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Analysis of Environmental Impacts of Dam Projects to Determine Optimum Alternative (Case Study: Kalat Dam and Hydropower)

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Expanded Abstract

Introduction

Kalat Dam and Hydropower Plant, is located in Maroon River Basin, Kohgiluyeh and Boyer-Ahmad Province, in the southwest Iran. In this research, three alternatives, namely Kalat, Sarkooh, and Zirna, are investigated to select the optimum alternative for this Project, with emphasis on the environmental criteria. This plan has the objectives of securing reserves, flood control, and production of hydro-electric power (HEP), from the potentials of Maroon River discharge. Table 1 illustrates the most critical technical specifications of the considered alternatives.

Table 1. Technical specifications of the considered alternatives to Kalat Dam and Hydropower Plant Project

Alternative	Reservoir Volume (MCM)	Reservoir Area (ha)	Dam Height (m)	Dam Crest Elevation (masl)
Kalat	1313	2119	130	830
Sarkoh	704	1339	180	1020
Zirna	423	751	170	1070

Materials and Methods

The study area of this research is located in Maroon River basin. The survey of soil erosion in the reservoir shows that the classification of erosion is not significantly intensive in the study area. Thereby, from the viewpoint of erosion, the alternatives are in a desirable condition.

In the limits of the dam reservoir in Kalat, Sarkooh, and Zirna, there are a number of 15, 8, and 2 villages. Only within the limits of the reservoir of Kalat alternative, there exist two shrines and a historical bridge, which shall be submerged during the water-intake of the reservoir.

To determine the ecological capacity of reservoirs, we have used slope, bedrock permeability, and density of vegetation, and land cover maps. Ecological model is classified into three groups: suitable, semi-suitable, and unsuitable. After overlaying the maps, the ecological capacity of the region is prepared. In order to determine the optimum alternative, the Analytic Hierarchy Process (AHP) is utilized. The first step in this method is to create a structural formation at three levels, which are: Level 1. Objective: in selection of the optimum alternative, Level 2. Factors: in the way of criteria, and Level 3. Plans: considered for the selection.

To determine the criteria, check-list method is utilized. Subsequently, in accordance with the results of the check-list, the primary criteria are determined. In this research, by taking the environmental observations into account, 9 key criteria are selected.

In the second step, weighting or coefficient importance of the criteria is determined. To evaluate a criterion in relation to another criterion, a numerical value of 1 to 9 is taken into consideration such that two criteria, which are of an equal value, are evaluated numerically as (1). However, if the importance and priority in applying a criterion are infinitely more than those of another criterion, its comparative evaluation is considered 9 and the intermediate digits are determined based on the relative importance of the criteria.

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In the third step, on the basis of the implication of the criterion coefficients and utilization of Expert Choice (EC) software, the weighting or significance of each of the indices, relative to those of a higher level (relative weight), are computed. Such comparison and weighting are implemented in pairs between the criteria.

In the fourth step, the alternatives are separately compared with the form of pairs in each criterion and are weighed. However, in the ultimate step, by combining the comparative weights of the alternatives and criteria, the final weighting of each alternative is calculated. Finally, the alternative that gains the optimum weight shall bear a critical degree of importance with respect to the other alternatives.

Results and Discussion

According to the results of assessment in Figure 1, ecological capacity map shows that 100% of Zirna alternative and more than 91% of Sarkoh and Kalat alternatives are located in suitable and semi-suitable zones. Because of different criteria, multiple criteria decision analysis is applied to determine the optimum alternative.

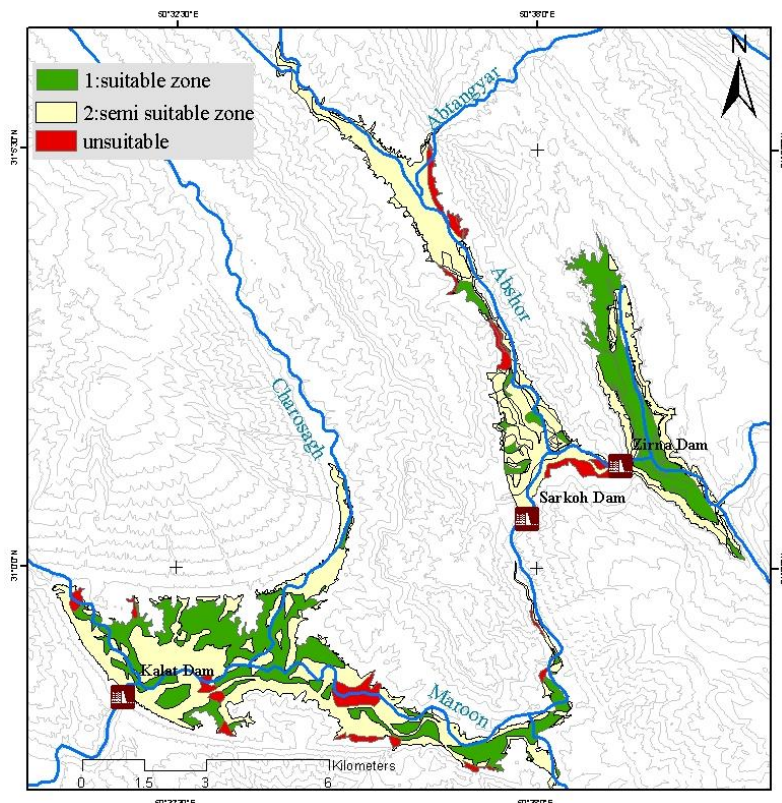


Fig. 1. Ecological capacity map of three alternatives

In accordance with the basic studies and environmental conditions in the study area, the environmental consequences of the plan are investigated in order to determine the environmental criteria (indices) using check-list method.

Based on the results obtained from the predicted impacts in Kalat, Sarkooh, and Zirna alternatives, it can be concluded that, despite the high importance of some criteria, they are not selected to determine the selected criteria, since all the three alternatives have the same or similar conditions. Therefore, the most critical environmental criteria selected from the check-list method are: land use, threatened species of index flora with ecological value, index fauna, rural population centers, and limits of the operational area influenced from the viewpoint of environmental destruction, land ownership, cultural heritage sites, other development plans and seismicity of sites.

In the subsequent phase, by utilizing Expert Choice software, the weighting of the criteria with respect to each other is mutually performed in such a manner that an increment in points, from 1 to 9, illustrates a more critical value in one criterion compared with another. With all the aspects and criteria, the alternative relative to Zirna has attained the highest points of 0.347. It is the selected option, whereas the alternatives of Kalat and Sarkooh with the ranking of 0.339 and 0.314 points, respectively, are the second and third priorities. The results of comparison and points of the three alternatives demonstrate that the alternative of Sarkooh which has a noteworthy variation relative to the other two options has minimum points. The results attained in the developed model in the 'Expert Choice software is demonstrated in Figure 2.

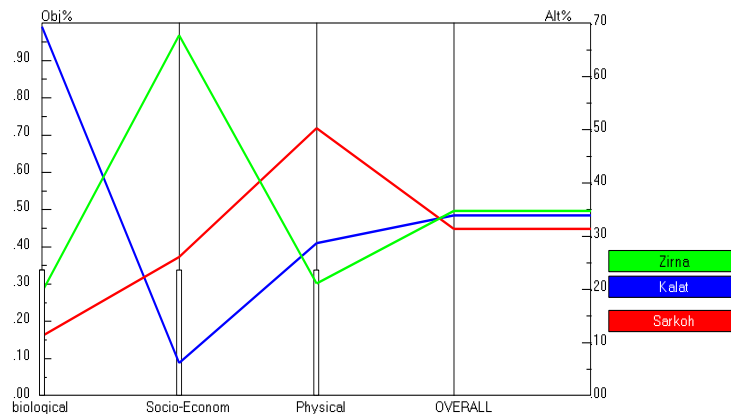


Fig. 2. Results of the final weighting of the alternatives in the 'Expert Choice' Software

Conclusion

The results obtained from this research illustrated that, conditions relating to land use, index flora, seismic conditions, and regional population specifications are of greater importance in order to determine a choice of alternatives from the environmental point of view. Hence, they had an immense impact on determination of the ultimate site. Comparison of the final points, which were determined for the three axes, indicated that the sites of Zirna, Kalat, and Sarkoooh, which attained 0.347, 0.338, and 0.312 points, respectively, gained the first to third priorities in terms of being selected for the dam location.

In the preliminary survey and without specifying the significant coefficients of the criteria, it seemed that, due to a few distinctions such as presence of accessible roads and less amount of damage to the reservoir, Sarkoooh alternative gained the first preference for the dam construction. With the disclosure of all the major criteria in decision-making and with the critical coefficients as well as coupling comparison between the alternatives, it was specified that this alternative would be at farther distance than other options, ranking the last priority. Thereby, in all the projects in which a selection should be made between several alternatives which are subjected to numerous factors, it is essential to utilize appropriate multiple criteria assessment methods.

Finally, it is proposed that, since numerous dam and power plant projects are simultaneously studied or implemented in this basin, in order to prevent biased attitudes toward a specific project, strategic environmental assessment studies and regional planning must be performed.

Keywords: check-list, dam, environmental impacts, multiple criteria decision making, optimum alternative, prioritization.

Great Cormorant (*Phalacrocorax carbo*) as a Monitor of Heavy Metals Contamination in Hara Biosphere Reserve

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Expanded Abstract

Introduction

Environmental pollution, especially marine pollution, is one of the complex and minatory problems that human is faced at the present time. Many of human activities have irrecoverable outcomes and affect the marine environment in such a way that destruction of marine zones has become a significant warning. One of the most important ecosystems in Iran is Hara biosphere reserve, located in the southern part of the country, and in the northwest Qeshm Island in the protected zone of Hara. Since it is situated near the city of Bandar Abbas (the largest southern port of Iran in the Persian Gulf) and because of its location at the margins of the northern coast of Qeshm Island (the largest island and commercial-industrial free zone of the country in the Persian Gulf), this region has been subjected to urban and industrial pollutions. One of the most important pollutant sources, which have jeopardized the life of this ecosystem with serious threats in the recent decade, is the entry of heavy metals from various pollutant sources. Heavy metals are the most important contaminants that enter into the sea through rivers and shore zones and aggregate in the aquatic body through the food chain.

Most of these elements are not necessary for animals but have high toxic properties. One of the most imperative problems about the heavy metals refers to their insoluble characteristic in the body. Indeed, heavy metals never excrete from the body, but they sediment in fat, muscles, bones, and joint tissues and may cause illnesses and various other phenomena. Birds, in comparison with other animals, are much more sensitive to environmental pollution. They may distribute chemicals, such as heavy metals, through direct connection or using polluted water or food. In other way, because of their indirect connection to polluted sources, they can determine the level of toxic element concentration in the marine ecosystem food chain. Therefore, the birds' pollution of heavy metals can be used to anticipate the pollution level in the food chains. Among different tissues, mostly the soft tissues of birds are used for the monitoring operation.

In many studies, the tissues of muscle, liver, kidney, spleen, heart, lungs, fat, blood, brain, and bone, and in some others, the feather and egg have been used to investigate the concentration of heavy metals in the environment. The selection criteria for choosing the suitable bird species (generally the suitable environmental monitors) include: sedentary species, proper distribution, easy identification, long life, and availability during the whole year, carnivorous species, stability against fluctuations, and physiochemical features.

The birds that have most of these characteristics are not numerous. In fact, the maximum reflection of the heavy metals ratio is the purpose of these limitations. Therefore, according to the above conditions, Great Cormorant (*Phalacrocorax carbo*) was selected as a suitable species to evaluate the heavy metals concentration. Great Cormorant is a species dependent on the aquatic ecosystem with a plentiful population and a wide distribution. In addition, its special piscivorous behavior has been always attractive for researchers.

The purpose of the present study is to compare the concentration of heavy metals (i.e. nickel, cadmium and lead) in the kidney, muscle and liver of the great cormorant between the male and female cormorants, and also to compare the concentration of heavy metals between the mature and immature cormorants.

Materials and Methods

Hara Biosphere Reserve is located in the south part of Iran in the Strait of Khuran, between Qeshm Island and the mainland of Iran, in the Persian Gulf, with 86,581 hectares in area. Its latitude and longitude coordinates are 36°40' to 37° and 55°21' to 55°52' E, respectively. It is situated in the Mehran River delta and hosts the largest

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seabirds along the Persian Gulf shoreline and, therefore, it would represent a center of biodiversity in Iran. The variety in this biosphere reserve and its unique mangrove trees provides a diverse habitat for birds like egrets, herons, pelicans, and plovers. Based on the available statistics, in 2010, the biosphere reserve had been the host of 36 species and 13,000 water birds and wader birds. Hara also serves as a breeding and spawning habitat for fishes, shrimps, and other crustaceans.

After primary studies about the studied areas, we collected 12 Great Cormorant samples in November and December 2012 from Hara biosphere reserve.

After collection, we separated kidney, muscle and liver then, placed in the oven at 65°C for 24 hours. In the digestion phase, 8 ml of nitric acid (65%) and 2 ml of per chloric acid (60%) (I.e. at the ratio of 4:1) were added to each sample (1 gram of the weighted sample). In a hot-block digester, they were digested firstly at 40°C for 1 hour and then, at 140°C for 3 hours. Afterwards, samples were screened by Whatman paper No. 1 and the solution's volume reached 25 ml by using distilled water. At the end, all samples were kept in the refrigerator in polyethylene jars in order to later evaluate heavy metals concentration by atomic absorption machine.

In order to ensure about accuracy of the digestion process, in each digestion round, there was a control sample to subtract the sizable results from concentration of the metal in different samples. In this study, measurement of heavy metals concentration was performed by atomic absorption machine (model contrAA 700).

Results and Discussion

The results revealed that the maximum and average concentrations belonged to lead and the minimum related to nickel. Also the results indicated that the average of heavy metals were the highest in kidney and lowest in muscle (Table 1).

Table 1. Values of heavy metal concentration (mean±SD, $\mu\text{g g}^{-1}$) in kidney, liver and muscle of *P. carbo* in Hara Biosphere Reserve, Iran

	Sample	number	Nickel	Lead	Cadmium
Kidney	Male	4	0.05±0.21	0.86±2.12	0.09±0.15
	Female	8	0.03±0.18	0.47±3.04	0.13±0.15
	t-test		0.04*	0.005*	0.01
	Adult	7	0.14±0.22	0.85±1.7	0.14±0.22
	Juvenile	5	0.1±0.13	0.48±2.91	0.04±0.06
	P Value		0.001*	0.48	0.02*
	Total	12	0.09±0.19	0.82±2.42	0.31±0.15
Liver	Male	4	0.08±0.17	1.02±1.25	0.06±0.91
	Female	8	0.02±0.12	0.67±1.44	0.22±0.6
	P Value		0.04*	0.02*	0.33
	Adult	7	0.02±0.14	0.92±1.5	0.26±0.54
	Juvenile	5	0.01±0.1	0.36±1.07	0.1±0.82
	P Value		0.04*	0.22	0.03*
	Total	12	0.02±0.14	0.7±1.37	0.23±0.7
Muscle	Male	4	0.04±0.09	0.28±0.69	0.19±0.15
	Female	8	0.02±0.05	0.18±1.08	0.39±0.46
	P Value		0.01*	0.003*	0.45
	Adult	7	0.02±0.06	0.33±0.91	0.33±0.41
	Juvenile	5	0.01±0.04	0.27±0.71	0.12±0.04
	P Value		0.005*	0.51	0.04*
	Total	12	0.01±0.07	0.31±0.82	0.22±0.25

Note: $P < 0.05$, indicates significant differences. (Confidence level 95%)*

In this study, the high lead concentration in some of the samples from Hara biosphere reserve demonstrated this fact that environment of the birds is under extreme pressure due to existence of lead.

Lead is a contaminant, which can be found everywhere and enters into the sea through various industrial wastes from the printing industry, oil refinery, etc. Human activities, along with the developments of the oil refinery and petrochemical plants, added to zinc and lead factories in Qeshm, and marine transportation in the south of Iran, may play the most important roles in absorption of this metal in the tissues of this bird. The existence of heavy metals in the tissues of the great cormorant in Hara biosphere reserve can be due to the presence of oil refineries and usage of petrol nearby the study area.

Burger and Gochfeld (2000) indicated that the undesirable effects of lead in birds occurs at the concentration of 4000 ppb, although aquatic birds are able to tolerate even the concentrations higher than this level. If the lead concentration in birds' tissues reaches over 4000 ppb, it would bring some problems, such as the decrease in the bird's perception, decrease of chickens' survival, inability in recognizing the sibling species, and the behavioral and nutritional problems. The behavioral problems of birds resulting from cadmium occur at the concentrations much lower than the lead and mercury concentrations. However, in the present study, the lead, cadmium and nickel concentration is much lower than the effective threshold.

In this research, the T-test results were used for comparing the concentration differences between two genders and it was shown that there is a significant difference among nickel and lead concentrations in three tissues of males and females ($P < 0.05$), but the results of the T-test showed that there is a significant difference between nickel and cadmium concentrations in adult and juvenile cormorants ($P < 0.05$).

Conclusion

The results of this research revealed that the maximum and average concentrations belonged to lead and the minimum related to nickel. Also the results indicated that the average of heavy metals were highest in kidney and lowest in muscle. The results revealed that age factor affected on cadmium and nickel accumulation and sex affected on nickel a lead accumulation in all of Great Cormorant's tissues. Heavy metals levels are below the range to cause behavioral change or reduce reproduction.

Keywords: great cormorant, Hara Biosphere Reserve, heavy metals.

Assessment of the Vegetation Restoration Potential on Coal Mine Wastes (Case Study: Karmozd Savadkoh Mines, Mazandaran Province)

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Extended Abstract

Introduction

Mining is traditionally regarded as the world oldest and the most important activity after agriculture. Despite being an important economic activity, mining causes substantial damage to the environment worldwide. The environmental impact of mining includes erosion, formation of sinkholes, dust, noise and water pollution, vegetation degradation, loss of local biodiversity, and contamination of soil, groundwater, and surface water by chemicals from mining processes. Mine reclamation is the process of restoration of the land that has been mined to a natural or economically usable state. Establishment of a vegetation cover is essential to stabilize the bare area and to minimize the pollution problem. Mine restoration can aid in maintaining native wildlife populations while providing other valuable ecosystem services, such as erosion control, carbon sequestration, wood production, water-quality improvement, and watershed protection. Area under mining are often characterized by high bulk density, low pH, low nutrient availability, poor structure, low water holding capacity, and low biomass productivity. Basically, there are two approaches to reclamation or restoration of a disturbed site: 1. allowing spontaneous succession or 2. using technical reclamation with sowing or planting target species, accompanied by restoration or improvement of site conditions. There is also a third approach when spontaneous (natural) succession is reasonably directed with the aim to reach a target community. However, until now most restoration projects have relied on technical measures more than on spontaneous natural processes. Main technical methods include the use of mycorrhiza, remediation, fly ash, hydroseeding, top soil, and compost.

The main aim of mine restoration is the permanent establishment of vegetation and soil quality improvement in order to increase the ecosystem function. In the first step, it is very important to identify the early successional species which can colonize on coal wastes. Spoil heaps after coal mining is an important component of the landscape in several parts of Alborz Mountains, where lignite coal is mined deeply or in open-cast mining. Therefore, we have studied the potential of plant establishment on spoil heaps and also compared the natural vegetation recovery on these heaps with nearby rangelands.

Materials and Methods

This study was carried out in Karmozd area in Savadkoh County, Mazandaran province (52°57'38" to 52°58'12" E and 36°05'57" to 36°06'53" N). This area has been one of the most important mining areas in central Alborz Mountains. The climate of the area is cold humid (536.5 mm annual rainfall, 10.9°C annual average temperature). Three spoil heaps were selected based on age and the amount of spoil. Spoil heap 1 was the oldest and the biggest one while spoil heap 3 was the youngest. Vegetation was samples in all three heaps and the rangeland nearby. Sampling was done along transects using 138 plots of 1 m². The cover (%) of each species was estimated in each plot. Data were transformed using ASIN (SQRT(x/100)) and then a combination of

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analysis of variance and t-test were performed for individual species response. Also, we compared the species diversity and richness indices among these sites.

Results and Discussion

A total of 43 species from 20 families were identified in study area. Gramineae, Asteraceae and Lamiaceae were the most common plants. About 60% of species were perennials. In spoil heap 1 there were 35 species of which 22 species were unique (Table 1). Greater number of annuals and prennials were found in spoil heap 1. It seems that the seeds of 22 unique species were dispersed from surrounding area to spoil heap 1. The germination and establishment of new arrived seeds in spoil heap 1 is possible as this spoil heap is in the vicinity of river and also it had been longer existed than other heaps. The pioneer species in spoil heap 1 are those reported in other studies worldwide. There were 10 species common between spoil heaps and nearby rangelands. *Alyssum linifolium*, *Artemisiascoparia*, *Bromus briziformis*, *Colutea persica*, *Hordeum vulgare* and *Rumex acetosella* were found only in spoil heap 1 and spoil heap 2. *Artemisia scoparia* was the dominant species in rangeland. In spoil heap 1 the dominant species were *Hordeum vulgare*, *Glaucium fimbriigerum* and *Artemisia scoparia*. The common species in spoil heap 2 were *Glaucium fimbriigerum*, *Melica persica* and *Artemisia scoparia* while *Kochia prostrata* was the main dominant species in spoil heap 3. Greater EC was found in soil heap 3 and this is the main reason for the establishment of *K. prostrata*.

Table 1. A summary of the species recorded in study area

	Spoil heap 1	Spoil heap 2	Spoil heap 3	Rangeland
Total number of species	35	13	5	17
Unique species	22	0	1	3
Number of annuals	13	6	2	6
Number of biennials	3	1	0	1
Number of perennials	19	6	3	10
Common species between spoil heaps and rangeland	10	10	3	-
Common species among spoil heaps	10	11	3	-
Number of plots	72	24	18	24

Spoil heap 3 significantly had the least species richness and diversity (Fig. 1). There were no significant differences among spoil heap 1, spoil heap 2 and rangeland in terms of species diversity while species richness was significantly greater in rangeland than that in spoil heap 1 and spoil heap 2. The greater values of species richness and diversity indices were expected for rangeland, as it has a thin layer of developed soil. The soil heap 3 is the youngest coal waste. Thus, this can be the main reason for having less species richness and diversity indices.

The harsh environmental situation made this heap only suitable for *K. prostrata* establishment. *Artemisia scoparia*, *Bromus briziformis* and *Stachys laxa* significantly indicated greater cover values in rangeland than that in spoil heaps. In contrast, greater cover (%) of *Melica persica* and *Hordeum vulgare* were found significantly in spoil heaps than that in rangeland. The greatest cover (%) of annuals was found in soil heap 1 and 2 while spoil heap 3 had the least cover (%) of annuals. The maximum and minimum covers (%) of perennials were found in rangeland and spoil heap 3, respectively.

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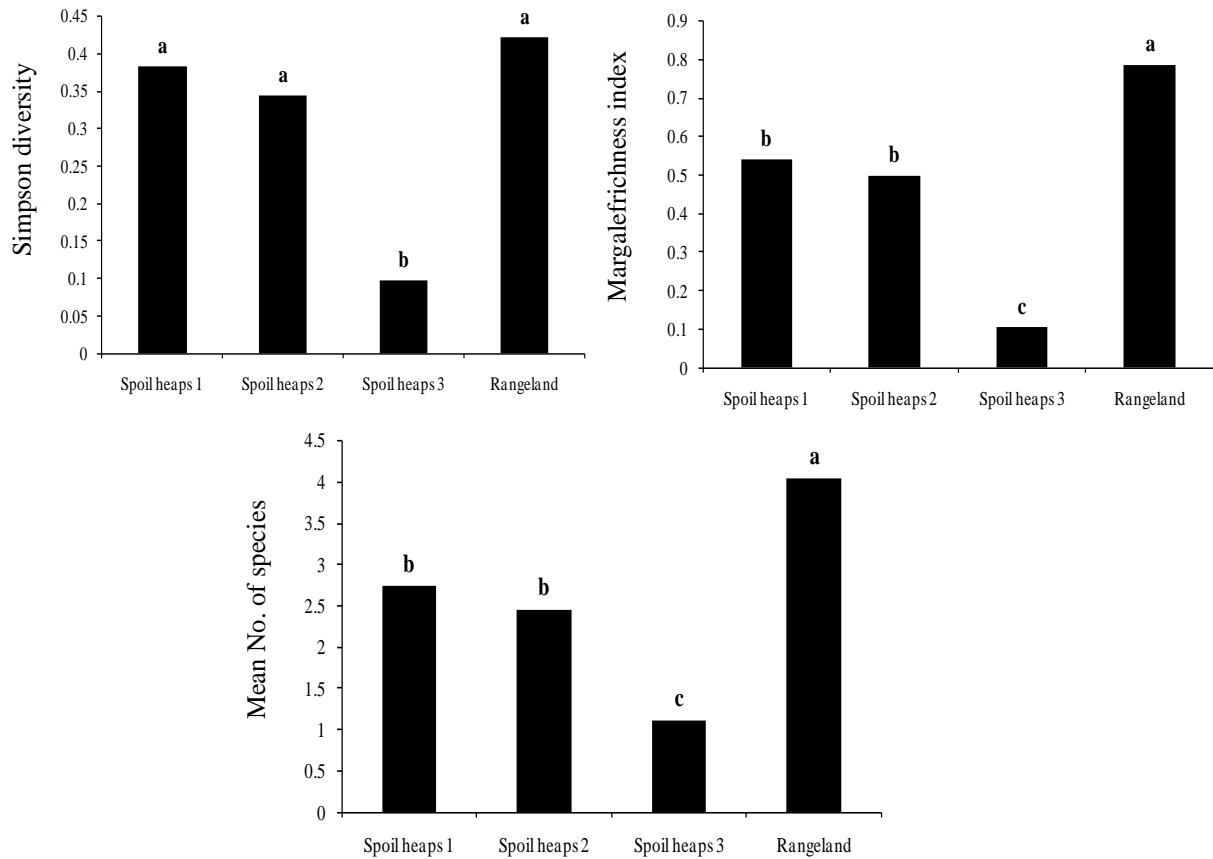


Fig. 1. Comparison of the species richness and diversity indices among spoil heaps and rangeland in Karmozd Savadkoh, Mazandaran province

Conclusion

Native species are recommended for long-term restoration of mine wastes as they have more potential for establishment. The establishment of early successional species is related to their seed dispersal from surrounding area. Thereafter, their potential for production of persistent seed bank is very important. The results of this study indicated that there is a potential of early successional species to establish on coal wastes. The amount of natural colonization was different among spoil heaps and we found this was related to spoil heap area and age after abandonment.

Keywords: pioneer species, species richness and diversity, spoil heaps, vegetation succession.

Investigation of Extent and Direction of Dense Vegetation Cover Changes of Gastroudkhan Protected Area with Landscape Ecology Approach

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Expanded Abstract

Introduction

Landscape structure means the pattern of a landscape, which is determined by its type of use, but also by its structure, i.e. the size, shape, arrangement and distribution of individual landscape elements. For delineation of these landscape elements, or so-called patches, often land use or land cover units are used. In this context, “‘land cover’ refers to the physical surface characteristics of land (for example, the vegetation found there or the presence of built structures), while land use describes the economic and social functions of that land. The heterogeneity of landscapes– as a parameter of landscape structure– is connoted as the quality or state of dissimilar elements, as with the mixed habitats or cover types on a landscape. It is the “‘opposite of homogeneity, in which the elements are the same. As indices of landscape structure, landscape metrics can be used to describe the composition and spatial arrangement of a landscape. They can be applied at different levels to describe single landscape elements by such features as size, shape, number or for whole landscapes by describing the arrangement of landscape elements and the diversity of landscape. The reason for using these metrics in spatial analysis may be to record the structure of a landscape quantitatively on the basis of area, shape, edge lines, diversity and topology-descriptive mathematical ratios; to document for purposes of monitoring; or to make the relevant information available as input parameters for landscape ecological simulation models.

Biological diversity in all its dimensions and facets is always tied to habitats, which need a concrete areal section of the earth’s surface for their existence. Biological diversity is therefore always defined for a certain reference area, and landscape structure is a key element for the understanding of species diversity. Spatial heterogeneity, as an expression of landscape structure, indicates the variability of the system’s properties in spatial terms. Since the complexity of biological diversity is difficult to describe, most ecologists have taken the practical way to research and to identify the biological diversity at the species level. Therefore, the selection of structural indicators was undertaken specific to the habitat type or tested species studied. Local data on species diversity can provide information as a proxy for regional biodiversity. An investigation of flora and fauna is, however, typically not comprehensive, but rather generally covers only a small proportion of all species. The clear determination of the diversity of various taxonomic groups requires very high efforts, knowledge and money. Hence a good substitute is needed. By combination of indicator species and groups with spatial environmental data and landscape structure, the power and deputy information can be increased and expanded geographically. Which parameters are suitable for the characterization and description of landscape diversity, and can therefore be used as an indicator for biodiversity? In principle, a few indicators are sufficient to ascertain landscape patterns. However, biodiversity cannot be described only by a simple number, as there are various qualities of spatial patterns. A set of indices representing the various aspects of biodiversity is much more informative and capable of interpretation. However, the use of many highly correlated indices provides no new information, and leads to problems in interpreting the results. For this reason, mutually independent indices should be selected. By means of indicators in monitoring, dramatic changes in values can be detected and serve as an early warning, and as an indication of the necessity for deeper investigation, even if no specific limit values can be defined. Landscape metrics may also be used to identify hot spots of biodiversity. Although they do not replace direct measurement of species biodiversity, these surveys can help make them more effective and less.

Area is the primary determinant of the number of species in a fragment. The size of the fragment will influence the number of species which are present when the fragment was initially created, and will influence the ability of these species to persist in the fragment. Small fragments of habitat can only support small populations

of plants and animals and small populations are more vulnerable to extinction. Minor fluctuations in climate, resources, or other factors that would be unremarkable and quickly corrected in large populations, can be catastrophic in small, isolated populations. Thus fragmentation of habitat is an important cause of species extinction. The fragmentation of large contiguous areas of habitat into smaller, dispersed patches is an important driver of biodiversity losses worldwide.

Habitat fragmentation also reduces the productivity of ecosystems because smaller areas of habitat are often less resilient to severe weather or disease shocks. Habitat fragmentation is often a cause of species becoming threatened or endangered. The existence of viable habitat is critical to the survival of any species, and in many cases the fragmentation of any remaining habitat can lead to difficult decisions for conservation biologists. Given a limited amount of resources available for conservation it is preferable to protect the existing isolated patches of habitat. The design of efficient and effective land conservation policies must therefore consider both the total amounts of habitat conserved and the spatial configuration of that habitat.

Forest fragmentation has become a global concern for conservation of important habitats as well as biodiversity. Protected areas that have been a cornerstone for safeguarding biological diversity are also facing enormous stress due to the increasing anthropogenic activities.

The impacts that fragmentation has on both wildlife and vegetation within a fragment and perhaps more importantly, the impact of loss of intact habitat and wildlife on the people relying on the remaining fragments, are important to understanding and slowing or preventing future decline. As fragments decrease and become more degraded, encroachment into the park and the number and severity of human-wildlife incidences may increase.

Establishing protected area is the primary mechanism used to protect forest biodiversity, particularly in regions with high human densities. Protected areas protect and maintain endemic, threatened or endangered, flora and fauna, geological features, and cultural heritage sites. In addition, they can generate income for the local and national economies, and provide important benefits associated with enhanced tourism sectors. However, many protected areas are also associated with negative social and ecological impacts. The processes that drive land cover change are complex and cannot be understood without addressing underlying cause and effect relationships. Changes in climate, population, and land use occur and interact simultaneously at different temporal and spatial scales, having major implications for both livelihoods and biodiversity. Forest loss and fragmentation are regarded as the greatest threat to global biological diversity.

Material and Methods

This study estimates the degree of spatial fragmentation in the protected area. Landsat TM 30 m satellite images of 1988 and 2014 were used as base maps in this study. The purpose of this study was to determine the extent and direction of changes in dense vegetation cover of Anzali watershed with using landscape ecology approach during period of 1989-2014.

Results and Discussion

As indices of landscape structure, landscape metrics can be used to describe the composition and spatial arrangement of a landscape. They can be applied at different levels to describe single landscape elements by such features as size, shape, number or for whole landscapes by describing the arrangement of landscape elements and the diversity of landscape. The purpose of this study was to determine the extent and direction of changes in dense vegetation cover of Anzali watershed with using landscape ecology approach during period of 1989-2014. This area has been selected for its habitat values and its role in sustainability of international watershed of Anzali. First Anzali watershed area extracted then dense vegetative cover area extracted from it. This area was classified in two classes of vegetation cover and bare. In following after separating Gashtrodkhan protected area, its dense vegetation cover was interpreted. After that vector layers of vegetation cover were built that it was used as input of patch analyst extension to calculate metrics.

Table1. Metrics of main patch of dense vegetation cover in Anzali watershed upstream during 1989-2014

Changes (%)	Changes (1989-2014)	Year-2014	Year-1989	Metrics
10	-15442.89	137433.48	152876.37	CA
102	4.67	9.23	4.56	ED
82	571431.85	1268257.72	696825.78	TE

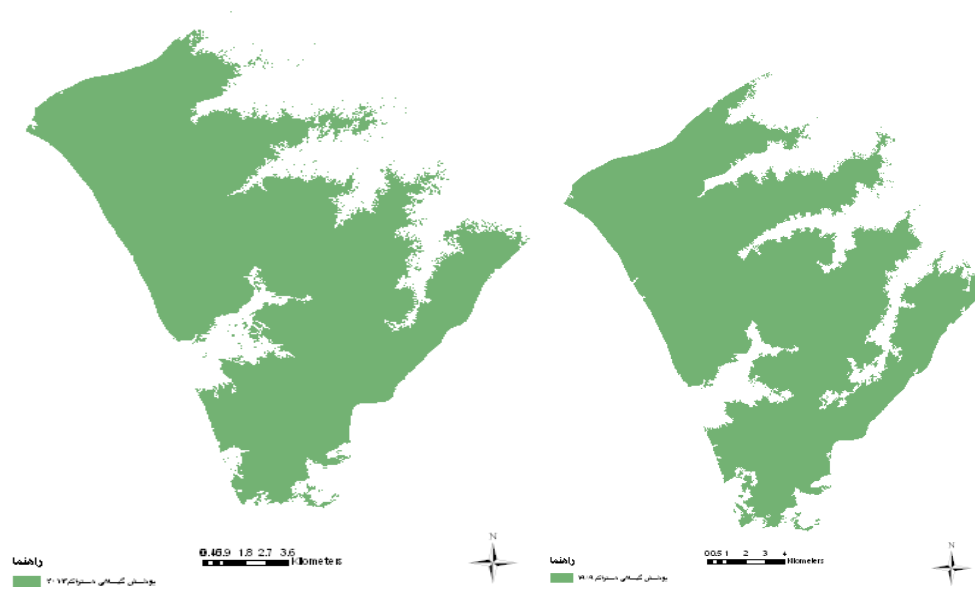


Fig. 1. Dense vegetation covers Gasht Roudkhan protected area 1989 (Right) 2014 (Left)

Conclusion

The results present considerable changes in CA, Numps, Mps, ED and TE metrics both in all patches and main patch that with the direction of change it can be concluded fragmentation process is rising (Table 1, Fig. 1).

Keywords: Anzali wetland, fragmentation, landscape, metrics.

Analysis of Polar Jet Stream (PJS) Location Associated with Heavy Rainfalls and Moisture Flux in West Iran

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Expanded Abstract

Introduction

Many aspects that strongly influence regional climate are including localized surface processes, large-scale patterns, especially mid and upper level tropospheric circulation and many factors of precipitation control in the west of Iran. These are including location of emigrate westerly winds systems, Jet streams location, Humidity Flux and topography. Upper tropospheric jet stream constitutes a significant factor influencing physical processes, including ascend or descend movements in the lower atmosphere in both synoptical and climatological time scales. Polar jet stream and subtropical jet stream are two main upper tropospheric jet streams affecting climatology in mid latitude atmosphere. Hence, formation of polar jet stream is related to thermal contrast in the polar front because of its proximity to the ground, it has greater role in providing ascendant atmospheric condition and precipitation. The Polar Jet stream embedded in the mid to upper tropospheric westerlies, 500 to 300 hPa levels. It is very variable in characteristics. It gains its energy from the thermal contrasts of the earth surface and is formed mostly over Polar Front. The Polar Front Jet stream through the vertical motion can control the development of surface pressure systems and weather or in long run the climate. But, sub-tropical jet stream is located at upper atmospheric level in tropopause and such condition can't have a prominent role as polar jet stream in ascendant condition, especially in precipitation. In addition, as the subtropical jet stream does not have other factors in polar jet stream such as polar front, dynamic properties of that does not affect climate feature of earth surface. Typically Jet stream potential can affect divergence and convergence, develop and steer the pressure systems and change control the weather patterns and climate. The Polar jet stream is one of main factors that affect climatology of Iran in winter.

In addition to jet stream location, the atmospheric moisture budget plays an important role in precipitation and hydrology. Water vaporflux in the atmosphereare is directly related to the atmospheric circulation and changes in rate and transmission paths of humidity are related to changes in atmospheric circulation during the year. Also, the moisture and other properties of atmospheric quantities are transferred by local circulation from other source to the given region. Existence of polar jet stream companied with adequate moisture can lead to heavy rainfall in each region. The objectives of the present study are understood by the location of polar Jet Stream during the heavy rains in Western Iran and characteristics of moisture flux from each region of moisture source and their contribution to the rainfall during the mentioned period.

Material and Methods

This study focus on western Iran, that is extended between the latitudes 33°N and 36°N and the longitudes 46°E and 48°E. The study area is covering an area about 100000 km². Many states of this region are located close to the Iranian border with Iraq and the area is largely occupied by the middle Zagros Mountain system with elevation between 300 to more than 3500 m, which is located across the paths of the prevailing moisture bearing and emigrate westerly systems, with annual precipitation between 300 to 600 mm. The area has a similar regimes for the amount of precipitation.

There are two main approaches in synoptic climatology: the environment to circulation and circulation to environment approaches and researcher atypically for precipitation base studied using environment to circulation. In this study, to determine the days with heavy rainfall, Mofidi et al., method have been used. Hence,

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the heavy rainfall was the amount of rainfall during the day with equal to or greater than 5% of the average annual precipitation (note: average annual precipitation in the study area was 450 mm) and also over 50 percent area of western Iran must receive heavy rainfall. Therefore, the 75 days with heavy rainfall for current study have been extracted. The location of PJS were analyzed according to atmospheric circulation types in 75 days with heavy rainfall using daily mean of the 500 hPa geopotential height data for these days between 10°–80°E, 10°–60°N, with a 2.5° (lat) × 2.5° (lon) spatial resolution with 841 grids. Thus, a 75 × 841 matrix was created. These data were retrieved from the National Centers for Environmental Prediction/National Center for Atmospheric Research (NCEP/NCAR) reanalysis archive. To determine the atmospheric circulation types and location of PJS during heavy rainfall over western Iran an agglomerative hierarchical cluster analysis was applied to the 75 × 841 matrix using the ward algorithm with Euclidean distance to identify atmospheric circulation types; because using hierarchical cluster analysis it can maximize within-group similarity and to minimize between-group similarity in data to determine the groups of days with similar characteristics. Then, it calculated the within-group correlation to identify representative days. The day with the highest within-group correlation was representative day of atmospheric circulation types. We analyzed the synoptic condition of these days. Using the grads software, we turned the geopotential height data from .nc format to .txt and also all calculation performed in the MATLAB.

These representative days represent each of the atmospheric circulation types due to heavy rainfall in the study area in winter. Finally, 4 groups of atmospheric circulation types affect the location of polar jet stream in both 300 hPa and 500 hPa levels associated with heavy rainfall in western Iran.

The convergence and divergence of moisture flux from two days prior to representative days was investigated. The convergence and divergence of moisture flux was calculated in 1000 hPa to 500 hPa levels to determine the main source of moisture flux in various atmospheric circulation types and arrangement of polar jet stream in time of heavy rainfall in western Iran. For this purpose, four daily NCEP/NCAR reanalysis data including specific humidity, zonal and meridional wind speed components (U; V components) for 1000 to 500 hPa have been used.

Results and Discussion

According to the results of hierarchical cluster analysis, we detected that four groups of atmospheric circulation types affect the location of polar jet stream in both level of 300 and 500 hPa, associated with heavy rainfall in western Iran. Usually, the annual rainfall in western Iran is associated with location of polar jet stream and emigrated systems of westerly winds. In the first pattern, the heaviest rainfall occurred at 00Z. Formation of deep trough in westerly winds on the East Mediterranean region lead to the formation of cut-off-low atmospheric circulation pattern in the both of 500 and 300 hPa levels. Existence of this trough with polar jet stream leads to intensification of the unstable condition in the atmosphere of western Iran. Therefore, in both level of 300 and 500 hPa, the west Iran is located in the second quarter zone of polar jet stream. In this pattern, existence of polar jet stream core in the west of Iran has taken a meridian curve and this issue provides more favorable conditions for convection and ascendant condition in atmosphere. In this pattern, the main sources of moisture are West Arabian Sea, Persian Gulf, Red Sea, and East Mediterranean is the secondary source that is less important.

In the second pattern, formation of a deep trough on the Red Sea convergence zone provides more favorable conditions for ascendant condition in the west Iran. The location of polar jet stream in this pattern is in lower latitude in comparison with the first pattern and intensification of polar jet stream is less than previous pattern. In this pattern, like previous patterns, western Iran is located under the second quarter zone of polar jet stream. The main sources of moisture in the second pattern are Arabian Sea and Red Sea, and also Persian Gulf and Oman Sea are secondary sources for this pattern.

In the third pattern, the reduction of depth and zonal expansion of westerly waves trough the wide area, from the Mediterranean Sea to the West of Iran, typically should cause decrease of ascendant condition in Middle Eastern atmosphere. But, the expansion of the core of polar jet stream from east of Africa to Iran causes intensification of unstable condition in the western Iran. In this pattern, similar to others, west Iran is located in the second quarter zone of polar jet stream and such condition caused increase of unstable condition in the western Iran and if the moisture supply be sufficient, this condition lead to heavy rainfall in the study area, like other patterns. The main sources of moisture in this pattern are Arabian Sea, Gulf of Aden, Red Sea, Persian Gulf and Oman Sea.

In the fourth pattern, existence of a deep trough on westerly wind waves over the Red Sea leads to increase in intensity of polar jet stream located in Middle East. Thus, this condition caused increase of unstable atmospheric condition in western Iran. According to moisture flux, the condition led to heavy rainfall in this region. The main sources of moisture in this pattern are Arabian Sea, Gulf of Aden, Persian Gulf and Oman Sea.

Conclusion

In this study, 4 groups of atmospheric circulation types have been detected. The types affect the location of polar jet stream in both levels of 300 and 500 hPa in time of heavy rainfall in western Iran. Many studies indicated that during super heavy rainfall in Iran jet streams are mostly extended from 250 to 600 hPa levels that have provided baroclinic conditions. Additionally, the northern half of Saudi Arabia was a major location of jet streams when super heavy rainfalls occur and we prove this result. In all patterns, core of Polar Jet Stream is located in close to middle of northern part of Saudi Arabia and its tongues come to western Iran. Such condition cause unstable atmosphere conditions.

Additionally, results of this study show that in all atmospheric circulation types that lead to heavy rainfall in western Iran, this region was located under the second quarter zone of polar jet stream. In all synoptic patterns, in time of heavy rainfall in Western Iran, the core of Jet Stream area perverted in direction of longitude. This will cause warm advection of temperature in western Iran. This state provides more favorable conditions for convection and ascendant condition in atmosphere and cause increase in precipitation. In all cases, if this condition has moisture supply, the super heavy rainfall will occur in the western Iran. Generally, the formation of a deep trough during the heavy rainfall days caused the jet tracks to concentrate close to the study area and this region has the most rainfall in the Middle East.

Major source of moisture for heavy rainfall is the Arabian Sea, especially in the west of this sea and the secondary sources are the Red Sea, Persian Gulf and Oman Sea. Mediterranean Sea has a negligible role in heavy rainfall in west of Iran. Moisture supply comes from the levels in 1000 to 850 hPa that there is moisture convergence flux in these levels. Whereas, in higher atmosphere levels there are moisture divergence flux. Therefore, in the 1000 to 850 hPa, lower atmospheric level, plays an important role in moisture supply for heavy rainfall in western Iran. The results of this study indicated that the water bodies in around Iran (such as Arabian Se, Persian Gulf) have more important role than water bodies in a way of Iran (such as Mediterranean Sea) to moisture supply for heavy rainfall in western Iran. Whereas, previous studies indicated that the Mediterranean Sea is one of the most important moisture supply sources for heavy rainfall in the west Iran.

Keywords: heavy rainfall, moisture flux, polar jet stream, west of Iran.

Modeling the Distribution of Suspended Particles in the South Tehran by AERMOD Model (Case Study: Tehran Cement Factory)

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Expanded Abstract

Introduction

Air pollution is the introduction of particulates, biological molecules, or other harmful materials into the Earth's atmosphere. This can possibly cause disease, death to humans, and damage to other living organisms such as food crops, or the natural or built environment. The atmosphere is a complex natural gaseous system that is essential to support life on planet Earth. Stratospheric ozone depletion due to air pollution has been recognized as a threat to human health as well as to the Earth's ecosystems. The cement industry has 79 years record in Iran and with total cement annual production capacity of 66 million tons is the largest cement producer country in the Middle East. In the various stages of production process of the material, many pollutants are released to the environment. Cement industry has always been associated with air pollution. From types of pollutants releases, particulate matter is the most important pollutants of cement plants. In the recent years, the cement plant is located in the southern Tehran; it is one of the most polluting industries in our country and is numbered as one of the most important cause of air pollution in the region.

Material and Methods

From the first steps for the control and reduction of air pollutants emissions, their distribution is specified and detected. Air emissions modeling studies, provide possibility to get useful information for strategies implementation for air pollution control in the future. Pollutants dispersion modeling in a variety of emission sources, weather conditions, and pollution source location can be capable to provide the desired output for the planning and management of reduction and control of the emission pollutants. Air quality models are widely used in recent several decades based on calculations by the computer.

Computer modeling of air pollution dispersion model was used by AERMOD. AERMOD is a steady dispersion state model to determine the concentration of different pollutants in urban and rural areas, smooth and rough, and the high level of emissions from point sources, the volume and variety of surface materials can be used. The model images show distribution and dispersion of pollutants from the source to the receiver. Thus, in this study, the model was used to simulate the particle dispersion and was used to evaluate the emission effects of various industrial sources. The model is applied to evaluate the emission effects from various industrial sources at distances less than 50 km and has been investigated by zoning the radius of dispersion of pollutants. AERMOD model uses two preprocessor. AERMET is a meteorological preprocessor and another named AERMAP is a geologist preprocessor. AERMET preprocessor is to process meteorological data and estimates atmospheric boundary layer parameters for use in the model and AERMAP preprocessor analyzes the regional topographic information.

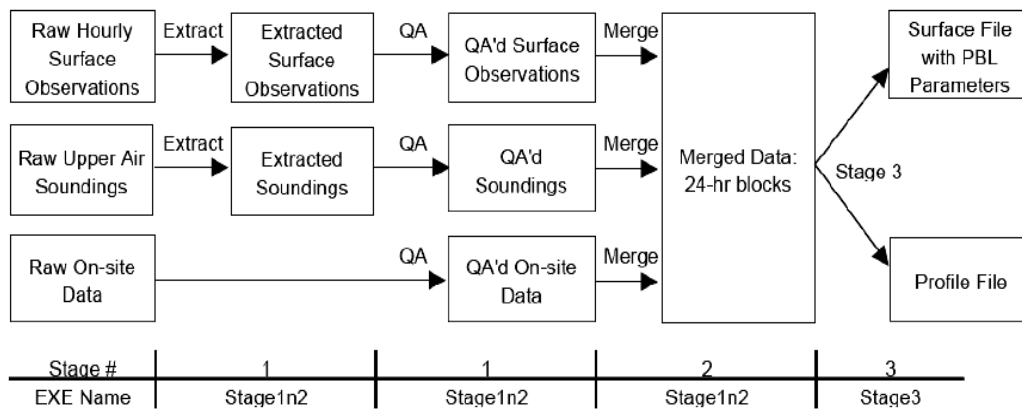


Fig. 1. Data preparation process in AERMOD by preprocessing of AREMET

Finally the model used the results of these two processors and supplemental information about the sources of emission and acceptor networks on the calculations and presents final results.

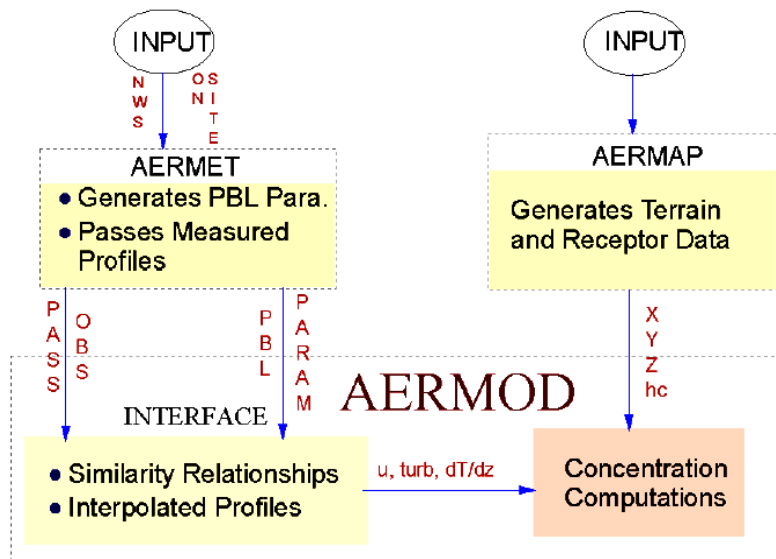


Fig. 2. General structure of AERMOD model

Results and Discussion

In this study, the basic data with measurement reports and output aerosol sampling of the stack and weather data was obtained from the meteorological organization (in this research we used climate variables such as temperature, relative humidity, wind direction and intensity, in daily scale for Doshan-tappe weather station on 2010). In the next step the pollutant sources location map was separately prepared with the proper resolution in the factory location (onsite) and nearest weather station. Then, distribution of particulate emissions for time average of 1, 3, 8 and 24 hours and a period of one month and seasonal for both summer and winter conditions have been carried out by entering the data related to each stack AERMOD model with emission rate (in grams per second) by calculating the flow on the scale of Micrograms to the seconds and multiply by the values for each output aerosol concentration in micrograms per cubic meter. As a matter of fact, emissions variables and pollutants properties (chimney height, speed and exhaust gas temperature, the volume of pollutants, etc.) of the cement plant, according to a quarterly sample results were received from 12 sources of pollutants that were all kinds of chimneys. Findings of air pollution dispersion modeling show that the greatest impact of suspended particles is occurred at a distance of 1 to 5 km from the emission source. The particles in the summer entry to Tehran from the plant origin had been further increased and covered to 15 km of the source.

In this study, simulation was done for 2 meters height or surface to breathe. Simulated altitude is assumed in a flat mode. By referencing to the results of modeling, in both summer and winter periods, the highest value is for the hourly average. In both hourly cases, the prevailing point is emission source eastward. In the summer case, due to heat and the more intensity wind blowing, the more range of area around the plant is located within the dispersion of pollutants. Dominant point of factory pollutants spread is south east and east. The concentration because of the high density of suspensor solid particles from air decreases more rapidly with increase in distance from the stack. After a long gap, pollutants dispersion to surrounding is caused to reduce its concentration. As it is known, the concentration minimum, respectively, was recorded at monthly and seasonal averages and particle volume maximum is occurred in hourly average, especially on the one-hour. Therefore, in the meantime, a considerable difference was seen in levels of particulate pollutant concentrations.

Conclusion

With the concentration of particles standard in Iran and EPA, it is observed that result for the model output is multiplier than the standard rate. In the hourly and daily measures in the vicinity of the emission source and a factory space, particle size is high. It is proposed that cement plant use hybrid filters in their product lines to reduce significantly its dust.

Keywords: AERMOD, air pollution modeling, cement plant, particulate matters.

Modelling of the Petroleum Hydrocarbons Concentration Variation in Different Depths of a Contaminated Soil during Phytoremediation Using Fuzzy Logic

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Expanded Abstract

Introduction

Isfahan Oil Refinery (Isfahan, Iran) is responsible for the production of huge amounts of oil waste. As the released organic compounds are highly toxic, carcinogenic, and mutagenic, they can potentially contaminate the soil and groundwater resources of the adjacent areas. This is particularly important in Isfahan where arid/semi-arid climate has limited the access to adequate surface water resources. Among the various methods proposed for oil-contaminated soil remediation, phytoremediation has been identified as an efficient and cost-effective technique. Limited access to soil samples from various depths during phytoremediation along with the cost, time, and effort required for quantitative measurement of TPH necessitates the development of a mathematical model to overcome the existing obstacles. Fuzzy logic is a feasible method for modeling systems with inadequate or vague and non-specific information. The fuzzy set theory, introduced by Zadeh in 1965, allows the user to define the rules and understand the relations between parameters and the existing decision-making process. Consequent to its constant evolution, the fuzzy set theory has found various applications. While fuzzy logic techniques have not been as extensively applied in the environmental field as in other fields such as industrial control systems, their diversity and progression increase their potential to affect environmental policy making.

Therefore, in recent years, numerous studies have evaluated the application of fuzzy logic methods to assess air quality and pollution, quality of surface waters, health of the rivers, groundwater contamination. River water quality classification has also been investigated. In Iran, however, fuzzy logic has not been commonly practiced due to the unfamiliarity of environmental experts with the subject. The present study applied fuzzy logic to model TPH concentrations at different depths of soil during phytoremediation. Considering the inaccessibility of all soil depths, high costs of measurement, and the existing ambiguities, such a model will facilitate the evaluation and control of soil contamination.

Materials and Methods

Determining physical and chemical properties of soil

Soil samples were collected from the contaminated lands contiguous to Isfahan Oil Refinery's Sulfur Recovery Unit where oil waste was accumulated. The samples were air dried and ground to pass a 2 mm sieve. Soil structure, electrical conductivity, pH, organic matter, available potassium and phosphorus, cation exchange capacity (CEC), total nitrogen, the concentrations of TPH and polycyclic aromatic hydrocarbons (PAH) were measured according to standard methods.

Phytoremediation experiment

Phytoremediation experiments were conducted in 130-cm long polyvinylchloride pipes (width: 20 cm) with 20-cm sand filters on the bottom. The pipes had holes at 25, 50, 75, and 100 cm depths to make the final sampling possible. The prepared soil columns were planted with either sorghum or barley seeds or left unplanted. In order to assess the resistance and stability of the plants in contaminated soil, they were maintained for 17 weeks after seeding. TPH concentrations at 25, 50, 75, and 100 cm depths of all soil columns were measured 120 days after seeding.

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Fuzzy modeling

Data modeling with fuzzy logic was performed in three phases using MATLAB.

1. Fuzzification of the inputs and the output. The inputs and the output were defined using linguistic variables and membership functions (MF). Depth was defined with four linguistic variables, i.e. very low (0-25 cm), low (25-50 cm), average (50-75 cm), and high (75-100 cm). Time was also defined through two linguistic variables, namely short (0-20 days) and long (20-120 days). The output (TPH concentration) was defined with four linguistic variables including low, average, high, and very high. While the Gaussian MF was applied on depth and TPH concentration, the triangular-shaped MF was used for time. The functions were determined following trial and error.
2. Defining fuzzy rules and application of fuzzy operators. According to the measured values, the fuzzy intersection (Min) and union (Max) functions were used to multiply the inputs and combine the outputs, respectively.
3. Defuzzification. Defuzzification involves the production of a quantifiable output. As we applied Mamdani fuzzy inference method, we used the center of gravity technique for defuzzification. All defuzzification calculations were performed using relevant software and the output was quantified for various inputs.

Results and Discussion

TPH concentrations in treatments with sorghum and barley and also unplanted (control) treatments demonstrates that, increasing depth was associated with higher concentrations of TPH and smaller differences between the treatments. More precise, TPH concentrations of control and planted treatments were significantly different at the 0-25 cm depth ($P < 0.05$). However, as both sorghum and barley spread their roots at this depth, no significant difference was observed between planted soil columns. In fact, the extensive root systems of the two species enhanced the microbial activity in the rhizosphere and accelerated the decomposition of petroleum compounds. Compared to baseline, sorghum and barley decreased TPH concentrations by 64% and 52%, respectively. These values were 23%-35% greater than those detected in the control soil. At the 25-50 cm depth, the difference between TPH concentrations of the control and planted soils was still significant ($P < 0.05$). Meanwhile, considering sorghum's higher root penetration, the planted treatments were also significantly different in terms of TPH concentration at this depth. At 50-75 and 75-100 cm depths, no significant differences were detected between TPH concentrations of the treatments. In fact, since the roots of sorghum and barley could not penetrate into such great depths, the three types of treatment had almost identical conditions (Fig. 1).

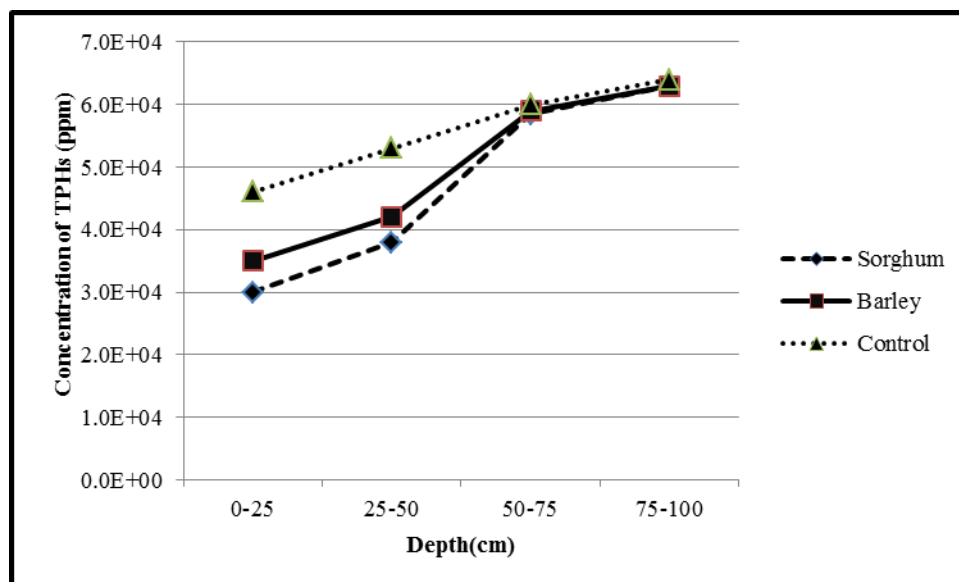


Fig. 1. Changes in the concentrations of total petroleum hydrocarbons at different depths of planted and unplanted soil columns

The output values were calculated after fuzzification of the inputs and the output, defining fuzzy rules and application of fuzzy operators to combine fuzzy relations and aggregate the outputs, and finally defuzzification. Comparison between the measured concentrations of total petroleum hydrocarbons and the values obtained from the fuzzy model after 120 days of phytoremediation with sorghum, barley and control treatment showed the fuzzy

model was well capable of determining TPH concentrations at various depths of soil during the phytoremediation process.

Conclusion

The present study designed a fuzzy model to determine TPH concentrations during the phytoremediation process in lands adjacent to Isfahan Oil Refinery. The measured concentrations decreased by 52%-64% in soils planted with sorghum and barley. These rates were 23%-35% greater than the values obtained from unplanted treatments. Since even small amounts of organic contaminants can seriously threaten human health, enhanced elimination of petroleum-based contaminants in presence of sorghum and barley plays a critical role in improving soil conditions in the area. On the other hand, not only is the quantitative measurement of TPH a difficult, time-consuming, and costly task, but it also requires access to different depths of soil during phytoremediation (which is not always possible). Therefore, we determined the concentrations at different times and depths by developing a fuzzy model. The applied model was actually able to mathematically formulate the existing limitations and facilitate decision-making and inference through its simple, flexible concepts.

With the novelty of fuzzy logic techniques in soil and water resources studies, particularly in Iran, further, more diverse research on the application of such methods in various fields of integrated soil and water resources management can lead to improved prediction and modeling accuracy at lower cost and time. As the values calculated by our fuzzy model were consistent with the measured TPH concentrations, this model can also be utilized in other contaminated areas. Meanwhile, the model comprised 10 different MFs (four for depth, two for time, and four for the output) whose parameters could be modified by the user and thus alter the numerical value of the output. Since selecting appropriate values for the parameters is complicated, future studies are suggested to use optimization methods such as genetic algorithms determine the best parameters for MFs.

Keywords: depth of pollution, fuzzy model, oil pollutants, soil pollution.

Performance Assessment of Natural Adsorbent Using Barberry Root in the Removal of Chromium from Aqueous Environment (Case Study: Groundwater Resource of Birjand)

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Extended abstract

Introduction

The potential sources of Cr (VI) are various effluents from metallurgy, electroplating, leather tanning, textile dyeing, paint, ink, and aluminum manufacturing industries. These industrial effluents can contain Cr (VI), in the concentration range of 10 to 100 mg/L, which is much higher than the standard limit; 0.5 mg/L in industrial wastewater (EPA). In aqueous systems, Chromium usually exists in both trivalent [Cr (III)] and Cr (VI) forms. Although Cr (III) is considered as an essential trace element, Cr (VI) is toxic, carcinogenic, mutagenic and teratogenic. Therefore, the removal of Cr (VI) from industrial wastewater is of particular concern. Advances in water and wastewater treatment technology need spur for the development of technologies that may be more effective and less costly. Nowadays, the contamination of water by toxic heavy metals through the discharge of industrial wastewater is a worldwide environmental problem that this pollution can also have a source of groundwater with the geological formation. There are various methods to remove heavy metals including chemical precipitation, membrane filtration, ion exchange, liquid extraction or electro-dialysis. However, these methods are not widely used due to their high cost and low feasibility for small-scale industries. The widespread industrial use of low cost adsorbents for wastewater treatment is strongly recommended at present, due to their local availability, technical feasibility, engineering applicability and cost effectiveness. Most agriculture wastes or by products are considered to be low value products. As an alternative, a variety of inexpensive biomasses have been studied for their ability to remove Cr (VI) from aqueous solutions. Among these low cost adsorbents are microorganisms, seaweed, clay minerals, agricultural wastes, industrial wastes and various other low-cost materials. The dynamics is an essential aspect of the adsorption process especially for practical applications. Therefore, the present investigation has been undertaken for studying the dynamic behavior of adsorption through batch experiments performed under different conditions of contact time, pH, adsorbent, initial concentration, particle size and temperature. A well-fitted kinetic equation was used to evaluate the suitable operational conditions for the removal process and a Langmuir-type isotherm was modeled using kinetic data and experimental results.

Materials and Methods

Preparation of the soluble metal

The stock solutions of Cr (VI) (1000 mg/l) were prepared by dissolving $K_2Cr_2O_7$ (analytical reagent grade) in distilled water. The desired Cr (VI) concentrations were prepared from the stock solution by making fresh dilutions for each sorption experiment. The initial pH of the solution was adjusted by using a solution of HNO_3 or NaOH.

Preparation of adsorbent

Barberry roots were collected from South Khorasan Province, Birjand areas and soaked in distilled water for 24

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hr before putting in an oven at 70°C for 24 hours. Barberry roots using mill were powdered. The powders were sieved through a 100µm mesh and were stored in a container away from moisture.

Batch adsorption experiments

Adsorption experiments were carried out in batch mode. In order to investigate the nature of Cr (VI), initially the effect of pH on percentage removal was carried out and then further experiments on the effect of contact time, adsorption weight, initial concentration and temperature were conducted by using optimized pH. Only one parameter was changed at a time while others were maintained constant. In the first set of experiment, percentage adsorption was studied at various pH of (1.5–9) at constant adsorbent weight of 0.1 g/100 ml, initial Cr (VI) of 50 ppm. It was in the predetermined time (10min) in a rotary shaker at a speed of 200rpm using series of 100 mL erlenmeyer flasks. Next second set of experiments were conducted with various contact time, initial Cr (VI) concentration (50ppm) at constant adsorbent weight (0.1 g/100 ml) and at optimized pH 1.5. In the third set of experiment adsorption weight was varied (0.05–1 g/100 ml) while other parameters such as initial Cr (VI) concentration (50 mg/l), optimum time (90min) and optimum solution pH kept constant. In the fourth set of experiment Cr (VI) concentration was varied (25–200 ppm) and in the last set of experiment, temperature was varied at six different temperatures viz., 22, 25, 35, 40, 45 and 50°C in a thermostat attached with a shaker. The constancy of the temperature was maintained with an accuracy of $\pm 0.5^\circ\text{C}$ (22-50), and other optimum parameters kept constant. After completion of every set of experiments the supernatant was separated by filtration using Whatman filter paper and only 10ml of each sample was stored for residual Chromium analysis. The pH of each solution was adjusted using required quantity of HNO₃ or NaOH before mixing the adsorbent. Three replicates per sample were done and the average results are taken for calculation. The filtrate was analyzed using Atomic Absorption Spectrophotometry (AAS-Shimadzu AA-6300; 228.63 nm). All the experiments were performed.

Results and Discussion

Effects of initial pH

Solution pH is one of the most important variables affecting the adsorption characteristics. The effect of pH on the removal of Cr (VI) by Barberry roots was studied by changes in the initial pH between 1.5 and 9. The percentage removal of Cr (VI) decreased from 70.26% to 40% with increasing the initial pH from 1.5 to 9. These results were considered since the dominant form of Cr (VI) is HCrO₄⁻ and the surface of the adsorbent is positively charged at low pH (pH = 1.5), but on increasing the pH, the HCrO₄⁻ species shifts to other forms; CrO₄²⁻ and Cr₂O₇²⁻. The decrease in the adsorption of Cr (VI) with increasing pH may have been developed due to the competition between the anions CrO₄²⁻ and OH⁻. Similar observations have also been reported by other research groups.

Effect of contact times

The effect of contact times on the removal of Cr (VI) by Barberry roots was studied by variation in the contact times (10 to 180 min) for constant initial Cr (VI) concentrations. The percentage removal of Cr (VI) increased from 70.26 to 92.22% on increasing the contact times from 10 to 180 min for an initial Cr (VI) concentration of 50 mg/L.

Effect of adsorbent weight

The effect of the adsorbent weight on the removal of Cr (VI) by Barberry roots was studied by varying the adsorbent weight (0.05, 0.1, 0.2, 0.3, 0.5 and 1 g). The percentage removal of Cr (VI) increased from 91.45 to 92.26% on increasing the adsorbent weight from 0.05 to 0.2 g. However, it is observed that after a weight of 0.2 g, there was no significant change in percentage adsorption of heavy metals. The increased Cr (VI) removal on increasing the amount of Barberry roots was due to the increased surface area and adsorption sites available for adsorption. Similar observations have also been reported.

Effect of concentration

The effect of initial Cr (VI) concentration on the adsorption of metal ions by Barberry roots was investigated with varying solution concentrations (25, 50, 100, 150, 200 mg/L) using 0.2 gr adsorbent weight at pH 1.5. Cr (VI) adsorption was significantly affected by the initial concentration of Cr (VI) in the aqueous solutions. The percentage of Cr (VI) decreased from 95.68 to 85.44% with increase in the initial Cr (VI) concentration from 25 to 200 mg/L. The decrease in the percentage removal can be explained by the fact the adsorbent had a limited number of active sites, which would have become saturated above a certain concentration.

Effect of temperatures

The effect of temperatures on sorption on to natural biosorbent under optimized conditions has been observed

that sorption of Cr (VI) increases rapidly with increase in temperature from 22 to 50°C. The percentage of Cr (VI) removed increased from 95.7 to 97.85% on increasing the temperature from 22 to 50°C. The increase in sorption capacity of the biosorbent is attributed to the enlargement of pore size and activation of the sorbent surface with rise in temperature. A further rise in temperature increases the mobility of the metal ions and reduces the swelling effect in biosorbent, thus, enabling the metal ions to penetrate further.

Isotherms

Sorption isotherms were constructed by plotting the amount of metal sorbet (mg/g) against the equilibrium concentration of metal in solution (mg/L). Equilibrium studies were undertaken to understand the behavior of the adsorbent of Cr (VI) on to Barberry roots at equilibrium conditions. Three adsorption isotherm models, Langmuir, Freundlich and Temkin were used to describe the equilibrium between adsorbed Cr (VI) on the adsorbent and Cr (VI) in solution. The correlation coefficient for the Langmuir isotherm was significantly better than the Freundlich and the Temkin isotherm.

Kinetic modeling

The design of adsorption processes is linked to kinetic study. Kinetic sorption of Cr (VI) on to Barberry roots adsorbent were investigated by pseudo-first order, pseudo-second order, modified pseudo-first order were used to analyze kinetic data. Kinetics of adsorption was best fitted with the modified pseudo-first order kinetic model. These results demonstrate that roots of Barberry are effective and low-cost biomaterial for removal from aqueous solutions.

Conclusion

The major findings of this study were as follow:

1. The removal of Cr (VI) from aqueous solutions increased with an increase in adsorbent weight and contact time. This suggests the dependence of the efficiency on the amount of surface sites of the adsorbent.
2. The experimental results indicated that the pH of the aqueous solution was crucial to the adsorption of Cr (VI), possibly because the presence of various Cr (VI) species and the surface charges on the adsorbent are highly pH dependent. The results showed that the removal of Cr (VI) from aqueous solutions by Barberry roots was effective for solution pH=1.5.
3. The experimental results were analyzed using the Langmuir, Freundlich and Temkin equations. The correlation coefficient for the Langmuir isotherm was significantly better than that for the Freundlich and Temkin isotherm.
4. The adsorption kinetics of Cr (VI) on to Barberry roots was analyzed using pseudo first-order, pseudo second-order and modified pseudo-first order models. The Modified pseudo-first order model better explained the kinetic of Cr (VI) adsorption.

Keywords: barberry root, Cr (VI), heavy metals, removal, wastewater.

Preparation of Engineered Nano Adsorbent with Organic Removal Capability for Water Treatment Sand Filters

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Extended abstract

Introduction

Conventional water treatment consists of unit processes including coagulation, flocculation, clarification, filtration and disinfection. The goal of the treatment is removal of turbidity, color and certain bacterial species. In filtration process, flocculated substances that have not removed in pervious stage are sediment. Filter media is often silica sand that removal mechanism is complex and consists of mechanical filtration, sedimentation, and adsorption, chemical and biological oxidation. The effective removal mechanism in filtration process is adsorption. Two basic factors for adsorption are van der Waals force and mass attraction. Sometimes for quantifying and qualifying upgrading of filters, we use other media such as granular activated carbon and anthracite. In these cases filters have dual media. Activated carbons (ACs) are effective adsorbents in water treatment, because of high removal capability toward soluble and particulate pollutants but slow adsorption kinetics and difficulty for regeneration limited extensive application. Today's progress in new technology result in production of other carbon structures such as carbon nano tubes (CNTs). CNTs with mesopore structures and diameter about 2-50 nanometer have high potential in organic materials and pathogens removal. Removal of organic matters with carbon nano tubes are in groups such as organic dyes, pharmaceutical, pesticides, phenol, aromatic amines and natural organic matters. Adsorption mechanisms of CNTs are driving including hydrophobic effect, π - π interaction, π - π electron-donor-acceptor (EDA) interaction, electrostatic interaction and hydrogen bonding. Although good potential in organic removal, using in slurry state is a problem that it is necessary to remove CNTs in final treatment. Therefore, if we can be capable to deposition of these CNTs on media, we can solve these problems. One way to use is deposition of CNTs on silica sand. Although silica sand has adsorption capability, with deposition of CNTs, it can remove soluble organic matters. Similar to this coating, graphene oxide (GO) was deposited on silica gel. One of the shortages in this research was inattention to stability of the coating. In other research, pristine single wall carbon nanotube was coated on silica sphere and a method based on non-covalent bonding was represented. The result of this research shows that, bonding has a strong stability.

Materials and Methods

For deposition of CNTs on silica sand, physical and chemical processes were used. In physical process heat and in chemical process covalent bonding is effective factors for bonding. Materials that used in this research are carbon nano tube (purchased from nanosov), hydrochloric acid 37% (Merck, Germany), nitric acid 65% (Merck, Germany), silica sand (gift from Tehran pars plant) and 3 (triethoxysilyl) - propylamine (Merck, Germany).

To evaluate adsorption effects, 4 parameters (pH, adsorbent dose, and adsorbate dose and contact time) were investigated. In this study, initial pH at neutral condition, initial adsorbent in 5-40 gr, initial adsorbate in 2-12 mg/l and contact time in 10-60 minutes were adjusted. For preparation of different concentration of TOC a 1000 mg/l stock solution of TOC was prepared and TOC analyzer (model -VCSH, Shimadzu, Japan) was also used for determination of TOC.

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For reversibility of humic acid we investigated surface of new adsorbent adsorption/desorption studies. Therefore, in some series 20 g of engineered nano adsorbent was entered into 200 ml solution of humic acid with initial TOC of 10 mg/l and when adsorption process was equilibrated the adsorption capacity was measured. After that, the new adsorbent was poured in 200 ml solution that pH was adjusted from 10-13 with 0.05 and 2 molar NaOH to attain optimum pH. Also desorption time for 10-50 minutes was done to evaluate optimum time. Finally, desorption process at 25°C, 120 rpm and for 5 cycles was repeated.

Chemical bonding

For chemical bonding of CNTs on silica sand raw silica was washed with hydrochloric acid. Then, amin groups was produced on silica sand with heat and 3(triethoxysilyl) – propylamin. Furthermore, pristine carbon nano tube was oxidized with nitric acid. After that, the oxidized carbon nano tube and silica with amin groups was combined and CNT_{sand} (new adsorbent) was produced.

Silica acid treatment

For silica acid treatment, first 500gr of silica sand, 250 ml tap water and 250 ml hydrochloric acid were entered into a 1000ml beaker. Then, beaker was heated for 100°C for 3 hours. Acid treatment not only removes impurities of silica sand, but also active OH groups. After 3 hours silica was washed with deionized water and was dried under vacuums for 24 hours.

Combination of silica with amin groups

1000 ml of toluene was putted on heater for 0.5 hours to evaporate H₂O, because presence of water can react with OH silan groups and be hydrolyzed. 100gr of silica sand was heated under a reflux condenser. Then, 1 ml of 3 (triethoxysilyl) - propylamin was poured and was heated in a temperature control box in 100-120°C about 48 hours and then the sand was washed with methanol for several times and finally dried under vacuum for 48 hours in room temperature.

Oxidation of carbon nano tube

The oxidation of carbon nano tubes not only purify and enhance the chemical reactivity of graphitic network, but also increases the solubility in polar media. Therefore, 1 gr of pristine multi wall carbon nano tube (MWCNT) was dispersed in 75 ml of HNO₃ (Synth, 65%) under a reflux condenser and magnetically stirred for different times under nitric acid reflux at different temperatures. To prevent the major alteration of the structural integrity of carbon nano tubes and exfoliation bundles reduced the times with increases of temperatures. The temperatures was 80°C, 100°C, 120°C and 140°C in times 20, 12, 8 and 5 hour, respectively. After each time of treatment the dispersion was placed into an ice bath in order to cool down that to room temperature. Then, dispersion was centrifuged for 10 min at 5000 rpm for several times and in each times add some deionized water into the sample. The solid residue was washed with deionized water so that the excess of nitric acid was removed from the sample. Finally, MWCNT were dried under vacuum for 72 hours.

Deposition of MWCNT on silica with amin group

Deposition of MWCNT on silica sand does with direct heating. 10 gr of silica sand with amino groups was poured in 100 ml beaker. 0.01gr oxidized carbon nano tube was dispersed in 25 ml deionized water and was putted in ultrasound bath (HWASHIN, Power Sonic 420, 50HZ, 700W, Seoul, Korea) for 20 minutes. After that, 5 ml of dispersion was poured on silica sand and the mixture was heated until the dispersion of oxidized carbon nano tube was dried on sand and then this work was repeated to finish the 25ml completely.

Physical deposition

In physical deposition silica treated with hydrochloric acid and pristine carbon nano tube was oxide, but 3(triethoxysilyl) – propylamin don't used. Thus, silica sand without amin groups is combined with oxidized carbon nano tube and directly heated.

Reinforce bonding with heating

Whereas heating may reinforce the bonding between carbon nano tube and silica sand, define temperatures 100°C and 200°C in addition to the first deposited carbon nano tube on sand was used to evaluate temperature effects.

Results and Discussion

Investigation method of chemical bonding

The method of chemical deposition is establishment of covalent bonding between amin groups of silica and hydroxyl groups of oxidized carbon nano tube. Thus, silica sand is initially hydrolyzed to active OH groups. Then, silica sand and amin propyl is combined to produce NH₂ groups and finally oxidized carbon nano tubes. The amin groups of silica sand are heated to be resulted –NH groups is a strong bonding.

Stability of MWCNTs coated on sand

To investigate stability of MWCNTs coated on sand, ultrasound method was used. Ultrasounds are mechanical waves with high power that disperse in adsorbent to detach CNTs from surface of silica sands. These waves have 40 khz dispersion power frequency. Thus, 6 samples, physical and chemical samples were initially heated in oven in 100°C and heated in oven in 200°C. Then, they were putted in the ultrasound bath for 30 min and after that the samples were dried and it was seen that physical deposition has not stability and the MWCNTs coated on sand detached from silica sand, but chemical deposition has a strong stability and in samples that was putted on it in 200°C in oven. This stability is very permanent that demonstrate high temperatures has good effects on stability.

SEM of MWCNTs coated on sand

SEM was used to detect possible morphological changes in pristine and oxidized MWCNTs and also for watching surface of silica sand and MWCNTs coated on silica sand. According to SEM, oxidized MWCNTs with nitric acid, some bundle appear exfoliated and curled and a major alteration of the structural integrity of MWCNTs is observed and length of tube was shortened. On the other side, observation of CNT_{sand} illustrate a non uniform coating of MWCNTs on silica sand that completely differ from surface of silica acid treatment.

Investigation potential of CNT_{sand} in removal of organic matter

Although MWCNTs potential in removal of organic matter has been demonstrated in some previous research, in this study humic acid was used for index of organic matter to define capability of this adsorbent. Therefore, response surface methodology was used for experiment design and initial concentration of adsorbent, adsorbate and contact time was investigated and 20 experiments were defined. According to response from RSM- X/M (mg/g) – with increasing in contact time and decreasing in adsorbent dose the adsorption capacity was increased. Also with increasing in contact time and increasing in adsorbate dose, adsorption capacity is increased that be because of increasing in adsorbate collision with adsorbent. The equilibrium time is about 60 minutes and adsorption capacity at equilibrium time is reached to above 70 mg/g.

Regeneration of adsorbent

To evaluating regeneration of adsorbent the adsorption/desorption process was investigated. Data obtained indicate at pH =10 the regeneration efficiency is about 26.3% and increases up 75.7% at pH=13. Also 30 minutes is the best time for regeneration time and after 5 cycles of regeneration, the adsorption capacity is about 40 mg/g.

Conclusion

Although silica sand is not applicable to removal of soluble organic matter, but by deposition of carbon nano tubes onto its surface, it can be capable of removing this organics. Stability investigations indicate that physical coating has a weak bonding between silica sand and carbon nano tubes. In chemical bonding that establish a covalent bonding between silica sand and carbon nano tubes, bonding has a strong stability. Scanning electron microscopy (SEM) on silica surface reveals a non uniform coating of carbon nano tubes on silica sand. Determination of TOC shows in sample with CNT_{sand}, adsorption capacity is higher than 70% and in sample with raw sand it is less than 1%. Regeneration studies indicate that the optimum pH is 13 and optimum time for desorption is 30 minutes. Also after 5 cycles of regeneration the adsorption capacity is about 40 mg/g. These experiments show that the new adsorbent - CNT_{sand} - has a good potential in organic matter removal and regeneration process is simple.

Keywords: carbon nanotube, organic, sand filter, silica.

Analysis of Effective Parameters on Electro Fenton System with Stainless Steel and Graphite Electrodes to Remove Acid Orange 7

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Expanded Abstract

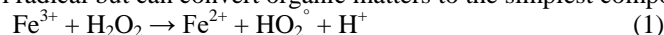
Introduction

Synthetic dyes and specially azo dyes are common pollutants found in textile and dyeing industries. Azo dyes are the most important class of synthetic dyes and represent about 70% of all world dyes consumption. Textile effluent can cause considerable pollution and rise high health risk factors due to loss of 20% of dyes in process and large scale of the dyes used in these industries. The characteristics of the textile wastewater are high color intensity and visibility in very low concentrations, complex chemical structures, and light resistance and hard to biodegradability, variability in pH range and above of these they have high carcinogenic and mutagenic potential.

Generally, the physical, chemical and biological methods were used for treating textile wastewater. They can be mentioned as electrocoagulation, adsorption, Fenton, photo-Fenton and photo-catalytic process. In recent years, advanced oxidation technologies have been described as efficient procedures to obtain high oxidation yields from several kinds of organic compounds. These methods mineralize and converse pollutants into CO₂, H₂O and inorganic ions, by the action of hydroxyl radical, which acts as a nonselective and strong oxidant of organics.

Electro-Fenton is a common advanced oxidation processes which contains electrochemical production of H₂O₂ and Fenton process. This makes each process more efficient. Its advantages are low operation cost, high potential for complete destruction and removal of organic pollutants into harmless compounds such as CO₂, water and mineral salts.

Electro-Fenton process is based on homogeneous reaction of organic components and strong oxidant due to generation of hydrogen peroxide by injection of air next to cathode electrode and iron ions as catalyst. Another strong oxidant of this method is hydro peroxide radical generated through reaction (1). However, this oxidant is not as strong as hydroxyl radical but can convert organic matters to the simplest components as well.



In undivided cell both anodic oxidation and electro-Fenton process would occur which increases the efficiency of both methods in decolorization of organic wastewater. Based on the previous studies, the aim of this study was cost reduction of electro-Fenton process by using graphite and stainless steel electrode for degradation of AO7 which also makes this method practicable for industries and examination of effective parameters such as current intensity, aeration rate, electrode area, initial pH and most important energy consumption.

Materials and Methods

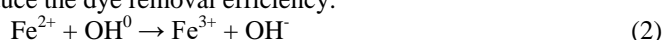
In this study, electrochemical process was developed at ambient temperature in a 500 mL rectangular plexiglass cubic reactor which includes two electrodes, an anode made of 304 stainless steel, a graphite cathode placed 3cm from each other and a PM-3005D power supply. Air was blown in the cathodic zone by an RS Electrical 610 air generator pump and an IKA RH- Basic 2 magnetic stirrer was used to mix and homogenize the sample. The other equipments used in this study include a Kern PLS 360-3 digital scale with 0.001 accuracy and Metrohm 691 pH meter. The amount of dye in solution was measured by using a Hach DR-4000 spectrophotometer at a wavelength of maximum absorption of acid orange 7 (485 nm) and the calibration curve of dye concentrations, respectively.

In this study, several parameters including current intensity (0.3, 0.6, 0.9 and 1.2 A), aeration rate (0, 3.5 and 7 L/min), electrodes area (30, 60, 90 cm²), initial pH (2, 3, 6.5 and 9) and energy consumption were examined. In order to maintain the flow of electricity in the cells, Na₂SO₄ (Merck) 0.01 M was used. All experiments were performed according to the method of analysis of water and wastewater and repeated at least 3 times.

Results and Discussion

Effect of current intensity

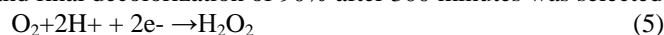
The influence of current intensity has been investigated in the range of 0.3 to 1.2 A. As we can see, after 120 min reaction, when current intensity was 0.3, dye removal efficiency was 71%. Increase in current intensity to 1.2 A could enhance dye removal efficiency to 94%. This is caused by increasing production of ferrous ions and hydrogen peroxide that can enhance the production of hydroxyl radical. However, after 180 minutes there is a little difference between these current intensities and electro-Fenton process decolorization rate was reached to 95 percent in all the investigated conditions. This was also caused by reduction of dye removal. When the current intensity was increased further, excessive hydroxyl radicals would be consumed via following side reactions which may reduce the dye removal efficiency.



Because the dye removal efficiency at current intensities of 0.6 and 1.2 A was approximately equal, the current intensity of 0.6 A was selected as the optimum level with lower power consumption than other cases (0.24 KWh/ppm).

Effect of air flow

Air flow rate was examined from 0 to 7 L/min at the obtained optimum condition. As it can be seen, increase in the air flow rate from 0 to 3.5 L/min resulted in an increase in the acid orange 7 removal efficiency from 80 to 90 percent after 150 min. The removal efficiency remained constant when the air rate was increased further to 7 L/min. The experimental results indicated that increase in air flow leads to increase in hydrogen peroxide concentration and enhances dye removal efficiency by improving production of hydroxide radicals. However, further increase in air flow would lead to reduction in removal efficiency by consumption of hydroxide radical with exceed hydrogen peroxide (reaction 5). In order to reduce the energy consumption of aeration, electro-Fenton with no aeration and final decolorization of 90% after 300 minutes was selected as optimum condition.



Effect of electrode area

Electrode area of 30, 60 and 90 were investigated to indicate the effects of electrode area on degradation of AO7 in obtained optimum condition. The results showed that when the electrode area were 30, 60 and 90 cm², the degradation percent of acid orange 7 after 300 min were 68, 89 and 97 percent, respectively. However, by increasing time reaction, dye removal reaches to constant value. It was well known that the amounts of electro-Fenton reagents would be increased by enhancing electrode area which also would be resulted in increased dye degradation.

Another important parameter in electrochemical process is energy consumption. Energy consumption per dye removal for 60 to 95% of removed dye was investigated to optimize the electrode area and energy consumption of electro-Fenton process. It is obvious that achieving higher removal efficiency requires higher energy consumption too. But there were huge energy consumption difference from 90 to 95% degradation of Acid Orange 7 for electrode area of 30 and 90 with 60 cm². For 30 cm² electrode, reduction in dye concentration leads to decrease in degradation rate which enhance the time of reaction and energy consumption. But for 90 cm² electrode reduction of dye concentration increases the scavenger effects of H₂O and Fe which reduces the degradation rate and increases the reaction time which finally increase energy consumption.

Equation 6 was used to examine the amount of energy consumption for ppm dye removed, which E is energy consumption (KWh/ppm), V is potential difference (V), I is current intensity (A), t is electrolysis time (hr) and removed dye (ppm).

$$E = \frac{V \times I \times t}{\text{Removed dye}} \quad (6)$$

Therefore, electrode area of 60 cm² was selected as optimum condition with energy consumption of 0.25 KWh/ppm and decolorization efficiency of 95 percent after 300 minutes electrolysis.

Effect of initial pH

Due to the direct production of hydrogen peroxide in situ, the highest dye removal efficiency was obtained at pH=2 because in this pH, H_2O_2 is more stable and could be produced more efficiently. Anyway, increase in the initial pH leads to reduction of dye removal efficiency in the first 60 minutes. Dye removal efficiency is decreased by increasing the pH to the neutral and alkaline ranges because of the formation of ferric hydroxide species, reduction in the ferrous ions reproduction and reduction in hydrogen peroxide generation. The results show that the dye removals were 76, 64, 62, and 55 percent, with initial pH of 2, 3, 6.5 and 9 at 60 min electrolysis respectively. However with increasing time reaction, efficiency of dye removal improved at initial pH of 6.5 to 95 percent at 180 min electrolysis. Thus, initial pH of 6.5 was selected as optimum condition for reducing chemical material for releasing wastewater into the environment.

Conclusion

This paper has considered the electro-Fenton treatment of an azo dye with producing in situ hydrogen peroxide by oxygen reduction in graphite cathode. The effects of current intensity, air flow rate, initial pH and electrode surface were investigated. The experimental results showed that electro-Fenton process is able to decompose organic compounds without producing sludge as well as the oxidizing agent (H_2O_2) that produce only oxygen and water, so this process can be used for treatment or pre-treatment of wastewater containing toxic and non-biodegradable materials, especially textile effluents. From the obtained results, after 300 min of electrolysis, 90% dye removal was achieved under optimum condition (current intensity= 0.6A, pH=6.5, no aeration, electrode area= $60cm^2$ and energy consumption= 0.24KWh/ppm), which shows electro-Fenton is the proper way to degrade acid orange 7.

Keywords: acid orange, electro fenton, electrode surface, pH, wastewater.

Kinetic Equations for the Biological Removal of Lead from Industrial Wastewater Using Indigenous Species of Aquatic Plants in Khuzestan

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Introduction

Water pollution by heavy metals is a worldwide environmental problem due to the increasing exploitation of mining activities, industrialization and urbanization. It has increased around the globe. Lead is the most important environmental pollutants that can contaminate soil and water resources from different ways. This element is including the most toxic heavy metals in the United States Environment Organization. Therefore refining of soil and water contaminated with this element is from most important environmental policies of developing countries and Industrial countries. Lead metal is unnecessary for the body, so that trace amount in the body, indicating contamination with this element. Lead substitute for calcium in the cells and disrupt the activities of the body. Also cause liver and kidney dysfunction, genital organs and reproductive system, anemia, loss of intelligence interest and occurrence of the metabolic complications. Remove and control pollution of heavy metals is very difficult due to their multiple and different sources of pollutions. In that, each pollutant requires its refining process. Until now, many methods have been developed for the purification of sewage including can be pointed to the chemical precipitation, reverse osmosis and ion exchange of organic. Each of which has its own advantages and disadvantages. Including the optimal method of biological for the removal of pollutants is the use of plants and other expression Phytoremediation.

Materials and Methods

Project preparation and cultivation of plants

In order to implement this study, plastic pots prepared with 60 cm in diameter and 40 cm in height. Therefore, sand with grains diameter of 1 to 5 mm and a depth of 30 cm was used as the growth bed in pots that after preparing the pots and planting. They were placed a suitable interval each other. Selected plants included Phragmites, Thypha and Cynodon Dactylon due to their abundance. Young plant samples were collected from margins of wetlands, open surface drains and rivers and immediately were transferred to the site of the research in experimental field of Islamic Azad University of Dezful. After preparation of bed and adding nutrients to the cultivation medium, each pot was randomly assigned to a treatment in three replicates. The youngest seedlings were selected for cultivation in each medium sample. After gentle washing of seedlings with water, three plants at regular intervals, with the minimum distance of 5 cm from wall of the container and at a depth of 10 cm (density of 25 plants per square meter) were cultivated. After preparing the pots and planting the desired species were irrigated with the common water for 40 days because irrigation with synthetic wastewater in the early stages of cultivation caused stress to the plant due to lack of root stability and compatibility with the new culture medium. So after the elapse of this period time, irrigation with simulated wastewater in different concentrations of 5, 10 and 15 mgr lead/l is performed.

Results and Discussion

Exponential Association regression model

Exponential Association regression model using curvexpert software was used in order to simulate the kinetics of uptake in different treatments. The general form of this model is as $y=a.(1-e^{-b.t})$. In this equation, t in day and y lead uptake was defined in milligram per kilogram of soil. Lead absorption curves have been showed for Cynodon, Phragmites and Thypha in the treatments of average level of lead concentration. In this diagram, the

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regression coefficients a and b are variable constants for the different species and under different levels of concentration. According to this model, the kinetics of adsorption was highly correlated. Therefore, these equations can be used to simulate the removal of lead at different concentrations. The results showed that with increasing levels of concentration, the correlation coefficient was reduced. So this model in the medium and high levels had high precision. Comparison of model in the studied species showed a correlation coefficient of reed was much higher than the other two species so had better fit to this plant. Therefore, these equations can be used to simulate the absorption of lead at different times and in different plant species, especially reed with the high correlation coefficients.

Fitting with other models of the kinetics

Due to the lengthy process of phytoremediation, the use of appropriate models to simulate and calculate the necessary time is essential to refine the soil and reach the optimal level.

For this purpose, in addition Exponential Association model, models of zero order kinetics (linear function), first order kinetics and power function were selected and with the data collected were fitted (Table 1). Results showed the first order kinetic model in all treatments had a correlation coefficient (r) higher and consequently the lower from standard error (s) than the linear model. Comparison first order kinetic model with Power model showed that power function had a higher correlation coefficient. Therefore, it is suggested that from power model to be used simulating kinetic Lead with the high correlation coefficient.

Table 1. The results of zero-order, first-order and power kinetic equations in phytoremediation

Zero-order kinetic			First-order kinetic			Concentration levels	Plant
S	R2	Eq.	s	R2	Eq.		
0.07	0.91	$Y=0.134+0.0068.t$	0.06	0.93	$y = 1.975.e^{-0.00392.t}$	5 mg/l	
0.125	0.87	$Y=0.382+0.0138.t$	0.12	0.88	$y = 5.895.e^{-0.00176.t}$	10 mg/l	Bermudagrass
0.245	0.77	$Y=0.482+0.0133.t$	0.24	0.78	$y = 11.52.e^{-0.0014.t}$	15 mg/l	
0.09	0.94	$Y=0.169+0.0113.t$	0.07	0.96	$y = 2.016.e^{-0.00713.t}$	5 mg/l	
0.29	0.91	$Y=0.517+0.0276.t$	0.26	0.93	$y = 5.56.e^{-0.0062.t}$	10 mg/l	Phragmites
0.51	0.82	$Y=1.01+0.0325.t$	0.5	0.83	$y = 11.14.e^{-0.0332.t}$	15 mg/l	
0.08	0.93	$Y=0.127+0.009.t$	0.07	0.944	$y = 1.99.e^{-0.0054.t}$	5 mg/l	
0.24	0.83	$Y=0.417+0.0162.t$	0.23	0.85	$y = 5.611.e^{-0.0033.t}$	10 mg/l	Typha
0.43	0.77	$Y=0.817+0.0233.t$	0.42	0.78	$y = 11.23.e^{-0.00228.t}$	15 mg/l	

Continue Table 1. The results of power kinetic in phytoremediation

s	R2	Power kinetic	Concentration Levels	Plant
0.04	0.97	$Y=0.067.t^{0.5}$	5 mg/l	
0.07	0.95	$Y=0.104.t^{0.5}$	10 mg/l	Bermudagrass
0.18	0.86	$Y=0.17.t^{0.5}$	15 mg/l	

Continue Table 1. The results of power kinetic in phytoremediation

0.017	0.997	$Y=0.102.t^{0.5}$	5 mg/l	
0.15	0.97	$Y=0.268.t^{0.5}$	10 mg/l	Phragmites
0.36	0.9	$Y=0.387.t^{0.5}$	15 mg/l	
0.04	0.98	$Y=0.08.t^{0.5}$	5 mg/l	
0.15	0.93	$Y=0.178.t^{0.5}$	10 mg/l	Typha
0.32	0.87	$Y=0.294.t^{0.5}$	15 mg/l	

Conclusion

Experimental results showed that the kinetics of the reduction of lead in soil was mainly in the form of an association exponential model and then power model had the best correlation coefficient compared with the other models. The results showed that these two models had better performance and matching during the entire period of experiment. Zero order and first order kinetics models were not accurate at the initial and final times. The results of the calculation of the equilibrium time to achieve half the initial concentration in the soil ($y/2$) indicated that as the first order kinetics model, times 384, 190 and 100 days respectively by cultivation of Cynodon, Typha and Phragmites required in conditions treatment of the mean levels of wastewater concentration which implies that Phragmites had greater potential for Phytoremediation than the other two species. Therefore, bed concentration was reached in short time by half the initial concentration of the soil lead. The results indicated that the reaction rate constant for the three species is ranged from 0.0014 to 0.0071 day^{-1} . This amount was higher for Phragmites than the other species. Thereby reducing rate of soil lead by Phragmites cultivation was faster than the other two species and this constant coefficient in all cases was decreasing with increasing the different concentration levels of wastewater. In the end, it was concluded that the kinetics of phytoremediation should be simulated based on plant type, levels of concentration and type of contaminants.

Keywords: aquatic plants, kinetic model, lead removal, Phytoremediation.

Evaluation of Carbon Sequestration Ability by *Chlorella Vulgaris* in Water with Different Salinity

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Expanded Abstract

Introduction

Nowadays, cultivation of microalgae in order to reduce CO₂ has gained attention all around the world. One of the outstanding features is that photosynthetic efficiency of microalgae is greater than that of terrestrial plants. Carbon dioxide (CO₂) has been known as one of the most important greenhouse gases. Global warming is specially caused by Anthropogenic CO₂ emissions from fossil fuel utilization especially from coal combustion. CO₂ emissions are expected to rise in the coming years because of energy needs increasing in the developing worlds. So many attempts have been made to reduce atmospheric CO₂ including chemical absorption, physicochemical adsorption, membrane, cryogenics, chemical looping combustion (CLC) and biotechnology (e.g., terrestrial vegetation or hydroponic algae). Bio fixation via microalgae has been known as a potential and new method for CO₂ capture and storage. So one of the most understudied methods is carbon biosequestration whereby autotrophic organisms and plants convert this CO₂ into organic carbon through photosynthesis producing large amounts of biomass. Photosynthesis is the original process that created the fixed carbon present in today's fossil fuels, and microalgae are the origin of these fuels. They are among the fastest growing photosynthetic organisms, using CO₂ as their main building blocks. Environmental factors, particularly light, temperature, nutrient status, and salinity, affect photosynthesis and productivity biomass. In order to assess the potential of a microalgae system for directly removing CO₂, biomass measurement or growth rate evaluations are necessary. However most studies have focused on culturing microalgae in fresh water according to water quality in most part of Iran, in the present study, we tried to sequester CO₂ by *Chlorella vulgaris* under salinity water.

Materials and Methods

Pure stock culture of *Chlorella Vulgaris* was obtained from National Inland Water Aquaculture Institute Bandar-e Anzali, Iran and cultivated in Bold's Basal Medium (BBM). Culture of *Chlorella vulgaris* were individually cultivated in three (9.3 liter working volume) flat plate reactors (40*40*40) under three different EC; artificial seawater (EC34000 μS/cm), distilled water (EC 3 μS/cm), natural water in study area (EC 1500 μS/cm). (measured by EC meter, Istek Model 915 PDC). The cultures were maintaining under a 12h dark/light photoperiod with 3500 Lx of illumination for 8 days. The average pH of natural water was 7.83 and hardness of 1000mg/l, the amount of carbonate and bicarbonate were 4 mg/l 339.7 and its electrical conductivity was 1500 μS/cm. The amount of initial dissolved CO₂ was 8 ppm. Agitation and aeration were accomplished using air from a compressor with pressure of 0.12 MPa. All tests were taken on laboratory conditions and under ambient temperature so the temperature was 25-31°C with an average temperature 28°C. Direct microscopic cellcount by Thoma haemocytometer was performed in this study using optical microscope. Microalgae dry weight (g/L) was measured by centrifuging 10 ml of each sample at 4500 RPM for 30 minutes and then washed with deionized water. Finally, the dried at 105°C for 40 minutes. After measuring the dry weight, the amount of biomass productivity (P), growth rate (μ) and carbon biofixation rate (R) would be achieved by using equation 1-3.

$$P_{\text{overall}} (\text{g/L/d}) = (x_t - x_0) / (t_t - t_0) \quad (1)$$

$$\mu \text{ (day}^{-1}\text{)} = (\ln (x_t/x_0)) / (t_t - t_0) \quad (2)$$

$$R_{\text{CO}_2} \text{ (gCO}_2 \text{ L}^{-1} \text{ d}^{-1}\text{)} = C_c P \text{ (mCO}_2 \text{ m}_C^{-1}\text{)} \quad (3)$$

where, x_t and x_0 were the biomass (g/L) on days t_t and t_0 , respectively. C_c is the carbon content of the microalgae cell (% w/w) measured with elemental analyzer; m_{CO_2} is the molecular weight of CO_2 ; and m_c is the molecular weight of carbon.

Statistical analysis

In the present study, the raw data were stored in Ms Excel and then the relationship among biomass production; specific growth rate and bio-sequestration rate of CO_2 with the different level of salinity were interpreted by Tukey analysis using SPSS (version 17) software

Results and Discussion

Nowadays, use of micro-algae cultivation to reduce carbon dioxide has attracted a lot of interests around the world. The higher rate of photosynthesis in these organisms rather than plants and crops is one of the distinctive features. In the present study, the pure stock culture of *Chlorella vulgaris* cultivated in Bold's Basal Medium was used. The microalgae were cultivated in 3 treatments and 3 replications containing pure water, artificial sea water and natural for 8 days. Lighting conditions provided for this test were periods of 12 h dark / light with light intensity of 3500 Lux.

The results of maximum concentration of biomass, maximum specific growth rate and maximum CO_2 fixation for the cultures under different EC are presented in Table 1.

Table 1. The parameters of productivity, specific growth rate and carbon fixation rate of *Chlorella vulgaris* during 8 days

Carbon fixation rate (R) ($\text{gCO}_2 \text{ L}^{-1} \text{ d}^{-1}$)				Specific growth rate (μ) (d^{-1})				Biomass productivity (P) ($\text{g L}^{-1} \text{ d}^{-1}$)				Culture
1-8	6-8	4-6	1-4	1-8	6-8	4-6	1-4	1-8	6-8	4-6	1-4	
0.093	0.045	0.033	0.148	0.15	0.045	0.035	0.266	0.057	0.028	0.020	0.090	Pure water (EC= 3 $\mu\text{s/cm}$)
0.041	0.041	0.016	0.053	0.019	0.018	0.007	0.025	0.025	0.025	0.010	0.033	Artificial sea water (EC= 34000 $\mu\text{s/cm}$)
0.111	0.107	0.082	0.127	0.131	0.085	0.077	0.182	0.068	0.065	0.050	0.078	Natural water (EC=1500 $\mu\text{s/cm}$)

As Table 1 shows the biomass productivity of *Chlorella* sp. In pure water, artificial sea water and natural water was 0.057, 0.025 and 0.068 g/L/d, respectively. This presented higher biomass productivity in natural water. Specific growth rate of 3 cultures was 0.15, 0.019, and 0.13 (day^{-1}) respectively, which the lowest one belongs to artificial sea water (high salinity). Carbon fixation rate of 0.093, 0.041 and 0.111 g/L/d was observed in pure water, artificial sea water and natural water.

According to Table 2 the most number of cells were counted in natural waters at the end of the eighth day. In the artificial sea water because of the high salinity and inappropriate environment the cell growth and proliferation was slow, so that it shows the ability of carbon sequestration in the environment with high salinity was low.

Table 2. Average cell numbers of *Chlorella vulgaris* per liter counted during 8 days of cultivation

Culture media	Cell counted (per Liter)	1 st day	4 th day	6 th day	8 th day
	Pure water		3×10^7	7×10^7	8×10^7
Artificial sea water		3×10^7	5×10^7	5×10^7	6×10^7
Natural water		3×10^7	6×10^7	9×10^7	12×10^7

Tukey statistical results showed that there are significant differences at $P \leq 0.05$ between biomass production, growth rate, atmospheric carbon fixation rate, and also the number of cells in different salinity treatments. So amounts of salinity have resulted in different effects on the growth rate and carbon fixation rate.

Conclusion

Due to lack of enough fresh water sources, hot, dry climate of study area and inappropriate plants growing conditions, using microalgae is one the best solutions in order to stabilize greenhouse gases (carbon dioxide) and other applications such as the production of renewable fuels and medicinal uses. According to the results of present study, the maximum biomass and cell growth was observed in natural water, the environment for freshwater microalgae, so the carbon sequestration potential of microalgae in the culture medium with high salinity is low. Despite being a fresh water microalgae, *Chlorella vulgaris* presented high growth and fixation rate in natural water (EC=1500), so it could be cultivated in study area (South Khorasan, Birjand).

Keywords: birjand, carbon sequestration, *Chlorella vulgaris*, greenhouse gases, salinity water.

River Surface Size Fractioned Sediments Pollution with Heavy Metals (Case Study: Sefidroud River)

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Expanded Abstract

Introduction

In recent years, restrictions of fresh water resources in the world and protection of the quality of these resources cause attention of many scientists about pollution of aquatic fresh waters like rivers. One of the most river pollutants is heavy metals. Unlike the organic compounds, these elements do not disintegrate natural processes and have toxic potential risks for living organisms and environment. Metals are the natural components of water ecosystems and most of them are necessary for organisms. Only when the contents exceed the limitation, they can be water pollutants. It is general phenomenon that metal contaminants in aquatics are accumulated mostly in fine sediments. Accordingly, few studies have been done about heavy metals pollution in size fractioned sediments. This study aims to examine the changes of heavy metals concentration in Sefidroud size fractionated sediments as one of the most important and largest river in the country using some common pollution indices. Finally, It also assessed the sources of heavy metals by using multivariate statistical analysis.

Materials and Methods

The study area was Sefidroud river in south west of Caspian Sea ,that have been located within Gilan Province. Its catchment area is about 14041 km² and is located between 50°36'00" and 48°34'00"E longitude and 38°27'00" and 36°34'00"N latitude. According to Iran Meteorological Organization reports, Gilan Province is the rainiest province with an average of 580 mm rain per year in Iran.

The Talesh Mountains and the western Alborz belt as gigantic barrier is located between this territory and Iran inland. This is the only natural connection of the Gilan territory with Iran inside plateau, and is through the Sefidroud valley. Gilan Province is composed by two following regions: The lowlands, adjacent to Caspian Sea and the mountainous region.

Moreover, important and interesting particularities of Gilan Rivers include a massive hydrographic network with a large number of rivers as well as high range of water flow in the rivers. The inundating rivers, is created by transporting circular stone pieces and blocks through under-washing the ridges overlooking the farms and orchards, threaten the cultivated areas and gardens.

According to the data of Iran Ministry of Industries and Mines, 60 active and 19 abounded mines are located in study area. They may release heavy metals into the environment. Coal mining activities are of the examples of mine type in the catchment area.

Sampling sites were located on different geological formations in the catchment areas of the Sefidroud River. Five surface sediment samples were taken from this river from upstream to estuaries during June to July 2013. Surface sediment samples were collected by mini Ekman type grab sampler. All samples were transferred to the laboratory in sealed plastic bags under 1 to 4°C. Grain-size analysis was carried out using wet standard sieving methods for particles larger than 38 µm using sieve shaker (Analysette 3 Pro, Fritsch) and laser grain size analyzer for particles less than 38 µm (Analysette 22, Fritsch) at the Research center for applied geology, Geological Survey of Iran, Sediment logy Laboratory. The 5 collected river samples were separated into six particle size ranges; <38µm, 38-63 µm, 63-125 µm, 125-250 µm, 250-500 µm and 500 µm⁻¹mm by wet sieve shaker for chemical analysis.

Homogenous and powdered samples, bulk and fractional, (0.5 g) were treated with HNO₃/HCl/ HF according to ASTM. Metal concentrations (Cu, Zn, Cr, Fe, Mn, Pb, Ni and Cd) in solution were determined by an

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Inductively Coupled Plasma/Optical Emission Spectroscopy (ICP-OES-730, Varian). For assessing heavy metals pollutions in Sefidroud size fractionated sediments, some common indices (enrichment factor, modified degree of contamination, risk index, degree of sediment toxicity) and were used. In the present research, PCA and HCA were run to interpret obtained data, identify the contaminants probable origins to metal pollution by some common and reliable sediment quality indices and interrelationship size fractioned river sediment with metal risk assessment in aquatic fresh water.

- Assessment methods of sediment pollution

- Potential ecological risk (RI)

Potential ecological risk index (RI) developed by Hakanson to assess ecological risk in lake sediments. It has been used for assessing the degree of heavy metal pollution in aquatic sediments by considering the toxicity of heavy metals and the relation between aquatic systems and heavy metals. So, for assessing aquatic systems, the risk index (IR) has been introduced as a useful instrument in some researches.

- Modified degree of contamination (mCd)

Modified degree of contamination was first proposed by Abraham and Parker to modify degree of contamination suggested by Hakanson. Using mC_d , overall contamination of a sediment sample by multi metal can be assessed instead of assessment of contamination caused by one metal in one sample.

- Introducing the index of sediment toxicity degree ST_d

In the present study a new index of metal pollution in sediment is proposed based on the results of multivariate statistical analysis of the data from the study area. Based on ST_d equation, increase in contaminant concentrations causes an increase in ST_d value, which reveals more degree of contamination.

- Statistical analysis

After preliminary data analysis and specifying categories, multivariate techniques, namely, Principal Component Analysis (PCA) has been found to be appropriate. The PCA technique describes the complete data matrix in a reduced number of principal components (PCs) by transforming the original variables to a new orthogonal set of PCs for describing the relationships among variables and samples. So, PCA has been widely used in heavy metal pollution studies. In the present research, PCA and HCA were run to interpret obtained data, identify the contaminants probable origins to metal pollution by some common and reliable sediment quality indices and interrelationship size fractioned river sediment with metal risk assessment.

Results and Discussion

- Size fractioned river sediment

Generally, size fractioned river sediments are used for a preliminary physical characterization of sediment samples. This phenomenon is emphasized by more researchers because of higher specific surface area in fine particles; larger pollutants such as heavy metals can present them. It was found that more than 29.1% of the river sediment particles at all the sampling sites are between 250-500 μm .

- Size fractioned sediments and metal pollution

Total metal concentrations (Cu, Zn, Cr, Fe, Mn, Pb, Ni and Cd) and statistical parameters of 5 samples across the six particle size ranges, <38 μm , 38-63 μm , 63-125 μm , 125-250 μm , 250-500 μm and 500-1000 μm have been determined. To identify more precisely the status of stations, the obtained values are compared with average amount of sediments and Earth's crust. In particles less than 38 μm , concentration of all heavy metals are much higher than average amount of sediments and Earth's crust. In particles 38-63 μm , except Cu and Ni, concentration of all heavy metals are higher than average amount of sediments and Earth's crust.

- Potential ecological risk (RI)

In all stations, except for particles 63-125 μm , the ecological risk index was medium to significant. Particle size of 500 μm to 1 mm has been low ecological risk index. The particle size 63-125 μm had high ecological risk index.

- Modified contamination degree (mCd)

It can distinguished that all size fractioned sediments except 63-125 μm , have been low and medium contamination. High modified contamination degree has been find in 63-125 μm particles. Also, in these particles, the stations near the estuarine have more pollution index.

- Sediment toxicity degree (ST_d)

It has acknowledged that by decreasing the sediment size, sediment toxicity degrees become higher.

- Statistical analysis

The CA of variables (particles less than 38 μm) according to Pearson Coefficient identified that the main cluster A was made by joining the metals (Cr, Ni and Zn). This means that metals which are located in cluster A may have common anthropogenic sources.

Another main cluster made by Mn, Cd, Cu and Fe named B, originate from natural sources. Finlay, cluster C contains Pb. It seems that Pb originates from anthropogenic sources.

Conclusion

The aim of this research is recognizing the contamination of Sefidroud River sediments and the effects of particle size.

Heavy metals concentrations in six sediment sizes were measured to reach the purpose of this research.

Generally, the results of analysis showed that by reducing the particle size, the heavy metals concentration were more than average amount of sediments and Earth's crust.

Degree of sediment toxicity index showed that with decreasing of sizes, the indexes increasing. Finally, multivariate analysis showed that concentration of some metals like Cr and Ni were high because of anthropogenic sources. Other metals like Fe and Mn have natural sources.

Keywords: heavy metals size fractionated sediment, multivariate statistics analysis, pollution index.

Investigation of Contamination of Groundwater Sources Surrounding Landfill Sites (Case Study: Takestan City Landfill Site)

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Expanded Abstract

Introduction

Nonstop growth of urban population and concentration of industrial and agricultural activities in many parts of the world and Iran have given rise to increased demand for water for different uses. Furthermore, as one important factor for lack of exchange between human and environment resulting in wide exploitation from agricultural lands, mine extraction, and application of various industrial tools, increased population has no role except pollution and contamination. Within this framework, one can view the issue of pollutions from two perspectives of natural resource destruction and development of waste stemming from various consumer goods. It might even have caused great transformations in quality and quantity of waste in response to rapid development of human artifacts and production of chemicals after industrial revolution. Threat to groundwater by landfill sites has always existed in many parts of the world. In particular, in developing countries, as a result of industrial and household wastes, even when there is no hazardous waste at the landfill site, the resulting leachate is still a significant threat to groundwater.

Although through immuring waste, hygienic landfill sites have brought about beauty and cleanliness to the environment and provided people and environment with health and hygiene. They will cause potential adverse effects due to generation of two by products, gas and leachate.

Leachate consists of the extract from the passage of waters mainly ditch water through waste mass containing numerous contaminants. Gas is also produced at the landfill site in response to chemical decomposition and decay of perishable waste and food. This gas mainly consists of methane, some carbon dioxide and volatile organic acids. Although soil is the most important and widely used physical, chemical and biological filter for waters, waste recycler, and a host for many substances, its capacity is limited and many toxins and materials added to soil may become more concentrated and in turn create serious threats to the environment. Greenhouse effects of methane and carbon dioxide gases, development of global warming, suffocation caused by carbon dioxide gas, and explodability of methane are among the effects brought about by gases emitted from landfill sites. The influence of methane gas on world atmosphere and greenhouse conditions is about 21 times as large as the effect of carbon dioxide.

Materials and Methods

Study scope

Takestan city is situated in southwest of Ghazvin in 46° 42' east and 36° 4' northeast (Fig. 1) with an altitude of 1265 m. Except for northwest and west of the city with a relatively steep slope, other regions of the city have a moderate slope. The general slope of the region extends from west to east and gradual decrease of slope has resulted in subsidence of remaining water of Abharrood and Kharrood rivers in the southern part. The maximum slope extending from northwest toward Takestan is around 3% and its average is 1.7% towards northwest. The general slope of the region from Takestan toward Ghazvin northeastwards is approximately 0.3%.

Takestan city, located in the plain of Ghavzin is restricted to Alinaghieh, Aghdagh, and Abuhanifeh altitudes

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from northern, northwestern, and western fronts situated at 7-15 km distance from the city. Regarding the limitation for development of the city in eastern and southeastern fronts, due to presence of vineyards and industrial lands at northeastern front of the city along with artificial barriers of development such as railways at the southern front, the only appropriate direction for urban development is the northwestern front limited by Tehran-Zanjan highway. On the other hand, since the region is earthquake prone and there are some known faults including Parandak, Ipek, Shtehard, Geshlagh, and Abyek, vertical development of the city is only possible by following Earthquake Code 2800 in urban constructions. The general slope of the city is about 2% from northwest to southeast and is 0.3% from west to east.

Sampling network

Samples of groundwater and leachate were analyzed chemically in laboratory after sampling followed by measurement of heavy metal concentration together with BOD5 and COD.

According to the main objective of the research, 5 sampling stations were specified within the study area from which water samples were taken in Mehr of 1393. In order to investigate the trend of qualitative variations, the obtained results were further compared with the results of 1393. Four sampling stations were selected from Takestan landfill downstream (A,B,C,D) and the fifth one (E) was selected from landfill upstream so that the potential effect of leachate on groundwater resource contamination within the study area be investigated more accurately. The leachate sample was further analyzed and the results were then compared with discharge standards. The location of sampling Table 1 presents the coordinates of sampling stations used in the study area.

Table 1. Coordinates of sampling stations within the study area

Station	Coordinate	
	X	Y
A	379540	3999343
B	381776	3985909
C	385212	3994738
D	377755	3987955
E	346979	3960313

Determination of concentration of qualitative parameters

The studied parameters were electrical conductance, pH, TDS, TSS, BOD, COD, Na, Ca, and some heavy metals (including copper, zinc, iron, lead, chromium, cadmium, molybdenum, manganese, nickel, and aluminum).

Qualitative standards of water

In order to analyze water standards qualitatively, some valid standards presented by Iranian institute of industrial research and standard, the standard of potable water in the country water industry, world health organization, and European Union potable water standard were used for drinking usages.

Results and Discussion

The qualitative parameters measured with water sampling included pH, EC, TDS, TSS, BOD, COD, Na, Ca, and some heavy metals (including copper, zinc, iron, lead, chromium, cadmium, molybdenum, manganese, nickel, and aluminum).

Conclusion

The comparison of qualitative parameter values in Takestan landfill leachate in 2004 and 2014 indicated reduced value of most qualitative parameters, particularly heavy metals in 2014 in response to alterations of landfill reactions (acidic conditions to methanogen).

The comparison of qualitative parameters values in leachate with the national standard of discharge to surface waters and absorbent wells manifested that Takestan landfill leachate both in 2004 and 2014 has had values (for most contaminants) higher than national standard of discharge. Therefore, it should not spread into the environment easily and with no proper management.

The comparison of analysis results of groundwater qualitative parameters within the study area revealed a significant increase of some contaminants particularly heavy metals. The probable reason could be leachate leakage to the environment and permeation to groundwater resources in the vicinity of landfill.

Concentration of lead, cadmium, and nickel in water samples had the largest violation from national and international qualitative standards compared with other studied contaminants.

Regarding the ascending trend of many studied contaminants (especially heavy metals) in water samples next to Takestan landfill, it can be stated that the leachate emitted from the landfill may have had a significant impact on the contamination of water resources around the landfill.

Keywords: BOD5, heavy metals, landfill, leachate, Takestan.

Vulnerable Areas of Malekan Plain Aquifer for Nitrate, Using Random Forest Method

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Expanded Abstract

Introduction

Management of groundwater, especially in dry regions such as Iran, is essential and this concern becomes further important with development of agriculture, industry, population growth and climate changes. This can affect the quality and quantity of groundwater resources. Hence, groundwater contamination can treat the human health. Since groundwater moves slowly through the subsurface, the impact of anthropogenic activities may last for a relatively long time. As a result, the environmental measures should mainly be focused on the prevention of the contamination. One of the ways to prevent the groundwater contamination is to identify vulnerable regions of the aquifers and make a suitable management of land use. The assessment of groundwater vulnerability maps requires the application of diverse methods and techniques, based on the hydrogeological knowledge of the region under research and on the application of predictive models. With the aim of deciding which areas are vulnerable a large data volume can be collected which cannot be effectively analyzed without an adequate and efficient model. Several methods have been devised to vulnerability mapping that relatively using fewer data and based on evidence of contamination. In this study to overcoming the problems of other methods the random forest (RF) algorithms is proposed.

Materials and Methods

Malekan plain is located in East Azarbaijan Province, Southeast Urmia Lake in northwest of Iran, with 450 Km². This region is one of the very active cultivated areas which its water demands is supplied by groundwater resources. In recent years, groundwater quality of the area is encountered with degradation problem. Malekan region have different geological formations such as Lalon, Shemshak, Lar formations, and a large part of the area in the western part is alluvial deposits of Quaternary. Aquifer of this plain is unconfined, which mainly formed by old and recent alluvial terraces, alluvial fans and fluvial sediments. Based on drilling wells logs and geophysical data, the west part of the plain is made of fine grained material with low permeable deposits.

According to farming and existing of grape farms in this region and intensive use of fertilizers and manure, groundwater nitrate concentration of the aquifer is high (Fig. 1). To evaluate the quality of groundwater resources, especially the assessment of nitrate anomalies in groundwater of the Malekan plain, 27 samples were collected from groundwater resources in September 2014, and Hydrochemical analysis were carried out in Hydrology Laboratory of Tabriz University. In this study, the random forest (RF) algorithms are proposed. This is a learning method based on ensemble of decision trees. The RF technique has advantages over other methods due to having, high prediction accuracy, ability to learn nonlinear relationships and ability to determine the important variables in the prediction. In this paper, RF method is used to estimate the Malekan Aquifer vulnerability, with four sets of data,

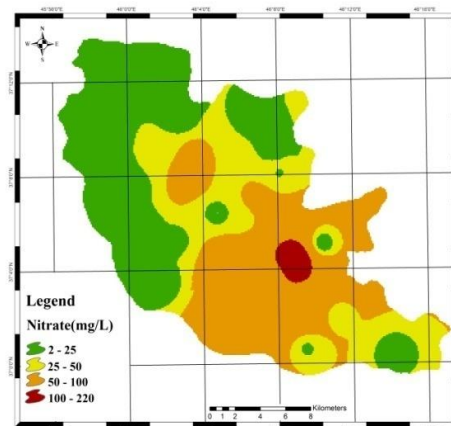


Fig. 1. Spatial distribution of nitrate concentration

including A model with all variables, B model with the variables related to characteristics of the aquifer, C model with driving forces variables, and D model with the variables related to the DRASTIC method. The predictions derived from all possible parameter combinations were evaluated using the Root Mean Square Error (RMSE) and mean square error. The area under the curve statistic (AUC) was used to determine which models and which combination of dataset is performed better. An AUC value of 1 is considered perfect.

Results and Discussions

From 23 explanatory variables used in the model, five variables (depth to water table, hydraulic conductivity, and distance to grape farms, hydraulic gradient, and transmissivity) can describe the nitrates behavior in the Malekan plain aquifer with more accuracy, since a smaller MSE was obtained. In order to obtain continuous and standardized variables for all area of the study, all data were transformed into a raster format, and were applied mainly three different approaches: 1. geostatistical techniques (e.g. hydraulic conductivity, hydraulic gradient and soil texture), 2. Euclidian distance raster calculations (potential point sources of contamination) and 3. classification of land cover from remotely sensed data and NDVI. In this paper, RF method is used to estimate the Malekan Aquifer vulnerability, with four sets of data, including A model with all variables, B model with the variables related to characteristics of the aquifer, C model with driving forces variables, and D model with variables related to the DRASTIC method. In order to set the value of k from which the error converges and also makes estimation more reliable, the models are made up of 1000 trees were generated from all explanatory variables. The parameter was optimized by changes in the number of split variables between 1 and the maximum number of variables of every subset. The resulting models were evaluated using the OOB error estimation. For the selection of the most accurate model the one in which the OOB error was the lowest is determined. Moreover, with the aim to reduce the dimensionality and improve the accuracy and interpretability of models, a FS strategy was adopted. The most significant predictive features were selected by using the importance measures of RF. These vectors formed the input to the RF algorithm and are known as input-feature vectors. The binary response variable (nitrate pollution) was used as target values for the training of the algorithm. In this study, which four models were used to predict nitrate contamination of groundwater, as shown in Figure 2, A and B Models, respectively, with RMSE equal to 0.11157 and 0.12214, predicted approximately 44 and 42 percent of the region's in the high vulnerability that located in the central and eastern parts of the aquifer. However, C and D models, respectively, with RMSE equal to 0.1392 and 0.1597, predicted approximately 15 and 24 percent of the region in the high vulnerability and could not be trusted in assessment of groundwater vulnerability.

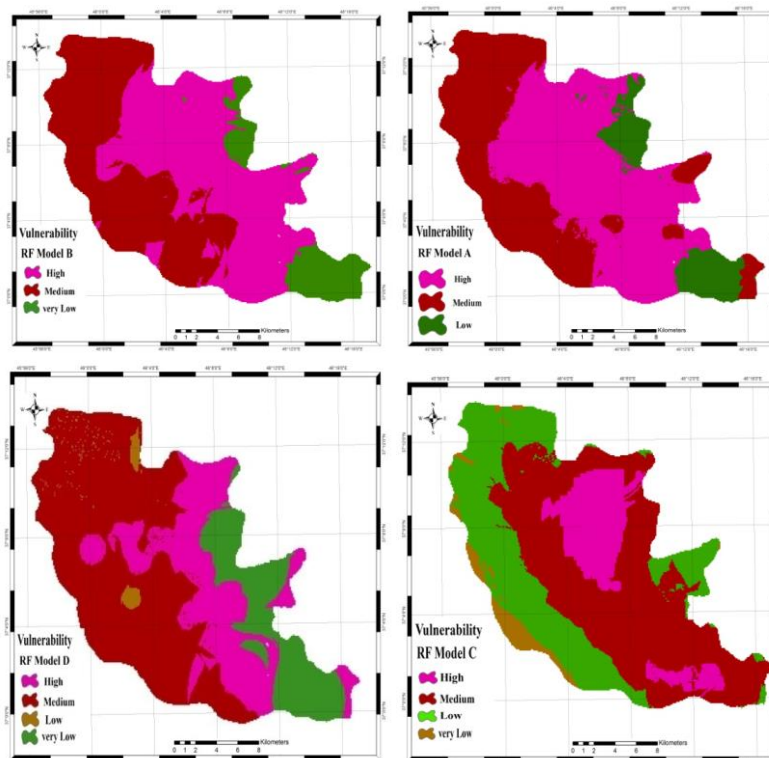


Fig. 2. Vulnerability Map of the four models. A) All variables, B) variables related to characteristics of the aquifer, C) driving forces variables, and D) variables related to the DRASTIC

Conclusion

The least significant explanatory variables of every subset were reduced until reaching the minimum error rate. Nitrate concentration was rescaled to a new response variable for every experimental sample: samples with nitrate concentrations higher or equal to the threshold value were given a value equal to 1 and samples lower to the threshold a value equal to 0. The explanative variables (predictors) and response variable were combined together into a set of input feature vectors.

Keywords: groundwater, Malekan Plain, nitrate, random forest, vulnerability.

Evaluation of Infill Development Capacity in City Center of Tehran

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Expanded Abstract

Introduction

New urbanization evolution in the world and emergence of new urban problems make downtown areas in adverse effects of urban development more than other urban areas. In the third world cities, this is due to rapid urban growth, influx of immigrants, lack of planning, etc... Problems of downtowns appear more severe when it is posed as a national issue. The old neighborhoods not only are considered as the memorial of culture and city history but they are also as an investment which can meet present and future needs of residents.

This attitude towards old neighborhoods assumes that these areas have the abilities and potentials such as infrastructure, vacant land and abandoned building which have the capacity of reuse and redevelopment. As a result, planning for redevelopment of these areas is essential case in most cities.

Infill development can be associated with development of urban centers, where such projects are used to restore city center neighborhoods. In fact, infill development could be proposed as a response to sprawl, a process which makes urban centers remain stunted and away from urban development.

The first step towards infill development is to find a method to measure development capacity. Thus, it is essential to use an appropriate approach to evaluate the development potential. One of the references in measuring development potential is Solimar research group which analyze and evaluate infill potential development broadly.

The question that this study is formed for is that: "Does the capacity development measurement in city center of Tehran reflect that it has lands with redevelopment potential?" This study is aimed to evaluate infill development potential in city center of Tehran. This evaluation is based on the criteria which derived from theoretical and empirical literature on subject. After introduction of infill development's indicators, it is time to evaluate theme in region 12. To achieve this issue by using Geographic Information System (GIS), prepare layers of indicators, overlaying criteria layers, then by using analytical hierarchy process gives priority to divisions of region 12.

The results indicate that all six division of the region 12 have capacity of development and among these six divisions, division 3, 2 and 4 have the highest rank.

Materials and Methods

Region 12 of Tehran city contains historical core of Tehran. Center of Tehran as a focus of city, and center of trading, business, aggregation of social, cultural, religious activities is referred as correlation core.

Tehran city center is about 1600 hectares in area. Region 12 consists of 6 districts and 23 neighborhoods. About 27 percent of this region has 400-year history and 73 percent of that has over 200-year history. Despite these values, over one third of this area is depressed and out of work. In fact, the historical center of Tehran is increasingly vulnerable and in a process of deterioration.

The method of research is descriptive, and data collection method is document review and library studies. Document review and library studies include surveying data, books, journals, articles, urban plans etc. Data collection in the research theoretical frame work and deriving research indicators are used in development capacity assessment.

Geographic Information System (GIS), Microsoft Excel, Analytical Hierarchy Process and Expert Choice are used in analytical section to analyze quantitative indicators of this research.

Table 1. Conclusion of infill development point of view

	Principles		Approach	index
Infill Development	1. Housing Development	1. Zoning	Changing zoning regulation	1. Vacant Land
	2. Mixed Development	Regulation	Changing density regulation	2. Undevelopment Land
	3. Transit – oriented Development	2. policies of master plans		3. brown field areas
	4. Compact Development	3. regulation flexibility		4. abandoned lands
				5. abandoned building

The purpose of evaluation of infill development is providing a flexible method to identify potential lands and parcels. Thus, in order to assess development capacity, as mentioned before, the tools which is used in this study are Geographic Information system (GIS), Data base software (Excel), using Analytical Hierarchy Process (AHP) through Expert Choice software.

Indeed, using geographic information system, infill development opportunities in parcel scale are identified and these opportunities are assessed quantitatively (numbers of parcels, areas ...) by Excel. For this purpose, first, layers of each criterion are generated in GIS and layers of each group overlaid, and finally the map of potential parcels and areas are created. Next step is ranking of 6 districts of region 12 (city center of Tehran). They have the highest capacity of development achieved by using Analytical Hierarchy Process through Expert Choice software.

Results and Discussion

Population density criteria: Low population density has a high potential for development. Among the divisions of region 12, districts 1 and 2 have the lowest population density in the area. Dominant land use of these two districts is business zone. Due to dominant use and lower rate of residential use in these divisions, population density is the lowest among the divisions.

Land Criteria: Land criteria include three indicators: vacant land, abandoned area and brown field. In city center of Tehran, vacant land includes around 56 hectares, abandoned area 46 hectares, and brown field around 160 hectares. The most concentration of these three indicators is in the district 3.

Building Criteria: This criterion includes two indicators: quality of building and floors of building. Quality of building includes buildings and lands which encompass destructive structures. Among these 6 districts in region 12 of Tehran, district 3 is the most in area with low quality of buildings.

Floors of buildings used as an indicator in assessment of development capacity. Low story buildings can be considered as a development potential. Tehran city center unlike other downtowns around the world has a very low height. This suggests that Tehran's downtown has great potential in terms of development density.

Access to public transportation criteria: Access to public transportation is a basic feature of a successful infill development. Thus, blocks and parcels with convenient access to public transportation are considered as a potential development. Access to public transportation criteria has two indicators: access to bus stations and access to metro stations. Assessment of these two indicators represent that approximately most of the area has an appropriate access to public transportation stations.

Regulatory criteria: This criterion is covering five indicators including redevelopment lands, stagnant areas, high density zones, residential zones, mixed-use zones. These five categories are mentioned and determined in Tehran comprehensive plan and detailed plan of region 12. In this study, they are used as development capacity. In region 12, 9 parcels with 33 hectares are allocated to redevelopment land. In this category, division 4 has the most concentration of redevelopment lands.

The total area of stagnant area in region 12 is about 641 hectares and district 3 has the most stagnant area in the city center of Tehran.

According to master plan and detailed plan zoning, about 574 hectares is allocated to high density construction. Due to historic characteristic of division 2 and 3, in order to preserve and maintain valuable building, lack of high density zoning in these two districts is acceptable.

Residential development is a main element of infill development which causes revitalization and returning population to city centers. Among these 6 districts, districts 5 and 6 have the most potential of residential development in the region.

Mixed use development is a principle of infill development in order to enhance livability of neighborhoods. District 1 has the most potential of mixed use development in city center of Tehran.

After preparing the layers of criteria and indicators and overlaying them, it's time to rank these 6 districts to find out which of them has the most capacity of development in the area. Analytical Hierarchy Process through

Expert Choice software indicated that among the 6 districts of region 12, division 3, 4 and 2 have the highest potential for development.

Conclusion

In this study, surveying and analysis of infill development criteria and indicators in city center of Tehran represent these results:

Population criteria show that region 12 has a low population density so this area has a potential to attract population.

Surveying land and building criteria indicate that the city center of Tehran have the areas with capacity of development. It also reflects high dysfunction and deficiencies in the region 12.

Access to public transportation criteria indicates that the whole region has the appropriate and convenient access to public transportation.

Surveying and analysis of urban plan regulations show that these regulations not only act as a deterrent to development but also they have development capacity.

Assess and evaluation of development capacity in region 12 indicate that all divisions have five introduced criteria but in different proportions. The ranking results indicated that district 3 has the highest capacity of development among the 6 districts.

Keywords: city center, evaluation of development capacity, geographic information system, infill development.