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## Optimizing pulp and paper wastewater treatment by using of Fenton Advanced Oxidation Method

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### Expanded Abstract

#### Introduction

The complexity and diversity in paper production process and high volume of water consumption in each stage have made the paper industry as one of the largest industrial consumer of water after the chemical and metal industry. High water consumption is between 76 to 227 cubic meters for per ton of product. The wastewater, in addition to high flow, contains high concentrations of BOD, COD, pH, suspended solids, color and turbidity. More than 250 chemical substances have been identified in various stages of paper production. Apart from a large variety of pollutants and their complex structure, many of the wastewater compounds are poorly soluble in water, and their resistant to treatment methods, particularly biological treatment and reddish-brown color of the pollutants led to many problems for treatment processes. All of these factors have made the treatment of paper industry wastewater as the most difficult one that associated with the complexity in the processes. The majority of pulp and paper industrial wastewater arises from pulping process and depending on the type of pulping process, wood and paper and industry produces various pollutants. Raw materials for the pulp of OCC (Old Corrugated Container) unit supplied from waste paper and cardboard. Raw materials to produce Kraft pulp are from broad-leaved and conifer trees. The literatures reviewing show that a variety of methods have been used for pulp and paper wastewater treatment:

1. Physicochemical treatment: settling/ flotation, coagulation/ sedimentation, adsorption, chemical oxidation, membrane filtration, ozonation
2. Biological treatment: activated sludge, aerated lagoons, aerobic biological reactor (SBR), anaerobic treatment method (UASB), fungi treatment and combined treatment process.

Due to environmental consequences and low operating cost, biological treatment methods are generally preferred and these are conventional method for treating wastewater containing organic materials. The biological treatment method is activated sludge system. This system produces sludge with variable settling characteristics and often is sensitive to loading shock and toxicity and their capacity to remove biodegradable toxic substances is extremely low. In addition, the barriers to biological systems require large surface area, difficulty of microorganisms' population control, pH, temperature and nutrients control and sludge bulking. Using of biological treatment methods has been restricted for pulp and paper wastewater due to the presence of toxic compounds with low biodegradability. For this reason, using of chemical methods has become more acceptable. Among chemical processes, advanced oxidation processes are used for reducing organic load or toxicity of different wastewaters. Therefore, this method has become a competitive technology to remove organic contaminants that are refined by conventional methods. Based on hydroxyl radical's production chemical oxidation is the oxidizing agent in order to mineralize wastewater complex chemical compounds. Hydroxyl radical is a strong oxidizing agent with oxidizing power of 2.23 V compared with conventional oxidizers. Fenton process ( $H_2O_2/Fe^{+2}$ ) is one of the most common advanced oxidation processes, which are used for wastewater treatment that can be applied to different scales because of its ease of implementation, low reaction time, using of coagulation and flocculation process and non-toxic compounds and its low economic cost in comparison with the other methods.

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## Materials and Methods

Studied wastewater was prepared from pulp and paper mill in Iran. In the investigated factory, depending on the used process, a Kraft pulp or OCC pulp, two kinds of main wastewaters are generally produced, one of them is fiber wastewater and other is alkaline wastewater. Considering the type and volume of produced wastewaters, a mixture of the two wastewaters (the ratio of 3 to 1) was transferred to the laboratory to evaluate the treatability. In this study, for optimizing the variables, five pH, temperature, reaction time, iron concentration and hydrogen peroxide concentration factors are considered. For optimizing these factors, the response surface methods (RSM) of minitab17 software were used. Response surface methodology based on Central Composite Design (CCD) is one of the statistical methods in designing experiments, modeling, evaluating the effects of several factors, optimal conditions for an ideal response and reducing the number of tests. In this investigation, a three levels Central Composite Design was used including 33 experiments and studied variables in down, up and central levels that encoded with +1, 0 and -1. The number of 33 designed experiments related to the Fenton process was done discontinuously in a 500 ml pyrex cylinder as a pilot scale. The mixture of fiber and alkaline wastewater were transferred to the pyrex and it was placed on a magnetic stirrer equipped with a thermostat to adjust the temperature. Given that the Fenton reaction occurs in an acidic environment, to set the pH of wastewater with 1M sulfuric acid ( $H_2SO_4$ ), it was subjected to the specified concentrations of iron salt (II) ( $FeSO_4 \cdot 7H_2O$ ) as a catalyst and finally, the specified concentration of 30% (w/w) hydrogen peroxide ( $H_2O_2$ ) was added to it slowly. Thereafter, the wastewater was stirred at 10 rpm for 25 min. When hydrogen peroxide was added to the solution, it was considered as the start time of the reaction and thereafter, the stirring was stopped and the flocs formed were allowed to settle for 1 h. At the end of the reaction time, 1 M sodium hydroxide (NaOH) was added to the wastewater mixture to neutralize until the wastewater pH is raised to 8; then, 2 mg/L of polyelectrolyte was added into the separation tank of liquid from solid as a co-coagulant. COD measurement was performed by using of the reactor and closed reflux method (5220 D), according to the standard methods instructions.

## Results

The results showed that to remove organic matters and achieve to the maximum COD removal efficiency, the optimum values of pH, reaction time, reaction temperature, Fe (II) and  $H_2O_2$  concentrations are respectively 3.5, 17.5 min, 32.5° C, 6 Mm and 27.5 Mm. In these conditions, COD (chemical oxygen demand) removal percent of pulp and paper wastewater is more than 90.7% as the following diagram. The results of the variance analysis (ANOVA) to test the utility of the model are according to the Table 1.

Table 1. The results of the variance analysis of response surface quadratic model in COD removal

| Changes Source | Degrees of freedom (Df) | Sum of Squares | Mean Square       | F-Value   | P-Value               |
|----------------|-------------------------|----------------|-------------------|-----------|-----------------------|
| model          | 28                      | 3445.3         | 38.8              | 50.46     | 0.001 (significant)   |
| residual       | 5                       | 53.11          | 7.59              |           | –                     |
| Lack -of -fit  | 2                       | 23.6           | 0.91              | 1.4       | 0.878 (insignificant) |
| Pure error     | 3                       | 29.51          | 6.68              | –         | –                     |
| total          | 33                      | 3498.11        | 46.39             | –         | –                     |
| $R^2=0.985$    | $R^2_{predic}=0.83$     |                | $R^2_{adj}=0.965$ | Press=515 |                       |

The high amount of  $R^2$  and its proximity to the number one indicate that COD removal can be well defined by this model and the model is suitable. The significantly of the model for COD removal is expressed by the amount of F, which is equal to 50.46. Also, no significantly of the lack of fitting test is confirming data well-fitting with the selected model. This means that there is not any significant ratio between the lack of fitting and the amount of the pure error.

## Discussion

According to the studies, pulp and paper wastewaters have biodegradable indicators ( $BOD_5/ COD$ ) less than 0.3 and are resistant to biological treatment. In pulp and paper, industries where using wood pulping process, more than 40% of the produced organic materials have low degradability.

Surveying the research results shows that, RSM method is an effective way to optimize variables in Fenton process and the predicted values by the model is compliance with the results of the experiments. Fenton reaction has high efficiency for treatment of pulp and paper wastewater. This treatment depends on several variables. The pH value should be adjusted to provide the stability of the catalyst. Iron remains stable in an acid environment

and the potential of reaction system is reduced.  $(\text{Fe (II) (H}_2\text{O)})^{+2}$  is produced in pH lower than 3.5, which has less reactivity with hydrogen peroxide. Producing a smaller amount of hydroxyl radicals reduces efficiency of the organic matters decomposition. What is important at very low pH is the effect of aggregation hydroxyl radicals by hydrogen ions, which prevents the reaction of Fe (III) with hydrogen peroxide. At pH more than 3.5, the decomposition rate of the organic matter is reduced due to the decrease of free iron ions in solution, which is in order to formation of iron (II) complexes with preventing buffer of the free radicals. At this pH, Fe (III) begins to precipitate as ferrous hydroxide, degrades  $\text{H}_2\text{O}_2$  to  $\text{O}_2$  and  $\text{H}_2\text{O}$  and prevents the formation of iron ions. In addition, the oxidation potential of OH radicals decreases by increasing pH. So, Fenton process efficiency in degrading of organic compounds at very low pH and also at high pH is reduced and the optimal pH is 3.5. In this process, organic compounds will be removed in two stages of oxidation and coagulation. The hydroxyl radical  $\text{OH}^\circ$  is responsible for oxidation and coagulation of the iron complex formation. Relative importance of oxidation and coagulation depends on the initial ratio of  $\text{H}_2\text{O}_2/\text{Fe}^{+2}$ . Chemical coagulation in low ratio of  $\text{H}_2\text{O}_2/\text{Fe}^{+2}$  is dominant, whereas chemical oxidation is dominant in higher ratio. Review of the literature shows that the optimum ratio oxidizing to catalyst is 5:1 in Fenton reactions, which the optimum ratio in this study is very close to this ratio (4/6:1). In oxidation process, oxidizing dosage should be selected carefully. Applying the additional hydrogen peroxide leads to increasing COD and the presence of excess hydrogen peroxide is harmful to most of the microorganisms and if the Fenton process is used as a pretreatment before biological process, it reduces treatment efficiency. The concentration of  $\text{H}_2\text{O}_2$  and Fe (II) is two interrelated factors that affect the Fenton process. At higher concentrations, iron has deterrent role and because of production, radicals' consumption decreases the efficiency of the process.

There are not many studies on the reaction temperature, but the reaction temperature is an effective parameter in Fenton process; in fact, temperature arising increases the reaction kinetics. Fenton reaction has a short reaction time in advanced oxidation processes, so when high COD removal is desired, it can be used. Fenton process can be an appropriate alternative by the reasons of simplicity of technology and the iron and peroxide are relatively inexpensive and non-toxic. From an economic standpoint, applying the Fenton process as a pretreatment can reduce treatment costs and increase biological treatment efficiency. Several researches have studied the application of advanced oxidation processes as a pre-treatment of biological treatment. In a study (Vlyssides et al., 2008), the effect of pretreatment of pharmaceutical wastewater was investigated by Fenton process before biological treatment. The purpose of performing this study is investigating the treatability of pulp and paper wastewater by using of Fenton method and optimizing the experiences by RSM method, as it was mentioned in literatures reviewing. For further studies, combined method and the lower dosage of the oxidizing agent ( $\text{H}_2\text{O}_2$ ) and catalyst ( $\text{Fe}^{2+}$ ) can be used for decreasing the costs of chemical materials.

## Conclusions

So, considering the previous studies, to reduce the wastewater organic load, color removal, its bio-degradability improvement and also increasing treatment efficiency, is suggested that, first, the wastewater being pre-treated by using of oxidation process and after increasing the wastewater biodegradability, it enters into biological system. Generally, based on the results of this study and considering that the Fenton oxidation is able to remove 90.7% of organic matters in the wastewater and the final COD does not in accordance with the surface water discharge standards, it is suggested to use biological method after the oxidation method.

**Keywords:** fuzzy simulation, industrial wastewater, optimization, Zeolite.

## Biosorption of cadmium and lead from aqueous solutions using *Spirogyra*

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### Expanded Abstract

#### Introduction

Heavy metals are the most important pollutants for the environment and human and are a serious threat because these elements have properties such as toxicity and carcinogenicity. Heavy metals are accounted to cause universal and serious issues that have very high toxicity for the health of human being as well as environment. Though heavy metals are classified into two groups of essential and non-essential elements, nickel, iron, copper, zinc and manganese are namely the essential elements required for growth and development of plants, but cadmium is not essential for the living being. The cadmium element widely entered the environmental cycle from industrial wastewater, such as metal plating, phosphate fertilizers, minerals, paints, batteries (cadmium-nickel batteries), alloys and steel industries. Cadmium is simply absorbed by the human pulmonary and digestive system and accumulated in the human body, causing kidney failure, muscle contractions and nausea. It can also be causes to diseases such as lung and prostate cancer, anemia and bronchitis. Cadmium excretion is very slow and the biological half-life of this element in the human body is between 10 to 30 years. Among the various metal ions in wastewater, lead is one of the most common toxic metals. This toxic and deadly element mainly accumulates in bones, brain, kidneys and muscles. Different methods such as filtration, electrochemical purification, oxidation, reverse osmosis, coagulation and ion exchange are used to remove heavy metal ions from aqueous environments. Often, these methods have disadvantages and limitations such as time-consuming, low efficiency, high operating costs and production of secondary pollutants. Biosorption of heavy metals from environments and water resources is a strategy effective and environmentally friendly. The reasons for this are the removal of high efficiency, the low cost of the process and the possibility producing high amounts of adsorbent. The biological removal process of pollutants is carried out by organisms such as bacteria, fungi, single cells and algae. But due to the presence of polysaccharides in the cell wall of algae and their abundance in different ecosystems, these organisms have a higher ability to remove heavy metals from aqueous solutions. This is the case caused to more attention of the use of algae in the biosorption process. The aim of this study is use of *Spirogyra* algae to investigate its application to remove cadmium and lead from the aquatic environment.

#### Material and Methods

##### Preparation spirogyra algae

Biomass was collected from a subterranean Birjand city. Then washed with distilled water and remove the dirt direction of reducing the amount of water was filtered by the filter paper. After four days, biomass was exposed to sunlight and dolloved by oven dried at 70°C for 24 hours. Finally, biomass was sifting to particles with a size between 150 to 250 mesh.

##### Cadmium and lead adsorption experiments

The stock solutions of cadmium and lead (1000 mg/L) using cadmium nitrate and lead nitrate dissolve in deionized water were prepared. Then the standard solution in order to perform experiments using dilute the stock solution was prepared. At first in order to determine the optimal pH, dissolved in 6 ml Erlenmeyer flasks 50 ml metal cadmium initial concentration of 3 mg/l and six other Erlen containing 50 ml of solution with initial concentration of 3 mg of lead ions shed. Using 0.1 normal NaOH solutions of and HNO<sub>3</sub> at pH 3, 4, 5, 6, 7 and 8 set, to each amount of adsorbent was added 3 g/l. Solution for 30 minutes at 200 revolutions per minute on a

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shaker device was and after passing through Whatman filter paper has been that in the liquid fraction dissolved being separated from the solid part. Finally, in the concentration of pollution, this solution was conducted by atomic absorption. In order to check the call time, 3 g/l of adsorbent was taken and 50 ml of 3 mg/l of lead and cadmium solutions under conditions of pH optimum duration of 10, 20, 30, 40, 60 and 90 minutes was mixed and the amounts of cadmium and lead ions absorbed by the adsorbent during this time were measured by atomic absorption spectrometry. To determine the optimal amount of adsorbent, the values 1, 2, 3, 4, 5 and 6 g/l to 50 ml of solution of cadmium and lead were added. This step was performed at pH optimum contact time. At the end, after filtering and separating the solid phase by atomic absorption, spectrometry was used to measure the absorption rate. In order to determine the optimal concentration of cadmium and lead ions, dissolved in 50 ml in concentrations of 0.5, 1, 2, 3, 4 and 5 mg/l of cadmium.

The equilibrium absorbance capacity was calculated by using Equation (1).

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

In order to calculate the percentage of cadmium and lead removal (%R), Equation (2) was used.

$$\%R = \left[ \frac{C_i - C_e}{C_i} \right] \times 100 \quad (2)$$

Today, different equations and isotherms have been developed to investigate adsorption and describe the adsorbent behavior. In this study, Langmuir isotherms, Freundlich and Temkin were used.

Absorption kinetics is used to determine the control mechanism of adsorption processes. Two kinetic models including pseudo-first-order and pseudo-second-order kinetics models were used to study the kinetics of cadmium and Lead adsorption.

## Results and Discussion

Results related to the influence solution pH on cadmium and lead ions shows the minimum efficiency of adsorption of cadmium and lead equal to 42.15% and 37.15%, respectively happened in pH =3. The lead and cadmium uptake pattern by increasing the pH ascending finds. Then the pH above 6 performance adsorption process is reduced, so pH=6 and pH=5 for cadmium and lead were determined as an optimal pH. Results related to the influence contact time on cadmium and lead removal efficiency show that the highest adsorption rate at the initial time has taken place. This is identified the speed and high ability adsorbents in the removal of cadmium ions are and lead. According to the results, maximum removal time of 30 and 40 minutes for cadmium and lead were obtained. By increasing the amount of adsorbent, adsorption percentage of cadmium ions lead increases. Because increased adsorbents, the number of places available adsorption increases. But this process reached a certain size of adsorption against certain concentrations of cadmium lead continues and after it was changed to increase the amount of adsorption which isn't observed in the adsorption. Lead and cadmium remove this increase due to an increase in the number of places available. With increasing concentrations of cadmium and lead ions removal efficiency is reduced, so that the concentration of 5 mg/l, the lowest level reaches. As a result, decreased adsorption of active sites on the surface is adsorbent. In the present study, with increasing the initial concentration of this heavy metals cadmium, lead removal efficiency is reduced. In fact, the results of this research showed that lead and cadmium removal efficiency with initial concentration is inversely. The reason for this is that the absorbers have a limited number of active sites and are saturated at high concentrations. The results of the Langmuir, Freundlich and Temkin isotherm models showed a high correlation coefficients for all. But, according to the data, Freundlich model for cadmium and lead has the highest correlation coefficient, that respectively the amounts of are 0.9914 and 0.9816. Thus it can be concluded that cadmium and lead uptake by the spirogyra algae process balance data is better follow in Freundlich model.

## Conclusion

Results of this research showed that under the optimum conditions, the highest removal efficiency cadmium (83.5%) at 6 pH, with initial concentration of 2 mg/l and 3 g/l the adsorbent for 30 minutes and the highest percentage of removal of lead (75.84%) at 5 pH for 40 minutes with initial concentration of 2 mg/l and 4 g/l adsorbent happened. Compare isotherm models Langmuir, Freundlich and Temkin adsorption process showed that Freundlich model is better in cadmium and lead follow. Also, results of kinetic studies showed that removal of cadmium and lead from pseudo-quadratic models comply. In general, the results of this study showed that the algae spirogyra efficiency and high ability in remove heavy metals cadmium and lead has its aquatic environment.

**Keywords:** adsorption isotherms, aquatic environment, cadmium, lead, Spirogyra algae.

## Investigation of heavy metals concentration in vermicomposting of soft peel of pistachio, municipal activated sludge and spent mushroom compost

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### Extended Abstract

#### Introduction

Solid waste management is one of the biggest challenges faced by the whole world. Increase in the world population which itself leads to the increase in solid waste production has made this problem more and more complex (Singh et al., 2011). Vermicomposting technology using earthworms for recycling organic wastes has been recognized as an eco-friendly and suitable approach for recycling and managing biological wastes (Padmavathiamma et al., 2008). But, the presence of heavy metals in the vermicompost and the danger of the entry of these metals into the food chain is a genuine threat as far as the living beings are concerned (Azizi et al. 2013). Heavy metals such as nickel, cadmium, copper, zinc, manganese, chromium, and lead in a limited amount are required by the plants for a normal growth. On the other hand, high concentrations of these elements have devastating effects on plant growth (Nayak & Kalamdhad, 2013). One of the ways for the removal of these elements from the contaminated soil is using tissues of organisms such as plants or invertebrates such as earthworms (Edwards & Arancon, 2004). Due to the accumulation of heavy metals in the intestines of earthworms or due to deformation of metal complexes in the process, these heavy metals change from an accessible to an inaccessible form and the danger of these metals in the agricultural wastes is neutralized (Song et al., 2014). In this study, soft peel of pistachios has been used for vermicomposting. According to the report submitted by Food and Agriculture Organization (FAO), Iran is the world's largest producer of pistachios. As being witnessed in the last few years, the total by-products obtained from pistachio cultivation has increased by a rate of 310,000 tons which in itself has changed into an environmental problem (Ghasemi et al., 2012). As no practical solution is available for this issue, in this study we have tried to make an optimal use of soft peel of pistachios for vermicomposting thus changing it into a useful material and we have also studied the change in heavy metals concentrations in vermicomposting of these wastes.

#### Materials and Methods

Pistachio waste was collected at the time of pistachio harvest. So as to remove any present phenolic compounds, the waste was mixed with coal powder and then was subjected to pre-composting. Municipal sludge and spent mushroom compost (SMC) were used in order to adjust the C/N ratio. In the next step, 2.5 kg of the dry weight of the main raw material comprised of different percentages of soft peel of pistachios, municipal activated sludge and SMC were filled in 12 beds and about 120 gr of the worm "Eisenia fetida" were added to each of the treatments. These treatments were analyzed and studied for a period of 70 days. Composition of various treatments shows in Table 1.

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Table 1. Composition of various treatments for the vermicomposting experiment

| Treatments | SMC (%) | Municipal activated sludge (%) | Soft peel of pistachios (%) |
|------------|---------|--------------------------------|-----------------------------|
| A          | 0       | 0                              | 100                         |
| B          | 0       | 100                            | 0                           |
| C          | 100     | 0                              | 0                           |
| D          | 30      | 30                             | 40                          |
| E          | 20      | 20                             | 60                          |
| F          | 10      | 10                             | 80                          |
| G          | 60      | 0                              | 40                          |
| H          | 0       | 60                             | 40                          |
| I          | 40      | 0                              | 60                          |
| J          | 0       | 40                             | 60                          |
| K          | 20      | 0                              | 80                          |
| L          | 0       | 20                             | 80                          |

### Analysis of heavy metals

At the end of the process, a sample of about 1 gr of dry and powdered vermicompost was gathered from all beds and was reduced to ashes in a furnace at a temperature of 550°C. 10 ml<sup>2</sup> NHCl was added to the sample, after the absorption of the acid, the quantity of the acid was increased to 50 ml. Atomic absorption spectrometer was used to calculate the amount of heavy metals such as copper, cadmium, zinc, nickel and lead etc. (Salimi et al., 2016).

### Statistical analysis

Statistical analysis of the data collected was performed using the software “Minitab version 17” and the average data analysis was done using one-way ANOVA and the Fisher’s method.

### Discussion and Results

In this study, a significant reduction was observed in the final treatments as far as nickel is concerned. As is evident from Table 1, the maximum proportion of nickel during the final phase of the process was observed to be 0.021 ppm which is related to the treatment B and in the final phase rest of the treatments lacked nickel in them. This study illustrates the fact that the reduction of nickel in the final treatments was because of the earthworm and microorganism activity present in the vermicompost heap which had led to the decomposition of the organic matter. During the saturation process of organic matter, nickel gets absorbed and accumulates inside the bodies of earthworms and other microorganisms. Also, it is seen that due to rinsing of the beds with latex an amount of heavy metals get removed through the poles of the bed thus reducing the overall heavy metal concentration. Singh reports that the concentration of heavy metals in the vermicompost decrease with the increase in time of the decomposition process (Singh et al., 2011). Also, with the formation of organic complexes a significant amount decrease is observed in the heavy metals formed due to the sewage sludge except iron and magnesium (Hait & Tare, 2012). In a study about the comparison of heavy metal concentration in composting and vermicomposting of organic waste, it was reported that the risk of heavy metals accumulation in the body of the earthworms is reduced in the case of vermicompost that in the case of compost (Mohee & Soobhany, 2014). In this study, at the end of the process, the concentration of copper was observed to increase in all the treatments. As is observed in Table 1, highest concentration of copper was found out to be 2.36 ppm in treatment H and the lowest was about 0.377 ppm in treatment C. The concentration of heavy metals in the vermicompost is related to the concentration these metals in the raw materials present in the bed. The increase in the concentration of copper in the vermicompost is due decrease in volume and mineralization of the organic matter by the earthworms. Vig also referred to decrease in volume and increase in organic waste to be the reason for the increase in heavy metal concentration in the vermicompost (Vig et al., 2011). Also, as per the studies of Nayak and Kalamdhad, the increasing in heavy metal concentration can be a result of loss of initial weight due to the decomposition of organic matter and emission of CO<sup>2</sup> gas during vermicomposting. As per the studies of Yadav and Garg (2013), contents of metals like iron, copper, lead and zinc in vermicomposting of mixed raw waste were higher than the initial level. The concentration of cadmium, zinc and lead decreased in some treatments and increased in some others at the end of the process. Maximum concentration of cadmium at the end of the process was observed to be in the treatment “L” and was about 0.024 ppm whereas the minimum concentration of cadmium was 0 ppm in treatments “A”, “E” and “H”. The maximum concentrations of lead at the end of the

process were about 0.67 ppm in treatment “B” and 0.65 ppm in treatment “H”. No concentration of lead was found in treatments “A”, “C”, “E”, “F”, “I”, “K” and “L”. The concentration of zinc was also observed to be different in different treatments. The maximum concentration of zinc at the end of vermicomposting was found out to be 14 ppm in treatment “B” and varied drastically from other treatments. The minimum concentration of zinc was observed in treatment “A” and was about 1.26 ppm. The concentration of heavy metals in the first bed, decomposition of organic matter, rate of adsorption and microbial activity directly affect the concentration of heavy metals in the final bed.

### **Conclusion**

In this research, reduction of heavy metal concentration due to leachate leakage, absorption of the metals in the substrate material by earthworms and accumulation of these metals in their tissues has been reported. On the other hand it is quite possible to say that during vermicomposting, heavy metal concentration increases due to volume and weight reduction of the materials in the bed due to organic decomposition. Finally, it was found that the concentrations of these metals are within the limits of the national standards of Iran and the use of these fertilizers in agriculture does not have any harmful effect.

**Keywords:** *heavy metals, municipal activated sludge, soft peel of pistachios, spent mushroom compost, vermicompost.*

## Kinetic and thermodynamic study of cadmium (Cd) adsorption by grape and apple pruning residues biochars

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### Expanded Abstract

#### Introduction

Cadmium (Cd) is a toxic heavy metal that has been released to the environment through the combustion of fossil fuels, metal production, application of phosphate fertilizers, electroplating, and the manufacturing of batteries, pigments, and screens. Given pervasive cadmium contamination and the low drinking water guideline, there is considerable interest in the development of techniques to remove cadmium from contaminated water. Several treatment processes such as adsorption, chemical precipitation, ion exchange and membrane filtration have been developed to remove the heavy metals dissolved in industrial wastewaters. Adsorption has been developed as a simple and effective technique for the removal of heavy metals from contaminated water and soil (Ahmaruzzaman, 2010). Biomass is a renewable energy resource and has a growing interest as a chemical feedstock source. Biochar is a fine-grained carbonaceous solid residue produced by pyrolysis of carbon-rich biomass under oxygen-limited conditions. Biomass-derived biochar is considered as a new potential, low-cost and effective adsorbent for heavy metal adsorbent, due to abundance of polar functional groups, such as carboxylic, hydroxyl, and amino groups, which are available for heavy metal removal (Sukiran et al., 2011). Biochar has many properties, such as a relatively structured carbon matrix, high degree of microporosity, extensive surface area, and high pH and cation exchange capacity (CEC); therefore, it may act as a surface adsorbent (Zhang et al., 2014). In the past few years, many reports on adsorption of various contaminants on biochar have been published including Peat moss biochar (Lee et al., 2015), sugarcane bagasse biochar (Yang et al., 2011), rice straw biochar (Han et al., 2013), sugarcane pulp residue biochar (Yang et al., 2014) and almond shells biochar (Kilic et al., 2013). Agricultural residues, especially grape and apple pruning residues, being produced in large quantities in the vineyards and founding ways of using such residues for the treatment of water by producing biochar are necessary. Therefore, the objective of this research is to investigate the equilibrium, kinetic and thermodynamic of cadmium (Cd) adsorption by grape and apple pruning residues biochars from aqueous solution.

#### Materials and Methods

##### Preparation of Grape and apple pruning residue

Grape and apple pruning residue used in this study was obtained from orchards located in the west Azarbaijan province, Iran. The small pieces of grape and apple pruning residue after drying in the oven at 105 °C for 24 h were placed in a vertical stainless steel reactor and heated at a temperature of 500 °C for 2 h in the absence of oxygen. The black residue was cooled and passed through a 0.5 mm sieve.

##### Characterization of biochars

The pH and electrical conductivity (EC) of the biochar were measured in a 1:20 (biochar: solution ratio) extract after shaking with deionized water for 1 h (Singh et al., 2010). The CEC was measured using 1 M ammonium acetate (pH 7) method (Lu, 1999). Ash content was determined using the ASTM D1762-84 method (ASTM International, 2013). Total C, H and N contents in the biochar were determined using an elemental analyzer

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(ECS 4010 CHNSO Analyzer). Specific surface area was analyzed by the Sear's method (Sears, 1956). The surface morphology of adsorbents was characterized by Scanning Electron Microscope (SEM, AIS-2100, 5.0 kV, Korea).

### Adsorption experiments

Batch experiments carried out with different initial concentration of Cd (0, 10, 20, 40, 60, 80, 100, 150 and 200 mg L<sup>-1</sup>) at pH (4, 5, 6), ionic strengths (0.01, 0.03, 0.1 M) and temperature (10, 20, 30, 40 °C) at different times (0, 0.08, 0.17, 0.33, 0.67, 1, 2, 5, 10, 20, 40, 60, 90, 120 and 240 min) with 0.03 M NaNO<sub>3</sub> as a background solution. Pseudo first-order, pseudo second-order, Elovich and fractional power were fit to experimental data to examine the adsorption kinetics of cadmium uptake by biochars. Non-linear fitness between experimental data and predicted values from adsorption isotherm (Langmuir, Freundlich, Temkin and Dubinin-Radushkevich) was performed using the solver add-in with Microsoft's spreadsheet, Microsoft Excel.

The amount of Cd<sup>2+</sup> adsorbed per unit mass of the adsorbent ( $q_{ads}$ ) was calculated by Equation (1):

$$q_{ads} = C_i - C_e \times \frac{V}{m} \quad (1)$$

where  $q_{ads}$  (mg/g) becomes  $q_e$  or  $q_t$  at equilibrium or at time  $t$ .  $C_i$  and  $C_e$  are the initial and the residual amount (mg) of Cd<sup>2+</sup>, respectively, added and remained in solution.  $V$  is the volume of the solution (mL), and  $m$  is the mass of adsorbents (g).

The removal efficiency (RE) was determined by computing the percentage sorption using the formulae in Equation (2)

$$\%RE = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

## Results and Discussion

### Effect of contact time

The experimental data indicated that Cd adsorption increased with increasing contact time and the equilibrium time is attained in 40 min for grape and apple pruning residue biochar. Equilibrium time of 40 min was also reported by Rao et al. (2006) for Cd adsorption by activated carbon derived from *Ceiba pentandra* hulls.

### Adsorption kinetics

Among adsorption kinetics models, pseudo second order model was better fitted for experimental data ( $R^2=1$ ) and the values of predicted equilibrium sorption capacities showed good agreement with the experimental equilibrium uptake values. Adsorption capacities ( $q_e$ ) obtained by pseudo second order model, were 9.8 and 9.0 mg g<sup>-1</sup> for grape and apple pruning residue biochars, respectively.

### Adsorption isotherms

Ionic strength and pH of background solution significantly affected Cd adsorption and the highest adsorption capacity was obtained at pH 6, ionic strengths of 0.01M at 40 °C. Sorption capacity factors ( $q_{max}$ ,  $K_F$ ,  $K_T$ ,  $q_D$ ) and sorption energy factors ( $n$ ,  $K_L$ ,  $B$ ) of grape pruning residue biochar was more than apple pruning residue biochar. The sorption energy parameter ( $E$ ) of Dubinin-Radushkevich isotherm and Gibbs free energy change ( $\Delta G$ ) indicated that the Cd adsorption processes were physical and spontaneous. The separation factor of Langmuir ( $R_L$ ) indicated that the sorption reactions of Cd<sup>2+</sup> by grape and apple biochar is favorable ( $R_L=0.15-0.50$ ).

## Conclusions

In this study grape and apple pruning residue biochars, produced in large quantities in the orchards of west Azarbaijan province, were evaluated as an alternative low-cost adsorbent for removal of Cd<sup>2+</sup> ions from aqueous solution. The results showed that cadmium adsorption increased with increasing contact time and the equilibrium time is attained in 40 min for grape and apple pruning residue biochars, respectively. The pseudo second order kinetic model accurately described the adsorption kinetics ( $R^2=1$ ). The highest adsorption capacity was obtained at pH 6, ionic strengths of 0.01M at 40 °C. It was observed that cadmium adsorption for grape pruning residue biochar was higher than apple pruning residue biochar. The separation factor of Langmuir ( $R_L$ ) indicated that the sorption reaction of Cd<sup>2+</sup> biochars ( $R_L=0.14-0.50$ ) is favorable. Results from this study suggest that grape and apple pruning residue biochars were able to substantially remove Cd<sup>2+</sup> from aqueous solutions.

**Keywords:** adsorption isotherm, adsorption kinetics, adsorption thermodynamic, cadmium, grape and apple pruning residue biochars.

## Comparison of artificial intelligence and geostatistics methods abilities for spatial prediction of Arsenic anomaly in Chahardoli plain

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### Expanded Abstract

#### Introduction

Groundwater spatiotemporal sampling has some limitations due to economic condition. So, it is better to use the interpolation methods to estimate variable in unknown point. The aim of the present study is modeling of the distribution of arsenic in the Chahardoli Plain of Naghadeh by using geostatistics, fuzzy logic, and genetic expression programming (GEP). As yet, different studies have been done in which the geostatistics is used to determine the distribution of heavy metals and trace elements (Corwin & Wagenet, 1996; Juang et al., 2001; Rodriguez et al., 2009). Artificial intelligence is a branch of computer science which is able to predict and simulate using models such as fuzzy logic (FL) and genetic programming (GP) models (Fallah-Mehdipour et al., 2013). Each of the models has its own advantages and uncertainty that can be used of the individual benefits of each these models (Labani et al., 2010).

Fuzzy method offers an appropriate way to reduce human and estimation error compared to other methods. In a comparative study on the performance of fuzzy inference with other techniques, it concluded that the fuzzy techniques are successful in moderating intrinsic uncertainty of data and also in the interpretation of complex situations (Chang et al., 2001).

Recently, gene expression programming (GEP) is developed based on the evolutionary algorithm. The GEP used to solve complex problems and compare its ability with different methods of artificial intelligence in hydrological system modeling. These researches results in supporting capability of GEP for hydrological system modeling (Ustoorikar & Deo, 2008; Alvisi et al., 2005). Many researchers cited GEP to study the process of forecasting and simulation of groundwater levels (Fallah-Mehdipour et al., 2013), river sediment transport (Aytek & Kisi, 2008), estimation of incomplete data (Ustoorikar & Deo, 2008) determine the unit hydrograph (Rabunal et al., 2007), daily discharge determination (Güven, 2009), flow forecasting (Shoab et al., 2015), simulate rainfall-runoff (Jayawardena et al., 2005), short-term and long-term weather forecasts (Kisi et al., 2011) and other studies.

In the Qorveh-Bijar area (small zone of Sanandaj-Sirjan), hydrothermal activity of area with young volcanoes diffuse the arsenic-rich outflow vapors into the system. Also, existence Travertine formation in this area is the main evidence high volcanic activity in this area. Therefore, volcanic activity is the main agent of arsenic release in watercourses in this zone. Since arsenic contamination in this area is a type of geogenic source, and considering the difficulty of controlling this type of pollution. Therefore, the study area should be studied carefully.

#### Materials & Methods

##### Study area

The study area is located in the Northwest of Iran, Kurdistan Province and the southeastern of Qorveh City . Based on Emberger method (1930) and average annual rainfall of 332 mm, the prevailing climate in the study area is arid-cold.

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## Geology

The study area is located in a small part of the Sanandaj-Sirjan zone, which have the features of this zone such as magmatic rocks and metamorphic activities due to tectonic movements on large areas. Lithology of the Rhyolite and Rhyodacite is related to the Jurassic and Cretaceous time that is exposed in the central highlands in the West of Chahardoli. Lithology of Nummulites lime and green Tuff which is related to Eocene visible is located in a small area in the eastern mountains of Chahardoli. Volcanic, sandstone, and conglomerate lithologies which is related to Oligomiocene visible in a broad area in the highlands of North-East region. The last magmatic phase related to the early Quaternary and it covers the study area from the East of Vinsar Village to the south of the Daskasan Village.

## Hydrogeology

In hydrological point of view, study area is located on a tributary of the river Taluoar. Watershed area of Chahardoli is 958 km<sup>2</sup> and the plain area is about 386 km<sup>2</sup>. The most important surface water resource in the study area (Chahardoli basin) is a Cham Shur River. The general direction of groundwater flow is from the highlands of East and West into the Central Plains and finally, it reaches to the northwest of the plain.

## Data analyses

To investigate the water quality, 31 water samples, including groundwater resources of well, spring and qanat were collected during October, 2014. These samples were analyzed at the hydrogeological laboratory of the geology department in University of Tabriz and water and sewage organization of Kurdistan. The water quality parameters of interest were Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, F<sup>-</sup>, As, Fe, Mn, Pb, Cr, Cd, EC and pH were determined by the standard methods. The correlation matrix shows that silica, potassium, and sodium ions is highly correlated with arsenic, respectively. The high correlation of arsenic with these elements is due to their common origin and role of these elements in increasing concentrations of arsenic in the watercourses of the region.

## Discussion of Results

### Geostatistics

Data distribution was evaluated using the Q-Q diagram and using logarithmic transformations, data distribution close to the normal distribution. Anisotropy semi-variogram was checked for changeability of the range and sill which were evaluated relative to different angles of plotting semivariograms and by preparing in it in four directions.

The ordinary kriging model was used for prediction of arsenic concentration in the study area. In addition to the main variable of arsenic, silica parameter that has the highest correlation with arsenic was used as a secondary variable for cokriging model. In geostatistics method, J-Bessel cross-variogram models having R<sup>2</sup> equal to 0.75 and the nugget effect of zero was selected to predict arsenic concentration.

### Fuzzy

Artificial intelligence models were used to improve efficiency of the arsenic estimation model. In this study, Sugeno Fuzzy Logic (SFL) has been used to predict the total arsenic values. In this model, the reduction method for data classification and determining of the membership were used. Fuzzy model by determining the optimal radius of 0.6 based on the lowest RMSE was accomplished that the value of R<sup>2</sup> for training and testing level is in order 0.91 and 0.78, respectively.

### Genetic programming

The parameters of sodium, potassium, silica and arsenic were used as input data and the arsenic value is output data of GEP model. The input and output data is divided to two class, train and test steps data which have the statistically the same characteristics. Production of the initial population of the program was carried out by selecting the number 20 chromosome with a head size of 7, 3 number of genes and 2 constants per gene. The mathematical operator of '+' was selected for the linking function between subtrees. To compare the results of the program, three sets of the function were used as the main operators. F<sub>3</sub> function includes default operators was selected as the major functions in the program and the best fitted compared to other functions. GEP model by providing the relationship between input and output, and more accurate results in the training and testing steps with R<sup>2</sup>, 0.93 and 0.87, respectively. It was evaluated as the most appropriate model than other models to estimate the arsenic values in the region.

## **Conclusions**

Geostatistical techniques (kriging and Cokriging) were used to estimate the amount of arsenic in the study area and the efficiency of model was not high and the results were not precise enough. The main reason of it can be find in the heterogeneity of the study area and special condition of data that cause the non-linear and unclear general trend. To improve efficiency, artificial intelligence models such as sugeno fuzzy logic (SFL) model and genetic expression programming (GEP) were used. In this study, the results of GEP and SFL model are acceptable for spatial prediction of arsenic anomaly, but the SFL model improved 18% efficiency of GEP model based on the RMSE value. Evaluation of other artificial intelligence model abilities in spatial prediction of arsenic anomaly, including Mamdani fuzzy logic, Larsen fuzzy logic and Neuro-fuzzy models suggested for future research topics.

**Keywords:** arsenic, fuzzy logic, genetic expression programming (GEP), geostatistics, Kurdistan.

## Evaluation of groundwater salinization and delineation of ion offspring in Malekan Plain Coastal Aquifer using ionic ratios

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### Expanded Abstract

#### Introduction

Degradation of groundwater quality, including salinisation, has become an increasingly serious global problem in coastal aquifers in recent years. With rapid economic development, population growth and increasing demand for freshwater resources, extensive groundwater withdrawals in these areas have led to water level declines and increasing groundwater salinization. In the cases that two or more factors affect increasing of dissolve solid, the source identification in groundwater could be usable in planning, managing and choosing the right strategies in exploitation and protection of water resources. In this study, hydrogeochemical, geological and geophysical investigations were carried out to assess the geochemical water composition and also governing processes groundwater hydrochemistry in Malekan Plain. The study area is located in the SouthEast the Urmia Lake, North western Iran. The main aims and objectives of the present study are evaluation of groundwater salinization and delineation of ion offspring in Malekan Plain Coastal Aquifer.

#### Materials and Methods

In order to assess the groundwater quality, including the source of salinity, and the hydrogeochemical processes affecting the quality of water, 41 groundwater samples were collected, in July 2016. Water samples were analyzed in the field for various physical parameters such as temperature, pH, Eh, and electrical conductivity (EC). All samples stored in polyethylene bottles and were transported to the water laboratory of the Tabriz University. Samples analyzed for hydrochemical parameters such as major, minor and trace elements. The location map of groundwater samples is shown in Fig. 1.

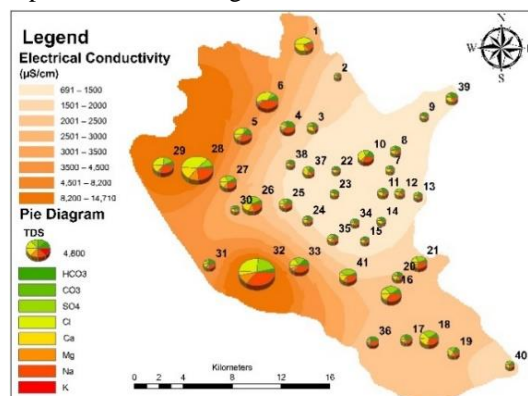


Fig. 1. The Pie diagram and the location map of groundwater samples



Statistical and geochemical modeling was performed to understand the processes controlling groundwater geochemistry. The chemical composition of groundwater was evaluated by several natural factors including aquifer lithology, interaction with geological formations. In addition, anthropogenic activities such as agriculture and industry have been shown to impact on the groundwater chemistry using hydrogeochemical techniques. Also, the hydrogeochemical diagrams were used to evaluate the source of salinity and geochemical evaluation.

## Discussion

The results of field and laboratory measurements of physicochemical parameters, major minor and trace elements showed that the high electrical conductivity (EC) (691-14710  $\mu\text{mhos/cm}$ ) in groundwater is due to high concentrations of gradual increasing in major elements,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{SO}_4^{2-}$ , through groundwater flow. Related to total dissolved solids (TDS) gave a variable response between the northwestern and southeastern parts of the study area. The northwest zone has a TDS values over 4000 mg/l. However, relatively low values of TDS (less than 1500 mg/l) have been recorded in east and southeastern part of the study area (Fig. 1).

On the basis of relative proportions of major-ions, the chemical composition of groundwater in the coastal aquifer is classified. The sequence of abundance of the major cations and anions is as follows:  $\text{Ca}^{2+} > \text{Na}^+ + \text{K}^+ > \text{Mg}^{2+} = \text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$  and  $\text{Na}^+ + \text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} = \text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$ . The Piper diagram was used to determine the groundwater types. Also, hydrochemical data were also plotted on a Gibbs diagram. Gibbs diagrams suggest that groundwater chemistry is controlled by rock-water interaction and evaporation, which the dominant factors are leading to poor groundwater quality. This is expected, as evaporation greatly increases the concentrations of ions formed by the chemical weathering of rock, leading to higher salinity.

Surface and groundwater evaporation has had a significant effects on groundwater salinity and solute increasing at the end of the plain. To understand the origin of groundwater salinity in Malekan plain, the values of saturation index of calcite, dolomite, gypsum, anhydrite and halite in all 41 groundwater samples have been calculated using the Phreeqc Interactive 3.0.0. computer code. Hydrochemical ratios was considered as a good indicator for groundwater genesis which could be used to detect a trend of salinization. The hydrogeochemical ratios such as  $\text{Cl}^-/\text{sum Anion}$ ,  $\text{HCO}_3^-/\text{sum Anion}$ ,  $\text{Cl}^-/(\text{HCO}_3^- + \text{CO}_3^{2-})$ ,  $(\text{Na}^+/\text{Cl}^-)$ ,  $\text{Na}^+/( \text{Na}^+ + \text{Cl}^-)$  and  $\text{Ca}^{2+}/(\text{HCO}_3^- + \text{SO}_4^{2-})$  were estimated to determine the origin of ions and salinity in the groundwaters. Chloride has been selected as a fingerprint element for saltwater intrusion because it is chemically conservative. The  $\text{Cl}^-/(\text{HCO}_3^- + \text{CO}_3^{2-})$  ratio values was introduced as a criteria by Revelle (1941), above 1 be considered to be affected by saltwater intrusion in coastal aquifers. The  $\text{Cl}^-/(\text{HCO}_3^- + \text{CO}_3^{2-})$  concentration indicates an increase of salinization towards the northwest, which is clearly reflected by increase in  $\text{Cl}^-$  value. The minimum ratio of  $\text{Cl}^-/(\text{HCO}_3^- + \text{CO}_3^{2-})$  is recorded at the central part of the study area, corresponding to the recharge area. This ratio was found to range from values 0.088 to 12.85 for representative samples taken in July 2016. The  $\text{Cl}^-/\text{sum Anion}$  ratio was found to range from values 0.06 to 0.88 for samples. In the process of a saltwater intrusion front progress, sodium often replaces calcium on the aquifer matrix through ion exchange. This distinguishes saltwater intrusion from domestic wastewater, which typically has  $\text{Na}^+/\text{Cl}^-$  ratios above 1. In the study area, the  $\text{Na}^+/\text{Cl}^-$  ratio ranges between 0.31 and 5.84. Low ratios (below 0.86) are noticed in northwest area. The rest of the groundwater has ratios consistently above 1. The  $\text{Na}^+/( \text{Na}^+ + \text{Cl}^-)$  ratio values lower than 0.5 explaining the magnitude of contamination by saltwater intrusion. This ratio was found to range from values 0.24 to 0.91 for representative samples. The ratios of  $\text{Ca}^{2+}/(\text{HCO}_3^- + \text{SO}_4^{2-})$  for groundwater samples in the plain ranged from values 0.11 to 4.53.

Studying the ion ratios revealed that sodium has been entered to the aquifer in consequence of salt water intrusion from the evaporate brines, contemporary playas and connate groundwater from northwest of aquifer adherent to southeast of Lake Urmia, and also weathering and leaching of salty-clayey layers. In other hand, calcium and magnesium ions originate from limestone and dolomite deposits. The hydrogeochemical ratios and saturation index which arose from geochemical modeling indicate that the dissolution of evaporation deposits and cation exchange are the most important processes affecting the chemical composition of groundwater.

The chloride ion, as an indicator of groundwater salinization, is highly correlated with EC, which plays a key role in groundwater quality. The ratios of  $\text{Cl}^-$  and  $\text{Br}^-$  have been extensively used to detect the dissolved salts in groundwater since both from the stable anions of  $\text{Br}^-$  and  $\text{Cl}^-$  in water and are not usually affected by water-rock interaction. The ratios of conservative elements ( $\text{Cl}^-/\text{Br}^-$ ) for groundwater samples in the plain ranged from 93 to 2184 and showed the effect of evaporation deposits, agricultural returned groundwater and domestic sewage.

$\text{Li}^+/\text{Cl}^-$  ratio is another of the most important used ratio to separate different salinity origins. Samples related to seawater can be distinguished by the value of  $\text{Br}^-/\text{Cl}^-$ . The  $\text{Br}^-/\text{Cl}^-$  relationship helps to identify the possibility of seawater intrusion since it is relatively constant in the seawater considering the extremely long residence time of Sea masses. Compound diagram of ionic ratios ( $\text{Li}^+/\text{Cl}^-$ ) vs. ( $\text{Br}^-/\text{Cl}^-$ ) were identified as an adequate criterion of separating different salinity sources. The groundwater samples located in evaporation playas (cluster 3) and

groundwater (cluster 4) part of diagram and have far composition than samples related to seawater or lake can be distinguished by the value of  $\text{Br}^-/\text{Cl}^-$  (Fig. 2).

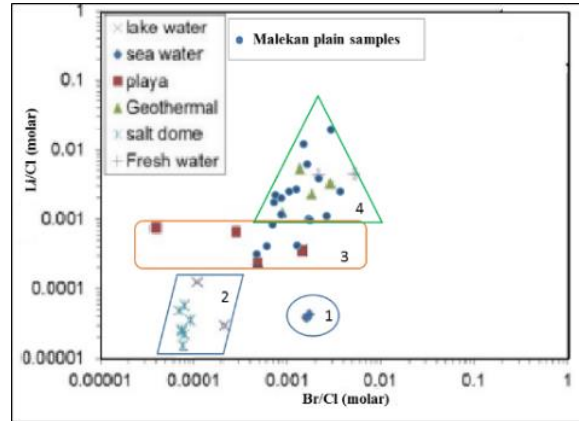


Fig. 2. Compound diagram of molar ionic ratios ( $\text{Li}^+/\text{Cl}^-$ ) vs. ( $\text{Br}^-/\text{Cl}^-$ )

## Conclusion

All evidences like certain ratios, hydrogeochemical graphs and saturation index indicate that the dissolution of evaporation deposits and cation exchange are the most important processes affecting the chemical composition of groundwater. The results of applying statistical and hydrogeochemical techniques confirmed that both the evaporation-crystallization reactions and water/rock interaction in the aquifer and exposed the effect of human activities on groundwater quality. Compound diagram of ionic ratios ( $\text{Li}^+/\text{Cl}^-$ ) vs. ( $\text{Br}^-/\text{Cl}^-$ ) indicates the groundwater samples which origin from different sources as different clusters. Based on results of the present study, factors like cation exchange, salt water intrusion from the evaporate brines, contemporary playas, and also leaching of salty-clayey layers from northwest of aquifer adherent to South East of Lake Urmia, and groundwater evaporation at the end of the plain could be the main causes of salinity regarding to used techniques.

**Keywords:** compound diagrams, coastal aquifer, evaporation, ionic ratios, salinity.

## The investigation of absorbing heavy metals self-purification in Watershed of Kaleibarchay River

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### Expanded Abstract

#### Introduction

Increasing of the urban, industrial, and thereby increasing the concentration of heavy metals in water and sediment of rivers and their role as a contaminant of concern for the country are considered industrial pollutants leave resulting from human activities and the adverse effects of animal and vegetable consumption left cheek. Heavy metal pollution in aquatic ecosystems and marine environments due to the accumulation of human life is a major concern. These metals are naturally through the weathering crust of the earth and atmospheric deposition into the marine environment. Pollutants are deposited on the substrate. They appear blue. In the lack of such studies about awareness of managers and planners, the aim of this study is determining the role of self-care Kaleibar River in removing heavy metals from water and sediment; the current situation of water resources and pollution of the river could manage it.

#### Materials & Methods

Kaleibar City in East Azarbaijan, Iran is mountainous walk, and with the cold weather. The area of this city is 4038.9 km<sup>2</sup> of the province covers an area of 8.92%. Whole area of the Aras River called watershed the northernmost boundary forms with North Arasbaran. Aras River basin in northern Arasbaran length 212.5 km, from the west to the east currently underway. The documents and extensive field studies was used in the period from July 2012 to September 2012. Tributaries into the river and urban and rural sewage were considered as a station and 10 stations, obtained including mineral water stations Olaus, Pole Kalalaq, Chelokhaneh, Kafshan Ivi Pole, terminal, Jilan river, Danesh town, Pole Emarat, Pole shah heydar, Janan Lu determined by using GPS and Google Earth software. According to studies conducted taken field operations and records, the number of three stations before entering the city, four stations within the city limits and three Stations outside the city were chosen to determine the pollution load of the river. The number of samples selected have been collected from each station was 10 water samples and 5. The study areas were chosen to cover the whole of the river.

#### Results

The minimum and maximum concentrations of respectively 0.03 and 3.8 micrograms of lead per gram of dry weight, respectively Jilan river and terminal stations respectively showed significant differences with each other ( $p < 0.05$ ). The next step was determined using the Dunnett test between stations 7 and 8. There was a significant difference in the concentration of lead deposits. Stations were calculated with minimum and maximum concentrations of cadmium respectively, 0.02 and 1.01 microgram per gram dry weight pole stations Kalalaq and Danesh town which showed a significant result with each other. The average concentration of lead in water, mineral water factory Olaus stations, Poles Kalalaq, Chelokhaneh, Kafshan Ivy Pole, terminal, Jilan river, Danesh town, Pole emarat, Pole Heydar Shah, Janan Lu was calculated, showing that between stations 2 and 8, 3 and 4, 3 and 7, 3 and 8, 4 and 8, 5 and 8, there is a significant difference in the concentration of lead in water. In average concentration of cadmium in water, mineral water was calculated factory Olaus stations, Poles Kalalaq,

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Chelokhaneh, Kafshan Ivy Pole, terminal, Jilan river, Danesh town, Pole emarat, Pole Heydar Shah, Janan Lu, which have significant differences ( $p < 0.05$ ). The next step is to determine if the difference between group Dunnett test was used. There were significant concentrations between stations 5 and 2, 5 and 3, 8 and 2 on water cadmium. The average concentration of copper in water, mineral water stations Olaus, Pole Kalalag, cello house, Kafshan Ivy Pole, terminal, Jilan river, Danesh town, Pole Emarat, Pole Heydar Shah, Janan Lu was calculated, which was significant ( $p > 0.05$ ). The results show that the amount of Pb metal in the water are significantly below the standard of all countries and with the standards of the Environmental Protection Agency, the World Health Organization for Standardization and Industrial Research of Iran different. Cd metal content in the water below the standard of all countries and with the standards of the Environmental Protection Agency, the World Health Organization and the Standards and Industrial Research of Iran are significantly different. Cu metal content in the water are significantly different than standard water standard for all countries and lower than EPA standard, World Health Organization and the Standards and Industrial Research of Iran. Cu in sediment is significantly different and below than the EPA standard, the international organization ocean and meteorology standard Canadian international standard organization, the World Health organization and the international food standard Standards and industrial Research of Iran.

### Discussion and Conclusion

The results of water samples at various stations Kaleibar river of Station 1 (mineral water Olaus) are the highest level of lead at a concentration of 1.45 milligrams per liter, the highest cadmium at Station 2 (pole Kalalag) at a concentration of 0.99 mg per liter and the highest amount of copper in 8 stations (pole Emarat) at a concentration of 3.87 milligrams per liter. The minimum amount of these elements were pooled at station 10 (Janan Lu), with concentrations 0.07, 0.00, 0.56 mg. According to the results, there was not a significant difference in sediment samples more than the standard amount of cadmium and Industrial Research Organisation of Iran. It can be concluded that in the years 1384 to 1391, concentrations of Pb in water and lead in our country were decreased. It can improve the quality of fossil fuels and increased standards attributed. There is no correlation between the concentration of metals in water and sediment. However, there are the correlation between elements in the sediment and water separately. Between cadmium, lead and copper in water sample, there is a significant correlation with copper in sediment samples. There is heavy metal concentrations along the river down stream of the city, despite the arrival of waste Kaleibar city and by reduced water and sediment absorbed. This shows the role of self-purification of the Kaleibar river watershed. The introduction of metals into natural waters usually takes place from urban, agricultural and industrial wastewater disposal sites (Ghavidel, 1393). Finally, it can be noted that the presence of vegetation around the margin of the Kalibir River tea and the volume of sediment accumulated in the bed and sides and also the amount of river flow can be effective in the rate of self-pollination of the river. Therefore, the amount of self-determination based on the year and month and other parameters mentioned above can be variable. Diagonanolin *et al.* (2004) showed that the highest and lowest concentrations for nickel, chromium and copper were 60.7-41, 19.8-0.7 and 28.7 in the spring, during the spring and winter seasons in 16 stations of Karun River -0.5  $\mu\text{g}/\text{l}$ . In winter this concentration was 110.7-69.3, 118.3-1.7 and 70.3-5.5  $\mu\text{g}$ . As a result, concentration is increased from upstream downward. Therefore, this could be a research field in relation to the examination of other heavy and toxic metals in water and sediment samples, investigating the impact of these metals on plants, aquatic animals and birds, studying the rate of self-healing of heavy elements in the river and vegetation, the evaluation of heavy metals in the soil around the river.

**Keywords:** heavy metals, river Kaleibar, self-purification, watershed.

## Good governance role and size of government on environmental performance in selected countries

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### Extended abstract

#### Introduction

The role of government in the environmental economy is more than anything else related to the delivery of public goods (such as environmental protection) and their quality. In the United Nations Development Program, environmental decision making has been the key to good governance in many countries. What is nowadays more prevalent in the environmental economy is the role of power in decision making and environmental policies. Governments must regulate environmental programs that are politically acceptable and economically viable. The first step towards achieving a good government and implementing the principles of good governance is to create a good law. This law should be in line with the principles that include the full cycle of executive and supervisory activity in society, including political development, drafting, authorization, enforcement and prosecution. This cycle can cover various areas including the environment. Governments should encourage public sensitivity and public participation by providing information to the public, providing effective access to judicial and administrative authorities, and ensuring judicial and administrative matters, including punishment and compensation. Governments, as environmental regulators, have a tool for the private sector to observe environmental considerations. The existence of bargaining power and the influence of some individuals and legal entities and, as a result, the emergence of a subject in the name of legislation can be a fundamental challenge to the rule of law and the requirement of law and government on the environmental performance of the private sector.

Therefore, based on the above discussion, the present study addresses the role of governance in societies (including cases of corruption control, accountability, public participation, rule of law and regulatory quality), and the performance and socio-economic performance of states (such as government size in the economy) in performance environmentalists.

#### Materials & Methods

The main concern of developing countries is to achieve development. What is the new harvest of the development concepts such as security, participation in social and political life, justice and the environment? The concept of development was beyond the accumulation of wealth and GDP growth and quality of the environment that could indicate improved living conditions of the population should be considered as one of the most important pillars of environmental justice and sustainable development. Environment is enormous and complex set of different factors that affect the performance and human activities and are affected as well. So, the socio-economic proper functioning of person's dependent on the proper functioning of environment.

Several factors can affect the quality of the environment, including economic variables (by degree of industrialization, trade and technological inequality), political variables (through democracy and dictatorship), social factors (the degree of urbanization and literacy rates) and government (by size and quality state) noted.

With a broader definition of environmental quality as environmental performance (EPI) (which represents environmental health, air quality, water quality, quality of productive natural resources, biodiversity and habitat, and sustainable energy), the role of individuals, governments and social relations between them is vital in determining environmental performance.

The occurrence of market failures, shortcomings in safeguarding individual rights and shortcomings in the international balance are based government intervention in the economy. In other words, it may market

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performance with regard to microeconomics approach, including allocative efficiency, however, in terms of macroeconomic views or development, represents a market failure. One example of market failure in the allocation of resources is public of environmental goods. Despite the more environmental resources have significant value, generally not considered precious to use them and if the price to be considered, these prices are not reflecting the price and the real cost of environmental resources.

Governments on one hand, by mechanisms such as the valuation of resources, internalize environmental costs, zero social costs of production and consumption and the use of legal instruments and monitoring can reduce pollution and destruction and stabilize economy by reducing pressure on resources. On the other hand, the more government presence can associated with problems such as weak institutions, governments inefficiency, lower quality rules, weaken regulatory agencies, administrative extensive bureaucracy, lack of accountability, corruption, rent-seeking, weaken public participation, undermine public scrutiny and participation and so on. Therefore, more attention should pay to the effect of government size and good governance and their mutual relations on the quality of the environment.

So, based on the above discussion, current study had been discussed the role of government in society (including for example control of corruption, accountability, public participation, rule of law and regulatory quality) and socio-economic performance of governments (such as the size of government in the economy) in performance environmental.

### Discussion of Results

In this study for examine the effect of government size and good governance as well as the theory of Kvzntsh, the following general model was used:

$$LEPI_{ij} = C + \beta_1 LEPI(1)_{ij} + \beta_2 Linst_{ij} + \beta_3 Lsize_{ij} + \beta_4 LGDPC_{ij} + \beta_5 LGDPC^2_{ij} + \beta_6 Lpopden_{ij} + \beta_7 Lopen_{ij} + \beta_8 DUM_{ij} + \varepsilon_{ij}$$

where LEPI represents the logarithm of environmental performance indicators, C: intercept, LEPI (-1): logarithm of the first continuous environmental performance index, Linst: log governance index, Lsize: logarithm of government consumption expenditure (% of of GDP) as an indicator of the size of government, LGDPC: log of per capita GDP (in constant price \$ 2005 America), LGDPC2: logarithm of the square of per capita GDP (in constant price \$ 2005 America), Lpopden: log the population density index, Lopen: logarithm of openness index, DUM: dummy variable to differentiate and compare developing and developed and  $\varepsilon$  is a disturbing regression model.

Good Governance Index (inst) consists of the sub-indexes which in separate models will be examined in this research. The sub- indexes include voice: voice and find best responds index, Gove: government effectiveness index, Regq: quality indicators laws and regulations, rule: the rule of law index, and control: corruption perception index.

### Conclusions

In this paper, six indicators of good governance in separate models were estimated on Environmental Quality. The results show that all these indice significantly positive impact on the quality of the environment.

So, improving good governance means accountability, public participation, rule of law, regulatory quality and control of corruption, can be achieved better in the shade of a small governments, because the larger government will be accompanied with bulkier and inefficient regulations and rules. When a private entity to harm the environment, treat and control, it much easier to monitor state institutions and the power. Basically, on the other hand, often the types of corruption finds relevant in government sphere. Finally, larger government will be accompanied with participation of fewer people, and so less accountability. Regarding trade openness index, it can have said first, business development can occur alongside smaller government and secondly, businesses make less damage to the environment.

Also, the results show that the size of government, population density and per capita GDP had a significant and negative impact on the EPI and the effect of economic openness on the EPI has been positive. The results of this study also demonstrated Kuznets curve theory. This means that, in the early stages of economic growth that reduces environmental quality; but continue on the path of economic development, by providing resources for the community to improve environmental performance.

The negative effect of government size is another channel to show the relationship between the inefficiency of government in the economy and the environment. This result is consistent with the effects of good governance and trade openness.

**Keywords:** environmental performance, good governance, the size of government.

## Predicting the impacts of climate change on Persian oak (*Quercus brantii*) using Species Distribution Modelling in Central Zagros for conservation planning

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### Extended abstract

#### Introduction

In recent years, climate change has affected on both ecosystems and the creatures that live in them. Hence, plant species may be expected to show marked redistributions in reply to climate change. This has estimated at various scales and in diverse places, usually by the use of bioclimatic envelope models. These models are often named distribution models (SDMs), climate envelope models or ecological niche models (ENM). They use climate factors as independent predictor variables and biotic data as dependent variables to produce a predictive model for species or ecosystem distributions. Modelling so appears the most practical and useful method to obtain efficient predictions. Assessing species range shifts are necessary for trees as they are a primary part of landscape composition, offer valuable services such as wood products and recreational opportunities, playing a crucial role in forest ecosystem functioning, and other important habitats for many animal and plant species. This is understood that shifts in vegetation zones are not entirely determined by shifts in climate. This has shown that soil, regional topography, groundwater surface, and other factors may influence plant species distributions. This is impracticable and unnecessary to estimate the total of these processes when modelling the effects of climate change on an extensive geographic scale. Climate envelope modelling can additionally be useful in another, the more effective method for ecosystem rehabilitation, conservation program, plantation forestry, or genetic source management. Climate envelope models can be informative, not by forecasting changes, but by quantifying differences among current distributions and potential habitats under potential climate change scenarios. Moreover, despite the deficiencies of climate envelope models, the overall patterns of predicted species range shifts often match observed biological tendencies. Temperature over south-west Iran may increase between 1.69 and 6.88°C by 2100. Summer temperatures may increase with higher rates than spring, winter, and autumn temperatures. The Zagros forests with an area of about 6 million hectares account for nearly 44% of the country's forests. These forests are the most important for water supply, soil conservation, climate change and the socioeconomic balance of the whole country. Seven first grade rivers, carrying 34.5 billion cubic meters of water and accounting for 40% of the entire groundwater of the country, rise in the Zagros Mountains and run into the rich plains. High ecological capacity, the possession of rich water supplies has resulted in a high population density in the region 9.8 million people live in this region, of which 1.5 million live in the forested areas, affecting the ecosystem. The main genus in the Zagros region is oak with a varied range of species distributed across the area. *Quercus brantii* Lindl. species is known as Persian oak. Persian oak species is endemic to temperate regions of Asia and western Asia, including Iran, Iraq, Syria, and Turkey and it's the boundary of Irano- Turanian vegetation region. Persian Oak is a prevalent species in Zagros forests. In the Zagros was showed that forest loss was more closely associated with climate change and urban human

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population increase. Recently, a large number of deaths among oak trees have been reported in their natural habitats. Therefore, this study aimed at predicting the effect of climate change on the geographical distribution of Persian Oak in Chaharmahal and Bakhtiari province in the Central Zagros region under future climate scenarios by 2050.

## Materials and Methods

The studied region in this research had the area of 1.6 million hectares in the central Zagros in Chaharmahal and Bakhtiari province. Field studies include harvest of geographical coordinates of the presence of this species in Central Zagros. In this study, 19 bioclimatic variable climate factors describing Persian Oak habitat, which have been used in many studies as the basis for monitoring impacts of climate change on organisms. Climate change RCP4.5 scenario, general circulation model HadGEM2-CC and three physiographical variables (elevation, slope and slope aspect) were applied to. These 19 bioclimatic layers must be derived from the three basic climatic variables. WorldClim provides monthly maximum (Tmax), minimum (Tmin), and mean temperatures, and monthly precipitation. Monthly precipitation was improved by average monthly precipitation obtained from weather stations across the province. Then 19 bioclimatic variables were created in DIVA-GIS. Digital Terrain Model (DTM) was used to generate slope and aspect data layers and as physiographic variables.

First, the presence of the correlation between variables modified by Pearson test was examined and the variables with over 80% correlation with each other were determined. After conducting Pearson's correlation analysis and removing variables with high correlation, it was found that eight variables (BIO9, BIO7, BIO3, BIO4, BIO12, and BIO17, percent of slope and slope aspect) were not correlated with each other and can enter the final model. In this regard, we used five modelling approaches, Generalized Linear Model (GLM), Classification Tree Analysis (CTA), and Artificial Neural Network (ANN), Generalized Boosting Method (GBM) and Random Forest (RF) to determine relationships between the occurrence of species and environmental factors. GLM is a mathematical extension of linear models. These models are not sensitive to different types of statistical distributions and are suitable for nonlinear relationships; besides, they use traditional practices used in linear modelling and analysis of variance (ANOVA).

In this study, we used biomod2 to run a stepwise GLM were Akaike valued to compute the best model. CTA is an alternative to regression techniques and has been used rather often in biogeographical and environmental studies. CTA uses recursive partitioning to split the data into increasingly smaller, homogenous, subsets until a termination is reached. The optimal length of the tree is selected by a 50-fold cross-validation. The advantage of CTA is that it allows capturing of non-additive behavior and complex interactions. GBMs were newly introduced in ecology. They are extremely useful in fitting the data. They are non-parametric and link the strengths of diverse modern statistical techniques. Here, GBM was carried out in R using the library GBM (Generalized Boosted Regression Modelling). GBM proceeds via sequential improvements.

Boosting is a numerical optimization technique to minimize a loss function (such as deviance) by adding at each step a new tree that best reduces the loss function. Environmental variables are input into an initial regression tree, which maximally reduces the loss function. For each following step, the concentrate is on the residuals. For example, at the second step, a tree is fitted to the residuals of the initial tree. The model is thus updated to consist of two trees, and the residuals from these two trees are calculated. The sequence is repeated as long as necessary. The maximum number of trees was set to 3000, and tenfold cross-validations were performed. GBM belongs to the class of learning methods. RF belongs to the machine learning methods. Random forest generates hundreds of random trees. A selective algorithm limits the number of implemented parameters in each tree. A training set for each tree is chosen as many times as there are observations, among the whole set of observations. For each node of trees, the decision is taken according to randomly selected environmental parameters. Trees thus constructed are not pruned and are as large as possible. After the trees have been built, data are entered into them and each grid square will be classified by all trees. ANN is a powerful rule-based modelling technique, which is increasingly used in bioclimatic envelope modelling. A network contains three different types of layers: the input layer (in which the environmental variables are input), the hidden (intermediate) layers and the output layer. Each layer is composed of independent neurons; each of them treats separately the outputs of all neurons from the previous layer as inputs of multivariate linear functions. The process is continued until processing of the output layer. Once the complete network is built, the different weighting factors of the multivariate linear functions are chosen by minimizing the quadratic error of the estimate. One difficulty with the use of species distribution models is that the number of techniques available is large and is increasing steadily, making it difficult for the user to select the most appropriate methodology for their needs. This is particularly true when models are used to project distributions of species into independent situations, which is the example of projections of species distributions under future climate change scenarios. BIOMOD is a computer platform for ensemble forecasting of species distributions. The main advantage of it lies in its capability to compare or combine a suite of algorithms. It also built on the power of R that now fully integrates geographic information



systems. In this study, we used the ensemble predictions of the models under the framework Biomod and R software. To do so, 20% of the species presence data was devoted to the evaluation and 80% to the implementation of these models. This process was repeated for 10 times for each of the used models. Evaluation and implementation parts were randomly selected from the data. Finally, for each model, the results were obtained from these 10 runs. The predictive model performance was evaluated using one main kind of accuracy measures, area under the receiver operating characteristic curve.

## Results and Discussion

All models assume a certain equilibrium, namely that the species occur in all environments where it is possible to survive, that it cannot survive outside this range and that it is in equilibrium with climate. In fact, due to many reasons (time delay in response, limited dispersal, anthropogenic influence), the situation is probably different from many species. Therefore, we report here the potential changes in suitable habitat for Persian oak, not the real range changes that will happen. However, a certain trend can be observed, which should influence decisions to be prepared for the species' response to climate change. Monitoring species distribution modelling can help us distinguish the most important factors in determining species presence and in designing conservation programs. This research showed annual precipitation (49.7%) and mean temperature of the driest quarter (27.7%) has played the most important role in habitat suitability of these species. Under RCP4.5 climate scenario Persian Oak might lose 35.7% of its climatically suitable habitats due to climate change factors, by 2050, while in a number of areas (61.4%), the currently unsuitable habitats may be converted into suitable. In the studied region as a result of climate changes, Persian Oak was moved to the higher elevation. Results have been similarly obtained in many of the studies in which the movement of species was affected by climate change. Among all the statistical techniques, RF was found to be the most reliable model for species prediction. However, the predictions from the different models varied a lot, even if for one given species, outcomes of prediction may change from model to model. In an opinion that each predictive model relied on different mathematical functions, SDM will give a variety of results without the doubt. Nevertheless, it was not so surprising because the RF model gives the predictions by producing thousands of trees and aggregated with an average. Thus, in this research RF was a robust technical modelling for species distribution prediction and ensemble modelling was also regarded as the best solutions to reduce the single model uncertainties and bias. To assess the accuracy of the maps produced by the model, AUC of ROC plot was used. Based on these results, all models are functioning well, because whenever an implemented model has the AUC values of more than 0.7 and 0.9, it will be considered a good and excellent model, respectively; otherwise, the model is weak.

## Conclusions

This research showed that ensemble modelling by Biomod could predict the current potential distribution of Persian Oak with high accuracy (AUC varies from 0.85 to 0.98). Among all the statistical techniques, RF was found to be the most reliable model for species prediction. This research showed annual precipitation and mean temperature of the driest quarter have played the most important role in habitat suitability of this species. These models could also predict the geographical shift of given species under climate change scenarios (RCP4.5). According to the results, Persian Oak is expected to move toward higher elevation, with a decreasing area of the current distribution. This study highlights the importance of climate change on the geographical plant species distribution. Persian Oak is one of the most important forest plant species in the Central Zagros of Iran, very crucial for soil conservation and biodiversity; hence, it requires an extra effort to protect species such as Persian Oak against climate change.

**Keywords:** Central Zagros, Chaharmahal and Bakhtiari province, ensemble method, habitat suitability, random forest.

## Monitoring and prediction of urban growth by using multitemporal images and GIS techniques (Case study: Bojnourd City)

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### Extended abstract

#### Introduction

Rapid population growth and human activities have resulted in unsustainable exploitation of natural resources. Studying land changes, change detection and prediction are essential in analyzing developmental consequences over time and also in decision-making and implementing appropriate policy responses relating to land uses.

Land-use change modeling has become a top research topic in many scientific field, recently. There are many approaches and models in use to perform spatially simulations, but among many land use modeling tools, LCM offers many advantages.

This modeler evaluates land changes between two different times, calculates the changes trend, gain and loses, persistence and displays the results with graphs and maps. There are three approaches to produce the probability map: logistic regression, multilayer perceptron (MLP) and a similarity-weighted (SimWeight).

Multi-layer perceptron (MLP) creates a transition potential map for each group of transitions in order to allocate the simulated transitions. It uses a Markov matrix to extrapolate the quantity of each transition and persistence.

Markov matrix generally obtains through the comparison of the land use maps from two dates. Markov chain projection provides the model with the estimated areas of each land use category for future dates and the amount of change for each transition.

LCM needs explanatory variables to improve the understanding of the causes, locations, and trends of land use changes. These variables are selected when they exhibit relatively high Cramer coefficient values for land cover categories. Cramer's Coefficient indicates the degree to which each explanatory variable is associated with the distribution of land cover categories.

This study demonstrated that human disturbance including road and urban distance was the key factor in determining transition model in land change prediction.

We predicted land use changes in Bojnourd city using multi-temporal remote sensing data and a multi-layer perceptron (MLP) neural network with a Markov chain model. Remote sensing techniques applied to classify satellite imagery in 2001, 2008 and 2015.

Several studies have developed different modeling methods to simulate the pattern and consequences of land use changes. Arekhi (2011) modeled deforestation using logistic regression, GIS and RS in the Iran's west forests. In this research, the effects of seven factors, distance from roads and residential areas, forest fragmentation index, distance from forest edge, aspect, elevation and slope were studied. The results indicated that by decreasing the distance from residential areas and roads, forest degradation will be more and the most of the deforestation occurred in the fragmented forest cover.

Joorabian Shoostari and Gholamalifard (2015) explored changes in landscape pattern in northern Iran's Neka Basin in 1987, 2001, 2006, 2011, and 2017. Their studies revealed that during 1987–2001, agriculture was the main contributor to the increased built-up area, between 2001 and 2006 agriculture converted to orchard and residential, and between 2006 and 2011 forest regenerated from orchard and agricultural lands.

Numerous studies have assessed urban growth with different modeling methods around the world. These studies though mapped and focused on determining whether a change has occurred and how the change has evolved over time.

Wilson and Weng (2011) studied impacts of urban land use and climate changes on surface water quality within Des Plaines River watershed, Illinois. Low density residential growth, normal urban growth, and commercial growth are three future scenarios in this study specified with Land Change Modeler (LCM).

Halmy et al. (2015) employed Markov-CA to predict future changes in part of the northwestern desert of Egypt. This studies results revealed more urbanization of the landscape with potential expansion in the croplands westward and northward, an increase in quarries, and growth in residential centers. Numerous research studies have used different modeling methods, for example.

## Materials and Methods

Land Change Models can be very useful tools for environmental and urban growth research concerning about land use change.

LCM was used in this research to predict the land use map in 2015 using the following procedure: change analysis and choice of explanatory variables, transition potential modelling, change prediction map and model assessment.

A total area of 14438.03 hectares of Bojnourd city was taken as study area which has potential for expansion. IDRISI Andes was used to determine land change using three different land-use maps from 2001, 2008 and 2015.

In this study, a series of satellite images of Landsat Enhanced Thematic Mapper Plus (ETM+) and Operational Land Imager (OLI) data (2001, 2008, and 2015) were respectively used to produce classified land use/cover map. It's necessary to assess the satellite data for their image quality.

Maximum likelihood classification was used to derive three land use categories in the study area. This way is based on the probability density function associated with a particular training site signature.

Accurate assessment land use maps, using ground control points, visual interpretation and Google earth were controlled. The classification accuracy and kappa coefficients was evaluated for land use maps.

The Land Change Modeler module in IDRISI software was utilized for land change detection and change trend analysis. For change analysis and prediction, first of all Land use maps for 2001 with 2008, 2008 with 2015, and 2001 with 2015 were used for analysis and detection of changes. Net change, gains and losses, persistence and other modules were used to evaluate map transition potential.

The study was used several variables including distance from road, distance from settlement, distance human disturbance, distance from vegetation edge, slope and qualitative variables.

The drivers of change were used to help understand what factors are major contributors to land change in study area. Identifying the factors is very important to predict and analysis the causes of change.

The Cramer's V coefficient was used to quantify the associations between classes and variables. It can indicate the degree to which each explanatory variable is associated with the distribution of land use classes. Two land cover maps of two different times (2001 and 2008) were applied to predict potentially transition in the future. LCM available (as IDRISI and ArcGIS extension) is a useful tool for the assessment and projection of land cover changes. Different modules are available to do this like cross tab module, gains and losses and etc.

## Results

The land-use maps were produced by supervised maximum likelihood classification and three classes (settlement areas, vegetation and barren land) were considered. Kappa coefficients obtained in this study was above 80%.

In this study, three major land use categories identified and mapped after field surveys, literature reviews and visual interpretation. Neural network training was carried out with the default setting (learning rate from 0.01 to 0.001, momentum 0.5, number of hidden nodes calculated as the average between numbers of input and output nodes, 10,000 iterations).

Four sub-models were identified including barren land to settlement areas, vegetation to settlement areas, vegetation to barren land and barren land to vegetation. Land use map of 2015 was predicted by using changes occurred during the years 2001 and 2008.

The analysis of changes shows the expansion in settlement areas (1203 ha), barren land (737 ha), vegetation area (554 ha) during the years 2001-2015. The land use change analysis for the next period (2008-2015), indicates that the area of settlement areas has increased. The transition from Burgenland and vegetation to settlement areas was 980 ha.

## Discussion and Conclusion

The objective of this research is to evaluate LCM as a land use model, focusing on its predictive power for the assessment of transition potential.

This study used Landsat ETM+ imageries of 2001 and 2008, and OLI/TIRS of 2015 to identify, classify, assess and interpret changes in a city area. The land cover categories and their changes for these years were generated and analyzed in the Idrisi environment.

Land use scenarios for 14 years from 2001 to 2015 was performed using Markov analysis in LCM module in IDRISI software.

Land Change Models can be very useful tools for environmental and urban growth research concerning about land use change. Rapid urban growth in last decades is a big problem which prompts concerns about environmental issues over the accompanied environmental issues and the degradation of economical sustainability.

Land use maps are very vital in decision makers and environmental management purposes to evaluate land changes and the causes of land degradation. LCM provides comparable and understandable maps and graphs to demonstrate natural and environmental conditions. Monitoring land changes can provide valuable information for regional management and planning, but it's not enough. Prospective simulation supports decision-making for urban planner and environmental management. LCM provides great advantages such as better monitoring changes, describe change trend, quantifying changes and also it can answer to questions with different scenarios like "what would happen if".

**Keywords:** *Land Change Modeler (LCM), Markov chain, multi-layer perceptron algorithm of artificial neural (MLP), transition potential, urban growth.*

## Assessment of landscape quality of urban public spaces (Case study: Imam Square in Hamedan)

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### Extended abstract

#### Introduction

Public space landscape has a multi-dimensional and complex nature, therefore people perception is different about it. Although we can spot urban landscape definition as an over scale of single building architecture in the simplest concept, but it shouldn't summarize at the physical and visual design. So, whatever can be understood by human senses, it influences on perceptual landscape quality. On the other hand, environment, people, and their activities have an important role in creating the urban space landscape. They create environment vitality. Hence, studying urban landscape need a comprehensive view about subject various dimension. In this comprehensive view, first we should identify urban landscape quality parameters, then we should assess factors relationship to improve them.

Imam Square in Hamedan has a special situation in urban structure and attracts the most number of various people. Hence, we knew it the most important public space in city that obtains a context for people daily activities. Although this square has a basic role in urban structure, but it doesn't have a suitable environmental quality and people aren't acquiescent than its quality, despite designed building sidewalls, presence of very population, and cultural-historical ceremony accomplishment. On the other hand, although Imam Square notes as a cultural heritage, but it sound people don't tally it as a "heritage" and "cultural" sign. In fact, verbal landscape of Imam Square doesn't have congruity with a thing we expect of it. So, it is necessary that we assess its landscape and reform it.

#### Materials and Methods

This paper is a descriptive-analytical and it is based on documental studies and field observations. Research theoretical studies were obtained through library studies and then parameters for evaluating the landscape quality of public space extracted. Then, extracted parameters were surveyed on the case study and main factors importance in quality of public space were specified by using factor analysis method. So, first we prepared questionnaire based on extracted indicators and five-level Likert method. In this research, people in the Imam Square are target society. We considered 200 questionnaire based on the Neyman sampling test in order to validity for SPSS analysis (The number of questionnaires are 6 times more than the number of indicators). After the completing questionnaires, we input data to SPSS software to analyze with factor analysis, extracting main factors, and calculating case study scores. Then, we used linier multi-variable regression method to assess relationship between extracted factors and landscape quality of square. At the end, we specified landscape quality improvement priorities of Imam Square by assimilating factor coefficient and people dissatisfaction mean.

#### Discussion of Results

People realize urban landscape and public space in various fields and views. So, for invitation of various people satisfaction presenting in urban spaces, it is necessary to identify whatever people percept truly and effort to improve them. Therefore, in first step, we need to identify landscape main parameters and then assess them in the case study. In a generic division, we can classify public space landscape parameters in four story: "physical",

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“functional”, “elegance” and “moral- conceptual- sensory”. After the completing questionnaires, we input data to SPSS software to create early data matrix. This matrix has 200 rows (one row per one questionnaire) and 32 columns (one column per one variable). Based on factor analysis method, two variables including “Details” and “Graffiti” have a score lower than 0.4 in Community Matrix. Hence, they don’t suitable for factor analysis method, so they lay away from variables set. Finally, when we run model with 30 rest variables, variable quantities in Community Matrix became larger than 0.4 and KMO value became equal 0.780 and Sig. value became 0.000. That these values mean correlation between variables is suitable to analyze.

At the end, the variables are classified in 9 landscape quality factors. That sum of aggregation variance of 9 factors are equal 74.78. After determine the number of factors, the Rotated Component Matrix is formed. This shows position of variables in each factor and we can do naming and interpreting the factors. These factors include:

- The first factor, Behavioral Landscape. This factor includes 12.93% of total variance and is related to “Sidewalls Activity & Land Use”, “Vendors & Peddlers”, “Vehicle Movement”, “Pedestrian Movement”, “Discipline & Arrangement”, “Sense of Security”, and “Noise Condition”.
- The second factor, Supplementary Landscape. This factor includes 11.83% of total variance and is related to “Urban Facilities & Equipment”, “Coloring”, “Urban Advertising”, and “Decorating”.
- The third factor, Space Formation. This factor includes 10.45% of total variance and is related to “Human Scale”, “Enclosure”, “Spatial Configuration”, and “Buildings Sidewall”.
- The fourth factor, Pedestrian Facilities, This factor includes 9.37% of total variance and is related to “Urban Furniture”, “Flooring”, “Pedestrian Direction”, and “Guidance Signage”.
- The fifth factor, Nightly Landscape. This factor includes 8.26% of total variance and is related to “Night Activity” and “Light”.
- The sixth factor, Natural Landscape. This factor includes 6.89% of total variance and is related to “Green Space” and “Fountain”.
- The seventh factor, Place Prestige. This factor includes 6.15% of total variance and is related to “Central Statue”, “Valuable Buildings”, and “Cultural & Artistic Events”.
- The eighth factor, Environmental Health. This factor includes 4.67% of total variance and is related to “Cleanliness” and “Olfaction”.
- The ninth factor, Semantic Landscape. This factor includes 4.23% of total variance and is related to “Identify” and “Vitality”.

When we specify landscape main factors of Imam square, we need to discover the relationship between these factors and landscape quality of Imam square. So, “Standardized Coefficient of Beta” is calculated by using the linear multi-variable regression analysis technique. Then three values include “Component Score Coefficient”, “Standardized Coefficient of Beta” and “Dissatisfaction Average of each Variables” being multiplied together and priority’s variables are specified.

## Conclusions

Research findings show basic parameters in landscape quality of Imam Square are regularity “Noise Condition”, “Vehicle Movement”, “Vendors & Peddlers”, “Urban Furniture”, “Sense of Security”, “Guidance Signage”, “Cleanliness”, “Light”, “Pedestrian Behavior”, and “Night Activities”. Therefore, we can offer these general conclusions:

- A significant proportion of space landscape quality is influenced by “Behavioral Landscape”. Therefore, we must notice to prospects of space perception and function besides offering two-dimension and three-dimension plans. So that in Imam Square, we observe beside physical and structural quality of square. Other aspects such as “Noise Condition”, “Sense of Security”, and “Cleanliness” don’t have a favorable condition.
- “Vehicle Movement” in public spaces is one of the most effective items on landscape quality. Hence, in Imam Square, vehicle movement is one of the organizing action priorities. Also, this variable effect on other variable such as “Noise Condition” and “Sense of Security” straightly.
- One of the main parameters to assess the landscape quality of public spaces is condition of them in different times. Hence, in Imam square, both “Nightly Landscape” variables are among landscape organizing priorities of Imam Square.
- Whereas urban public space landscape is percept by pedestrian view, therefore the facilities are considered for viewer (pedestrian) have a key importance. Hence, in Imam Square, pedestrian facilities such as “Urban Furniture” and “Guidance Signage” are as landscape organizing priorities of Imam Square.

Finally, we can offer bellow items to improve landscape quality of Imam Square in Hamedan:

1. Traffic adjustment and management in square

2. Preventing vehicle stops in square
3. Supervising on vendors and peddlers activities
4. Suitable designing and locating of urban furniture, panels, and guidance signage
5. Lighting organizing
6. Collection of garbage and disposal of surface water
7. Organizing the pedestrian movement directions.

**Keywords:** Hamedan, public space, urban landscape, urban square, visual comfort.

## Development of Environmental Flow Assessment Method for Rivers in Southern Caspian Sea Basin

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### Extended abstract

#### Introduction

Environmental Flow Requirement (EFR) is defined as the flow that is necessary to ensure the existence of habitats in water resources systems. Hydrological methods are almost the most straight-forward approach in rivers. These types of methods are also known as desktop methods that rely on annual, monthly or daily flow discharge data of the river. There are two main limitations for desktop approach. First, in this type of approach, regional ecological values are not considered directly. Secondly, this type of approach has little defense capability in interactions of water allocation, but because of having some advantages such as simplicity, it is used in many countries. But it is unequivocal which development of localized desktop approach is obligatory and also is salutary. It can be used as a flow index for environmental flow assessment in different projects. Main contribution of present research is development of new desktop method for environmental flow assessment in southern Caspian Sea basin with focusing on regional ecological values.

#### Material and Methods

The Lar National Park is located in 55 km at east of Tehran. Its mean elevation from open seas is 2531 m and its area is 27000 ha approximately. In this park, Brown Trout (one of Iran's most unique species) inhabits. This park is one of the original habitats of Brown Trout which has unique properties. In this park, predation of Brown Trout is forbidden and is protected by the Iranian Department of Environment (DOE). This park is an ideal place for development of hydrological flow index based on real life of aquatic in their habitats and physical habitat effects. Since the development of physical habitat simulation, physical habitat models became an important tool for river management. Aquatic habitat simulation models have been used for fish in water resource management, particularly in North America. The Physical Habitat Simulation is considered to be the first of these fish habitat models and is now being applied worldwide. In the present research, 1-D hydraulic simulation in combination of physical habitat simulation is used to simulate physical habitat for Brown Trout. Quantified ecological or habitat modeling describes flow changes in physical components of the system and translates them into an estimate of the quality and quantity of microhabitat for aquatic organisms. The most commonly used output from these types of models is Area Weighted Suitability (AWS). This factor is computed within the reach at a specific discharge from:

$$(1) \quad AWS = \left( \sum_{i=1}^n A_i \times C_i \right) / L$$

where  $A_i$  is the surface area of cell  $i$  and  $C_i$  is the combined suitability of cell  $i$  (i.e., composite of depth, velocity and channel index individual suitability). Common method in estimation of  $C$  is consideration of minimum value of depth, velocity and substrate suitability for development of combined habitat suitability in each habitat cell. Description of river condition is carried out in three main conditions which are maximum protection or outstanding, mid protection or good and minimum protection or poor. Two main habitats are selected for implementation of ecological modeling which are Elarm. Elarm is as a main habitat for fry and juvenile Brown



trout and Absefid is as a main habitat for adult Brown trout. Elarm stream slope is smaller than 2% and slope of Absefid is larger than 2%. Hence development of flow index for environmental flow is carried out based on these two types of rivers. Development of hydrological flow index was based on MAF in each river.

**Results and Discussion**

Habitat time series are shown in Figure 1. In this figure you can see the alteration of AWS in different months. According to habitat time series, environmental flow regime is assessed in two habitats in three stages. First stage was maximum protection or outstanding condition which maximum area weighted suitability is available for aquatics in river. Based on ecological negotiations, minimum acceptable AWS was 50% of maximum AWS, hence in stage 2 and 3, 75% and 50% maximum area weighted suitability is available. Estimated environmental flow regime is displayed in Figure 2. Lar method recommendations for assessment of environmental flow requirement are displayed in Table 1. It should be noted that seasonal scale is considered.

Table 1. Lar method recommendations in EFR assessment

| Winter                  |                        | Fall                    |                          | Summer                   |                          | Spring                  |                        | River condition |
|-------------------------|------------------------|-------------------------|--------------------------|--------------------------|--------------------------|-------------------------|------------------------|-----------------|
| 2>%.<br>135<br>35<br>20 | 2<%.<br>70<br>60<br>45 | 2>%.<br>300<br>60<br>25 | 2<%.<br>120<br>100<br>80 | 2>%.<br>425<br>100<br>30 | 2<%.<br>135<br>105<br>85 | 2>%.<br>130<br>35<br>20 | 2<%.<br>70<br>60<br>45 |                 |

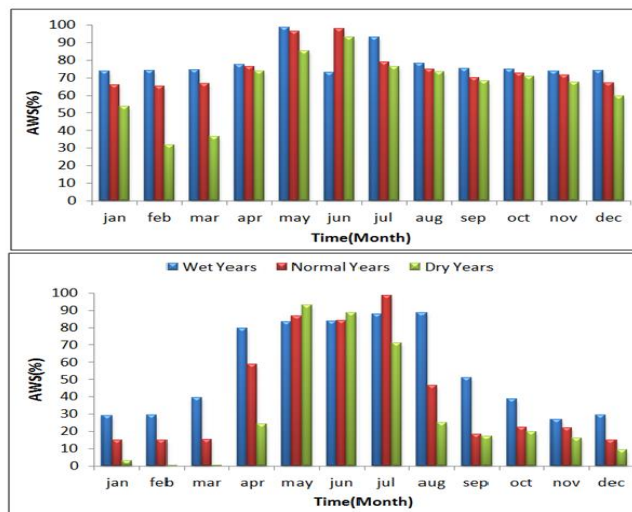


Fig. 1. Habitat time series in simulated habitats (figure above is Absefid and figure below is Elarm)

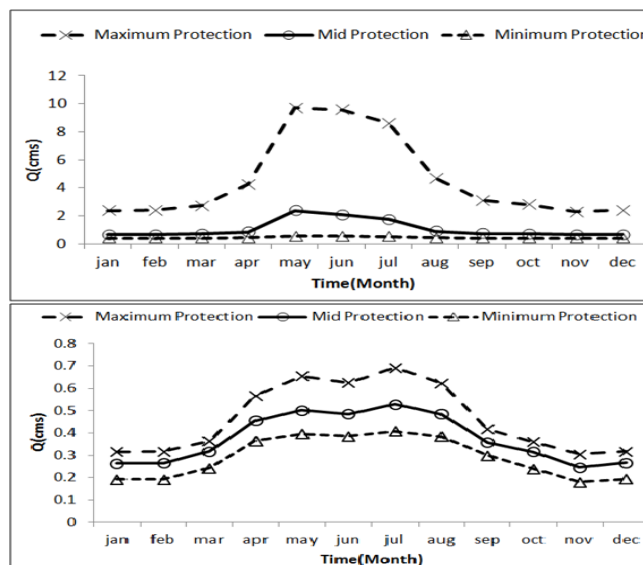


Fig. 2. Environmental flow regime (figure above is Absefid and figure below is Elarm)

**Conclusion**

In the present research, a desktop method is developed southern Caspian Sea basin. Because of special features of Brown trout habitats in Lar national park, this place is chosen for ecological modeling and development of hydrological flow index based on mean annual flow. According to results, minimum flow need for rivers which slope is larger than 2% are 20%, 30%, 25% and 20% of MAF in spring, summer, fall and winter respectively, but these values in river which slope is smaller than 2% are 45%, 85%, 80% and 45% of MAF.

**Keywords:** brown trout, environmental flow assessment, habitat simulation, Lar desktop method.