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# Regeneration of poor neighborhoods with an emphasis on spatial configuration (Case study: Hamedan)

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Received: August, 2016

Accepted: May, 2017

## **Expanded Abstract**

## Introduction

Attention to the city structure has been influenced since structuralism viewpoint from the early 1960s. At the beginning of the 1960s, Team Ten tried to consider the city like the whole unite, in contrast to the functionalism. In this viewpoint, theorists such as Edmund Bacon, Christopher Alexander and Kevin Lynch have underscored the importance of urban open spaces; So, streets structure has created the most area as the most important element of spatial structure that it can enhance connections between space and people. After that at the ending of 1970s, Bill Hillier and Joseph Hinson produced the Space Syntax theory for the cognition of spatial structure and urban configuration. They examined the relationship between space configuration and special behaviors. The mean of space configuration is the condition of spaces next to each other and makes connection between them. Thus, it can be concluded that each change on the arrangement of spaces will create changes in the whole of spatial configuration. In other words, in the city, each change on the city map (add or subtract a space such as streets, open space, etc.) will create changes on the relation of spatial configuration. These changes can vary the probability of activities and events. Recently, it has been proposed to improve the living conditions of residents of informal settlements, however it has not achieved the planned goals. One of the reasons for this problem is inattention to importance of knowing neighborhoods in various aspects of economic, social and physical ones. This study has tried to survey and analyze the different parameters of spatial configuration for a number of informal settlements of Hamedan through which we can identify the differences between neighborhood structures.

## **Materials & Methods**

This study has been done by using analytical-interpretive method, library research, and spatial configuration analysis of several case studies. At the beginning, the literature review was obtained through library research. In the next step, for analyzing the spatial configuration of neighborhood, we produced the map of urban blocks. This map separates full and empty spaces (streets and squares) from each other. After that, linear map is drawn for the city using the software of Depth Map. Then, various parameters of spatial configuration (including line length, integration, depth, connectivity, control and choice) are extracted by linear map of city. Finally, based on analyzing the various parameters, key strategies are suggested to improve the spatial configuration of case studies.

## **Discussion and Results**

In this study, the linear map of Hamedan has been drawn by using the software of Depth Map. The linear map is included structure of a series of urban open spaces being created based on the longest view line and connection. After drawing linear map of the city, the parameters of spatial configuration can be extracted for informal settlement. The main parameters of analyzing spatial configuration are line length, general integration, local integration, depth, connectivity, control and choice that their characteristics for case studies are as follows: *Hesar Neighborhood:* 

- The suitable situation in general integration
- The lowest local integration

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- The lowest average of connectivity
- The highest average and standard deviation of choice
- The suitable situation in depth

Khezr Neighborhood:

- The lowest average of line length like the Dizaj neighborhood
- The suitable situation in general integration
- The highest average of connectivity
- The lowest average and standard deviation of choise
- Dizaj Neighborhood:
  - The lowest average of line length
  - The lowest average of general integration
  - The highest average and standard deviation of local integration
  - The highest average and standard deviation of depth
- Mazdaghineh Neighborhood:
  - The lowest average of line length
  - The suitable situation of local integration
  - The highest average and standard deviation of local integration
  - The suitable situation of depth
  - The highest average of connectivity
  - The lowest standard deviation of control
  - The lowest average and standard deviation of choice

Manouchehri Neighborhood:

- The highest average of line length
- The highest standard deviation of line length
- The highest average of general integration
- The lowest average of connectivity
- The highest standard deviation of control
- The lowest average and standard deviation of depth.

#### Conclusions

According to parameters of spatial configuration (line length, integration, depth, connectivity, control, and choice) in Hamedan and five informal settlements (Hesar, Khezr, Dizaj, Mazdaghineh and Manouchehri), the results showed a significant difference between case studies. However, the situation of spatial configuration of neighborhoods was not satisfactory and it is essential to adjust and organize their spatial configuration parameters.

The following are some general strategies suggested for improving the spatial configuration of case studies:

- *Hesar Neighborhood.* It is essential to create structure of streets and texture for this neighborhood as a whole unit. Therefore, these strategies are suggested: promoting unity and solidarity in structure of streets and texture, developing the available vacant land in the neighborhood, and creating some main the east-west streets to increase local integration and decrease the isolation edges of neighborhood.
- *Khezr Neighborhood.* The dense texture and the north-south structure of this neighborhood has caused a lot of pressure on the street in western edge. Therefore, the following strategies are suggested: decreasing dense and massive texture, creating the north-nouth arterial street in the east of neighborhood for decreasing depth and isolating eastern part of neighborhood, and strengthening the relationship of neighborhood with ring road in east of neighborhood.
- *Dizaj Neighborhood.* The structure and inner configuration of this neighborhood is relatively stable and it seems essential to solve the problem of isolation of overall city. Therefore, these strategies are suggested: decreasing isolation of neighborhood from the whole of city, developing the vacant lands between neighborhood and the city, and promoting the order of street structure inner the neighborhood.
- *Mazdaghineh Neighborhood.* This neighborhood has the suitable opportunity in spatial configuration of city, but internal configuration of that is strongly influenced by the rural pattern. Therefore, these strategies are suggested: organizing and disciplining the inner streets of neighborhood, redesigning and aggregating of small blocks, and creating several cross streets in structure of neighborhood.

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• *Manouchehri Neighborhood.* The spatial configuration of this neighborhood is better than other informal settlements. It can be attributed to raster-like structure and small area. Therefore, these strategies are suggested: creating a hierarchy of streets by converting some public streets to semi-public street, and decreasing the uniformity of texture through creating a variety of streets and intersections.

Keywords: environmental quality, Hamedan, informal settlements, space syntax, urban regeneration.

Seyed Yousef Hejazi, et al.

## Investigating the effective factors on environmental behavior of environmental NGOs members in Tehran Province

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Received: November, 2016 Accepted: May, 2017

## **Expanded Abstract**

#### Introduction

In recent decades, environmental crises have caused increasing concerns about the safety of human life. Many believe that the solution crises should be searched in the change of human behavior and attitude's and his life method on earth. Researchers have suggested various solutions for environmental problems, most of which are technological. But nowadays due to the high cost of these projects, they are interested in changing people's lifestyles and behavior. Different models and theories have been used in various studies to explain the environmental behavior and different variables have been studied as the effective factors on environmental behavior.

Environmental NGOs have been stablished due to society needs and raising public awareness and knowledge about environmental issues is the main role of NGOs. These organizations play an important role in achieving the goals of protecting the environment, reducing pollution and recovering environmental damages. Therefore, environmental NGOs is one of the most important tools for environment conservation. The main goal of this study is to investigating the effects of environmental knowledge, environmental perception, environmental attitudes and environmental intention on environmental behavior of environmental NGOs members. The research conceptual framework is as follows:



## **Materials and Methods**

This study is a descriptive-correlational research and survey method was used to collect the data. The statistical population consisted of environmental NGOs members in Tehran Province which are active in environmental education field that has about 250 main and active members. Sample size determined 148 persons by using Krejcie and Morgan table and Sampling was done randomly. In this study in order to collect information, a questionnaire including 55 items in two parts was used: The questions of the first part was about the individual features and the second part questions were related to four factors influencing environmental behavior including environmental knowledge, environmental paradigm questionnaire: Dunlap et al. (2000), environmental knowledge questionnaire: Morrone et al. (2001) and Frick et al. (2004) questionnaire. Content validity was confirmed by experts and its reliability obtained based on Cronbach's alpha  $\alpha$ =88%. Data analysis is done by

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using SPSS 21 and Smart-PLS software. In descriptive statistics mean, standard deviation and coefficient of variation and in inference statistics, structural modeling based on partial least squares approach were used.

### **Discussion and Results**

According to Table 1, the independent variable (environmental attitude) has the most effect on the of mediator variable (environmental intention) and also the most impact on the dependent variable (environmental behavior), and then environmental knowledge is most effective. Environmental intention as mediator variable is explained 59.6% of the variance of the environmental behavior between environmental NGOs members in Tehran Province. Also, the four variables (environmental knowledge, environmental attitude, environmental perception and environmental intention), 33.4% of the variance of the dependent variable: environmental behavior is explained by four variables: environmental knowledge, environmental attitude, environmental perception and environmental intention. And the remaining percentage is related to factors that have not been identified in this research.

Table 1. Results of direct & indirect effects							
Dependent variable	Independent variable	Direct effect	Indirect effect	T Value	P Value	$R^2$	$R^2 Adj$
Environmental intention	Environmental knowledge	0.316	-	5.961	0.000		
	Environmental attitude	0.421	-	7.002	0.000	0.596	0.588
	Environmental perception	0.282	-	5.592	0.000		
	Environmental knowledge	-	0.183	5.429	0.000		
	Environmental attitude	-	0.243	4.876	0.000		
Environmental behavior	Environmental perception	-	0.163	5.341	0.000	0.334	0.329
	Environmental intention	0.578	-	10.518	0.000		
	Environmental behavior	-	-	-	0.000		

The results of the research hypotheses testing in Table 2 shows that all hypotheses have been confirmed.

Table 2. Results of research hypotheses testing							
hypotheses	Beta	T Value	Result				
Hypothesis 1: There is a significant relationship between	0.499	5.429	confirmed				
knowledge and environmental behavior.							
Hypothesis 2: There is a significant relationship between	0.664	4.876	confirmed				
attitude and environmental behavior.							
Hypothesis 3: There is a significant relationship between	0.445	5.341	confirmed				
perception and environmental behavior.							
Hypothesis 4: There is a significant relationship between	0.578	10.518	confirmed				
intention and environmental behavior.							
Hypothesis 5: There is a significant relationship between	0.316	5.961	confirmed				
knowledge and environmental intention.							
Hypothesis 6: There is a significant relationship between	0.421	7.002	confirmed				
attitude and environmental intention.							
Hypothesis 7: There is a significant relationship between	0.282	5.592	confirmed				
perception and environmental intention.							

#### Conclusions

The results showed that all four variables (environmental knowledge, environmental attitude, environmental perception and environmental intention) have a high mean in the environmental NGOs members in Tehran Province. Also, there is a positive and significant relationship between all four variables (environmental knowledge, environmental attitude, environmental perception and environmental intention) and environmental behavior. Environmental attitude has been identified as the most effective variable on environmental intention

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and environmental behavior in this study. So, awareness programs should be implemented for changing the attitude of the people and creating a proper environmental behavior culture. To create a positive attitude towards the environment in people, organizational goals should clarify and explain for all members. For this purpose NGOs can use seminars, question and answer sessions and periodically meetings for organization members. Environmental education in order to creating positive environmental attitude has to be considered because having knowledge and understanding about environmental issues are the necessary conditions for good attitudes and impacting on behavior. Environmental education is the most fundamental method for environmental protection that aims to find the most suitable and best systems of presenting contents and practices and implementation a structural promoting environmental awareness and knowledge and finally creating positive attitude in society and each person feels responsibility to preserve and protect the environment. Experts believe that knowledge, attitudes and perception's changes of people towards the environment will lead to develop and strengthen environmental behavior and reducing damage to the environment and reforming the environment crisis. One of the most important tools for making changes in effective factors on environmental behaviors is environmental education. Promoting environmental awareness in the society for each person creates a positive attitude toward environment, feeling responsibility for maintaining and protecting the environment and respects nature and knowledge about different approaches for environmental problems and participating in finding solutions. All of these are capabilities that can be achieved only with efficient environmental education. One of the important issues about environmental behavior and environmental conservation is pay attention to environmental NGOs education and training. NGOs according to their mission and objectives, has appropriate facilities to increase public awareness through education and training of their members and other people and should support these organizations in order to achieving their goals.

Keywords: environmental attitude, environmental attitude, environmental behavior, environmental conservation, environmental knowledge, NGOs.

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## Investigation acid mine drainage minerals using spectral characteristics and satellite image processing of Landsat- 8, a case study: Darrehzar mine, Kerman Province, Iran

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Received: November, 2016 Accepted: May, 2017

#### **Extended Abstract**

#### Introduction

Oxidation of iron sulfide is a common phenomenon in mining areas and sometimes generates acid drainage. Acid drainage is produced under certain conditions of pH and Eh when metallic sulphides (mostly iron) are exposed to oxygen and water. Copiapite  $(Fe^{2+}Fe^{3+}_{4}(SO_{4})_{6}(OH)_{2} \cdot 20(H_{2}O))$ , jarosite  $((SO_{4})_{2}KFe_{3}(OH)_{6})$ , schwertmannite  $(Fe^{3+}_{16}O_{16}(OH)_{12}(SO_{4})_{2})$ , goethite (FeO(OH)), ferrihydrite  $(Fe_{5}HO_{8}.H_{2}O)$ , lepidocrosite (FeO(OH)), and hematite  $(Fe_{2}O_{3})$  minerals are formed by oxidation of pyrite with increasing pH (from very acidic to neutral) and are frequently observed in mining areas with acid drainage pollution.

Landsat 8 can be used for environmental studies and detection of secondary iron minerals associated with acid drainage, as it has characteristics such as a relatively good temporal (16 days) and spectral resolutions in the visible and infrared (VNIR) ranges. This research focuses on the study secondary iron minerals associated with acid mine drainage using investigation of spectral characteristics of AMD minerals and image processing of Landsat 8 data in the Darrehzar mine.

#### **Material and Methods**

Spectra from USGS spectral library and Zabcic (2008) were chosen to identify the spectral characteristics of secondary iron minerals associated with acid drainage such as copiapite, jarosite, schwertmannite, goethite, ferrihydrite, lepidocrosite, and hematite. Furthermore, the resampled spectra of these minerals based on bands' centers of Landsat 8 were also investigated. Lepidocrosite, ferrihydrite, goethite, and schwertmannite have the same spectrum on the resampled spectrum of USGS spectal library. These minerals are created in acidic to near neutral conditions. Simillarly, jarosite and copiapite associated with very acidic conditions, have the same features in the visible range.

The Fast Line-of-sight Atmospheric Analysis of Spectral Hypercubes (FLAASH) correction applied on the images to compensate for the atmospheric effects. The NDVI masking was used to remove vegetation before performing principle component analysis technique. Then selected principal component analysis (PCAs) technique was used for image processing. The ferric iron absorption (Fe<sup>3+</sup>) of band 1 at copiapite, jarosite, schwertmannite, goethite, ferrihydrite, lepidocrosite, and hematite (0.433-0.453 micrometers), absorption of band 7 (2.100-2.300 micrometers) for copiapite and jarosite due to SO<sub>4</sub> and OH vibrations and reflectance values in band 4 (0.630-0.680 micrometers) of Landsat 8 for jarosite, schwertmannite, goethite, ferrihydrite, lepidocrosite, and hematite considered to perform this technique.

According to the eigenvector loading and spectral characteristics of Schwertmannite, goethite, ferrihydrite, lepidocrosite, and hematite minerals, PC2 is appropriate for discrimination of these minerals as bright pixels due to the high positive loading in band 6 and high negative loading in band 1. Jarosite will be presented by dark pixels in PC3 because of high positive loading in band 7 and high negative loading in band 6 which are absorptive and reflective bands respectivelly. This PC was multiplied by -1 to convert pixels related to Jarosite as bright pixels. Copiapite and jarosite will be presented by bright pixels values in PC4 based on high positive loading in band 1 which are reflective and absorptive bands respectivelly. Eventually, field survey was conducted for evaluation and verification of results of image processing. The rocks

Eventually, field survey was conducted for evaluation and verification of results of image processing. The rocks and water samples were taken out of the areas identified by image processing. Five water samples were taken

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from different parts of the mining area that consist of influx water to the mine (Da31), Piezometer well in the mine (Da32), water pit located in the eastern part of mine (Da23), accumulated water in the western part of mine (Da20), and discharging water from the mine (Da24).

Table 1. The sime second Matrix for the DCA second of London 49

	e eigenvector I	viatrix for the r	CA result of L	anusato	_
Eigenvector	Band 1	Band 4	Band 6	Band 7	_
PC 1	-0.2198	-0.49896	-0.69173	-0.47353	-
PC 2	-0.65757	-0.55888	0.423789	0.27505	
PC 3	0.023786	-0.0363	-0.5516	0.832982	
PC 4	-0.72022	0.66134	-0.19404	-0.0791	

Water samples were taken by Polyethylene bottles and recorded their temperatures in situ and transferred to Graduate University of Advanced Technology laboratory for EC and pH measurements. Their pH and EC were measured by Metrohm 827 lab pH meter and Metrohm 712 Conductometer EC meter. Rock samples were taken from southern, western, and eastern dumps and in the central part of the mine based on image processing results and transferred to Graduate University of Advanced Technology laboratory for spectroscopy measurements. Spectroscopy of rock samples was conducted by ASD FieldSpec<sup>®3</sup>. The measured spectra were compared with the spectra in USGS spectral library.

#### Result

Schwertmannite, goethite, ferrihydrite, lepidocrosite, and hematite detected in PC2, were located around the mine and pixels having high values (marked by red colour) have been presented in the east and northwest mine (Fig. 1C). Secondary iron minerals such as hematite and goethite were observed on the eastern and western dumps during the field survey. Spectroscopy results were presented goethite and hematite on the western dump and goethite on the eastern dump.

Jarosite detected as bright pixels in -PC3 covers the interior of mine and tailing dumps. Furthermore, the bright pixels in -PC3 correspond to argillic and phyllic zones in Darrehzar mine. Pixels having high values (marked by red color) have been observed within and eastern parts of mine (Fig. 1B). Copiapite and jarosite have been situated along the main stream in the middle part of the mine and southern dump (Fig. 1A).

EC and pH measurements of water samples determined that the water samples taken from eastern part of mine (Da23) and accumulated water in the western part of mine (Da20) have high EC and low pH while influx and discharging water of the mine have low EC and neutral pH. Water sampling areas having high EC and low pH (Da23 and Da20) conform to copiapite and jarosite in PC4. Despite precence of water with low pH and high EC inside of the mine, discharging water of the mine has low EC and neutral pH. It shows that during the sampling time acidic water inside of mine has no influence on the discharging water because acidic water is preserved in a reservior inside the mine. However, acidic water may be cause pollution during high rainfall period and it should be consider at the management planning of the mine.



Fig 1. The results of selected PCA on bands 1, 4, 6, and 7 Landssat-8, A: PC2 indicates schwertmannite, goethite, ferrihydrite, lepidocrosite, and hematite; B: -PC3 indicates jarosite; C: PC4 indicates copiapite and jarosite

#### Conclusions

Investigations spectral features of secondary iron minerals associated with acid mine drainage revealed that strong absorption of the minerals associated with very acidic environments such as copiapite (0.430µm) and

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jarosite ( $0.436\mu m$ ) is located at lower wavelengths than strong absorption of the minerals associated with acidic to neutral environments such as schwertmannite ( $0.489 \mu m$ ), goethite ( $0.480 \mu m$ ), ferrihydrite ( $0.489 \mu m$ ), lepidocrosite ( $0.480 \mu m$ ) and hematite ( $0.480 \mu m$ ). In addition, jarosite (associated with very acidic conditions) shows strong absorption feature in short wave infrared (SWIR) region ( $2.26\mu m$ ) due to SO<sub>4</sub> and OH vibrations while the other minerals such as schwertmannite, goethite, ferrihydrite, lepidocrosite and hematite do not have any absorption features in this region. The results of spectral processing revealed that despite there are some similarity between schwertmannite, goethite, ferrihydrite, and lepidocrosite, it is possible to discriminate AMD minerals using spectroscopic studies due to large numbers of spectral channel in spectrometers.

The result of Landsat- 8 image processing showed that the OLI sensor in this satellite could identify secondary iron minerals associated with acid drainage and determine environments having different acidic conditions. However, it could not separate hematite, goethite, lepidocrosite, ferrihydrite, and schwertmannite which have relatively the same spectra from each other and also copiapite and jarosite. Based on PCA results lepidocrosite, ferrihydrite, hematite, goethite, and schwertmannite that are associated with acidic to neutral conditions, were detected around mine while copiapite and jarosite that are generated in acidic condition (low pH), have been detected inside mine. Results of laboratory and field analysis conformed image processing results so that spectroscopy analysis on samples of eastern and western dumps revealed hematite and goethite which correspond to discriminated minerals like hematite, goethite, lepidocrosite, ferrihydrite and schwertmannite in PC2.

### Acknowledgment

The authors are sincerely grateful to the geologists and staff of the Sarcheshmeh copper mine especially Mr. Khosrowjerdi, Dr. Sahrayi, and Mr. Salajegheh for providing the facilities and kindly helping us during our field work.

Keywords: Acid mine drainage, Darrehzar, image processing, Landsat 8, spectral characteristics

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## Survey of the magnetic field effect on arsenic removal from drinking water with and without iron filings

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Received: August, 2016 Accepted: May, 2017

## **Expanded Abstract**

#### Introduction

Arsenic is a toxic metalloid and exists in nature in the two organic and mineral forms. Arsenate is the oxidized form and predominant in the surface waters, while arsenite is a reduced form and often found in the groundwater. Besides, toxicity and solubility of arsenite is more than that of arsenate. Excessive and prolonged human intake of inorganic arsenic, through drinking water and food, causes arsenicosis including skin disorders, skin cancer, internal organ cancer, arm and leg vascular diseases and diabetes. The World Health Organization (WHO) guideline value for arsenic in drinking water is set as 10  $\mu$ g/l. It should be noted that this standard is 50 µg/l in Asia and also in Iran. There are three main methods for arsenic removal from drinking water, including membrane filtration, coagulation-precipitation and adsorption. Water treatment by means of the magnetic field has been recently considered. Ma et al. (1998) investigated the arsenic removal via sulfide ions in the magnetic field. Coey and Cass (2000) carried out a study on water treatment using the magnetic field. Lipus and Dobersek (2007) surveyed the influence of magnetic field on the aragonite precipitation. Also, Ambashta and Sillanpää (2010) investigated water purification using magnetic assistance. Szcześ et al. (2011) carried out the effects of static magnetic field on water at kinetic condition. Gholizadeh et al. (2005) investigated the effect of magnetic field on scale prevention in the industrial boilers. Amiri and Dadkhah (2006) carried out a study on the reduction of the surface tension of water due to magnetic treatment. In addition, Banejad and Abdosalehi (2009) conducted an experiment on the effect of magnetic field on water hardness reducing. In this study, the efficiency of iron filings in arsenite removal from polluted water was primarily surveyed, and then the effect of magnetic field on the process was investigated. The innovation of this research will be to understand the importance of physical forces such as magnetic field in the field of water purification and its application in the water industry.

#### **Materials and Methods**

#### Preparation of adsorbent

The required iron filings were prepared in the turning workshops of Tehran, Iran. The iron filings were passed through a sieve with pores of 2 mm and were made wet using deionized water. Ferric hydroxide precipitation was allowed to be formed on the surface of the filings.

#### Making the magnetic column

A circular magnet with the magnetic field intensity of 0.01 T was primarily placed around a glass column and an iron spiral was located in front of the magnet inside the column, so that the sediments on it could be reacted (discharge velocity was 2 mm/s).

#### Preparation of the samples

The synthetically arsenic-polluted water samples were prepared by diluting 0.1 N sodium arsenite solution (Merck) with de-ionized water. In addition, to prevent the oxidation of arsenite to arsenate, the required solutions were prepared on a daily basis at 0.5 and 2 mg/l concentrations.

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The tests

The prepared arsenite solutions at 0.5 and 2 mg/l concentrations were reacted in contact with the iron filings adsorbent at 0, 2.5 and 5 g/l dosages over contact times of 5, 10 and 15 minutes within a beaker with the volume of 100 mL on the shaker at the velocity of 400 rpm. Half of the sample (50 ml) was then passed through the column at the velocity of 2 mm/s and a blank (without iron filings) was considered for each sample. Then, the arsenic concentration of the samples was measured by the ICP system. Moreover, the electrical conductivity of the samples was measured using EC meter. After data collection, the arsenic removal efficiency in any state was calculated. Mean and standard deviation of removal efficiencies were determined and the variables were compared with each other by means of paired t-test and one-way ANOVA.

## **Discussion of results and Conclusions**

#### Mixing

The results indicated that by increasing of the initial arsenic concentration, the removal efficiency also increased. It was due to the oxidation of arsenite into the insoluble arsenate ion. Via analysis of iron filings by extraction with hydrochloric acid, Hsing (Lien & Wilkin, 2005) showed that almost 28% of arsenic has existed in the form of arsenate, which revealed that oxidation has also been effective in arsenic removal.

#### Initial arsenic concentration

The results demonstrated that bu increasing of the initial arsenic concentration, the arsenic removal efficiency decreased. Zhang et al. (2003) achieved the adsorption capacity of 16 mg/g at the arsenic concentration of 1 mg/l, while Hsing (Lien & Wilkin, 2005) reported the adsorption capacity of 7.5 at the arsenic concentration of 50 mg/l.

#### Iron filings dosage

By increasing of the iron filings dosage, the arsenic removal efficiency increased as well. Tyrovola et al. (2007) showed that by increasing of the iron filings dose, the removal efficiency of arsenite ion increases.

#### Contact time

The results showed that by increasing of the contact time, desorption can occur at various times. In the samples with high arsenic concentration and iron filings, due to ferric hydroxide sites on the iron filings and therefore higher adsorption, the desorption process occurred at longer contact times.

#### pH

The iron filings, unlike the other adsorbents, have a high affinity to the reaction with arsenic at the normal pH of water. Ramaswami et al. (2001) removed the arsenite by iron fillings at the pH of 7 with the efficiency of 95%.

#### The magnetic field

The results showed that the magnetic field reduced the arsenic level of the samples without iron fillings but increased the arsenic level of the samples with iron fillings. The ferric hydroxide ion was formed on the surface of the iron fillings.

Sodium arsenite (NaAsO<sub>2</sub>) reacts with ferric hydroxide (Fe(OH)<sub>3</sub>) and forms ferric arsenite (Fe(AsO<sub>2</sub>)<sub>3</sub>) on the surface of the iron filings. Also, ferrous hydroxide ion is formed within the solution and can react with sodium arsenite and ferrous arsenite (Fe(AsO<sub>2</sub>)<sub>2</sub>) can be thus formed. Based on the physicochemical Hall Effect, when a multi-atomic ion placed within a fluid passes through the external magnetic field, the bond between the ions is weakened and they are dissociated and form cations and anions. When charged particles are placed in a magnetic field, a force is applied by the magnetic field to the particle, which is called "Lorentz force". After the blank or control sample (sodium arsenite) passed through the magnetic field, these two ions were dissociated based on the Hall Effect and finally reacted with the ferric hydroxide formed on the metal spiral. When the ferric arsenite ion passed through the magnetic field, the ions were dissociated and were affected by Lorentz force. Arsenite has one negative charge and ferric has three positive charges and since ferric ion has higher charge, more force is applied to it and it attaches to the spring inside the column. Arsenite was also affected by Lorentz force and reacted with the ferric formed on the spring, but as the dissociation level of ferric arsenite ion was more than its adsorption, the arsenite level in the outlet column increased. Ferric arsenite is insoluble and was not measured by the device. When the solutions were passed through the column, arsenite separated from ferric and changed into a solution which could be measured.

Electrical Conductivity (EC)

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The results of this study demonstrated that the magnetic field increased EC. When the ions of a solution are exposed to the magnetic field, they are dissociated and the solution forms more ions and thus EC increases. Ma et al. (1998) showed that EC of the samples before and after the magnetic field were 0.22 and 0.27  $\mu$ S/m, respectively.

It can be concluded that by applying a stronger magnetic field around the magnetic column, the arsenic in drinking water can be removed with high efficiency without adding any chemicals or adsorbents.

Keywords: arsenite, iron filings, magnetic column, magnetic field.

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# Effect of temperature on hydrothermal gasification of paper mill waste (Case study: The paper mill in North of Iran)

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Received: February, 2017 Accepted: May, 2017

## **Expanded Abstract**

#### Introduction

Many researchers conducted on fossil fuels indicate that the use of fossil fuels must be reduced and the use of renewable energy resources should be increased instead due to the climate changes and lack of energy. Fossil fuel resources include problems such as: 1. the limited resources of fossil fuels, 2. adverse effects on the environment, 3. volatility and instability of fossil fuel prices and energy security policy. The fossil fuel resources are going to be abandoned and replaced with renewable fuels.

One of the abundant and renewable resources is organic materials (biomass). During thermochemical processes, biomass can be converted into biofuels. One of these thermochemical methods is hydrothermal gasification method which is flammable products including  $CH_4$  and  $H_2$ . The extraction of energy from biomass can substantially meet increased energy needs in the future. It can also prevent wasteful  $CO_2$  emissions.

The purpose of gasification is producing quality (flammable) gas and producing more gas, in general. It means that the gas type and the amount of gas production will change due to the changes in hydrothermal gasification conditions. Hydrothermal method is introduced to eliminate the costly and difficult process of drying from extracting energy out of biomass.

Hydrothermal process can be divided into three parts. The first part is hydrothermal carbonization aimed at production of hydrochar and is performed in operating temperature range between 180-250°C. The other subject is hydrothermal liquefaction which is performed in operating temperature range of 200-370°C and aimed to production of heavy oil and in the end the last part, which contains super-critical conditions named hydrothermal gasification with the purpose of production of flammable gases and this is the matter of the article.

In this paper, the hydrothermal gasification process of waste production of Iran's paper mills is being studied. In this paper at first specifications of a waste production of a paper mill are determined as an example and then have been evaluated and focused on the effect of temperature on hydrothermal gasification process as an energy production method and as a waste management method.

## **Materials and Methods**

Samples are taken during a year in 2014 at the beginning of each season, in four times and from five paper mills in order to provide a model of paper mill waste which would be the closest to the real model. The sampled waste was gray, with the smell of wet newspaper and containing particles and fibers with dimensions of 1 to 5 mm. pH of the waste sample was close to the neutral pH=7. The moisture content of the paper mill waste was 39% and needed a pre-treatment to prepare for the hydrothermal gasification process.

In order to determine specifications of the investigation subject, raw materials are analyzed in dried form under the tests of proximate analysis, ultimate analysis and gross heating value. The moisture percent of all samples is carried out with the help of moisture analyzer (Sartorius) and under a certain temperature program at 105°C. The measurement technique is that the temperature of raw materials is retained to 105°C, while the material weight will not change any more and after that the difference between the basic weight and the secondary weight (after drying) has been reported as percentage.

Feedstock has been analyzed approximately (proximate analysis) before entering the reactor in order to measure the moisture, volatile substances, fixed carbon and ash of input material entering the reactor. The analysis was

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carried out by Thermo Gravimetric Analysis (TGA) and the device used for this purpose was Perkin Elmer Pyris 1 TGA with an automatic sampler.

Heat value of raw material in (MJ/kg) unit is obtained by Parr 6100 bomb calorimeter device and then the accuracy is being checked by Dulong's formula:

HHV (MJ/kg) =  $0.338 \times C + 1.444 \times (H-O/8) + 0.094 \times S$ 

C, H, O and S parameters situate in Dulong's equation as a percentage.

Then, after determining the area under the peak of each of the components, the produced gas is calibrated and converted to mol/lit. In the following the lower heating value (LHV) and carbon conversion rate and efficiency of the produced gas are calculated.

LHV  $(MJ / Nm^3) = (107.98 (H_2) + 126.36 (CO) + 358.18 (CH_4) + 59.036 (C_2H_4) + 63.772 (C_2H_6)) / 1000$  where H<sub>2</sub>, CH<sub>4</sub>, CO, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> were the molar percentages of components of product gas.

The carbon conversion efficiency (Xc) was calculated by

Xc (%) =  $[12Y(CO\% + CO_2\% + CH_4\% + 2 \times C_2H_4\% + 2 \times C_2H_6\%) / (22.4 \times C\%)] \times 100\%$ 

where Y was the product gas yield ( $Nm^3/kg$ ), C% was the mass percentage of carbon in ultimate analysis of paper mill waste, and CO, CH<sub>4</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> were the molar percentages of components of the produced gas.

#### **Discussion and Results**

The amount of output gas is directly related to the temperature and gas production increases when temperature rises. This increased efficiency is probably due to the cracking of heavy hydrocarbons. Another reason could be due to Char endothermic reactions, when conditions become suitable for the development of the reactions with increasing temperature. With enhancing temperature from  $500^{\circ}$ C to  $750^{\circ}$ C, gas output increases from 27.09 to 45.22 mol/kg. It should be noted that according to the papers in the field of gasification, efficiency improvements in gas production is also being observed in hydrothermal gasification technique. This increase in the volume of the gas begins from 3.034 lit and continues up to 5.064 lit. It means that the amount of the volume has increased of 66.9% at this temperature range and only under the effect of temperature changes.

The hydrogen gas production almost doubled during temperature rise. This change is more likely occurred because of the completion of Tar cracking process. The amount of hydrogen gas output is also higher than normal (dry) one in thermal gasification method.

One of the reactions in hydrothermal gasification processes is Steam Reforming reaction in which a large amount of hydrogen is generated in combination of water and methane. Therefore this reaction plays an important role in reducing hydrocarbons such as methane. In contrast to studies indicate that carbon dioxide gas decreases in the dry gasification state (pyrolysis), generally the amount of  $CO_2$  gas is in the uptrend. The amount of  $CO_2$  gas is 8.38 mol/kg at first and increases up to 17.21 mol/kg, ultimately. The increase in range of 600°C to 650°C is a sudden increase, which lies in performed reactions related to the production of  $CO_2$ . Thus more oxygen is used by the material in this temperature zone and more  $CO_2$  is produced as a result.

In summary, the changes of gas amounts are as below: the amount of  $CO_2$  and  $H_2$  is enhanced and the amount of CO and  $CH_4$  is reduced in whole and it illustrates a more optimized mode compared to the gasification mode without presence of moisture. Because in normal mode (the typical gasification), less hydrogen gas is generated and we can fetch up the result that water enters into this process as a catalyst and reactant helper to produce  $H_2$  and facilitates reactions to produce hydrogen as more as possible. In fact, water has a role in which more water-gas transfer reactions occur in the presence of water and the conversion rate of water-gas increases with increasing temperature as a result of increasingly breaking carbon bonds.

Efficiency, level of generated gas has been increased like typical gasification. The result was not unexpected because water evaporates due to the temperature enhancement and water presence and it generates more pressure in accordance with higher temperature, then in a high pressure cracking reactions occur in better conditions and materials break more easily. The changes are located in the range of 0.61 to  $1.01 \text{ (m}^3/\text{kg)}$ .

Due to the increase in temperature, the heating value rate reduces but the carbon conversion rate increases. That is while the heating value of these two must be in one direction according to the formula. This means that if carbon conversion increases, the heating value should increase too.

In general we can conclude that the amount of generated gas enhances by increasing temperature in hydrothermal gasification and in contrary its heating value rate decreases while carbon conversion rate is increased. As a result in order to achieve the aim of optimizing we need to consider a temperature in which the generated gas amount would be much and in addition its heating value would be high. Here, the acceptable heating value is considered more than 10 and its heating period is considered between 500°C to 600°C. In this period, the gas yield rate is placed in the range of 0.61 to 0.77. As we get closer to the temperature of 500°C, the heating value of the gas coming from the reactor increases.

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## Conclusions

In this study, North of Iran's paper mill wastes wasere examined and the testing process was hydrothermal gasification process. Wastes from five factories were sampled at the beginning of each season and after pretreatment phase they were imported into the hydrothermal gasification reactor in the waste to energy laboratory of Environment Faculty in University of Tehran. Results from studying waste characteristics before entering hydrothermal gasification process and its output products showed that changes are as below: The amount of  $CO_2$  and  $H_2$  is enhanced and the amount of CO and  $CH_4$  production is reduced in whole and it illustrates a more optimized mode compared to gasification mode without the presence of water.

Keywords: gasification, hydrothermal, paper mill, temperature, waste.

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# Determination appropriate model for estimating soil water characteristic curve (Swcc) in various moisture conditions in the one compacted clay soil

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Received: September, 2016

Accepted: May, 2017

## **Expended Abstract**

## Introduction

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Nowadays, the proper disposal of urban waste is one of the basic needs of human society. The most important part of landfills is clay covering and used to prevent leakage of leachate into external environment.

Population growth, expansion of cities, and many other environmental consequences have followed. Waste generated in urban areas is one of them. The most important issue in the engineering design of landfills is separation the contaminate environment from the outside environment by sealing layers (EPA, 1993). Compacted clay soils are commonly used as barrier materials in waste containment facilities. The selection of these soils as barrier materials is based on their unsaturated behavior (Miller et al., 2002).

In order to modeling the flow, having information about the characteristics of soil hydraulic is essential (Wang & Benson., 1995). One of the essential features is Swcc.

Hughes et al. (2005) conducted a study to determine the type of landfill liner systems. They found that moisture in compacted clay soil increases effect of compaction and therefore play an important role in reducing pollution and landfill. More moisture maskes less soil pollution.

Studing on hydraulic conductivity of the clay soil in acidic waste disposal sites shows that the clay soil is necessary component in the reduction of hydraulic conductivity at waste disposal sites. Naturally, compacted clay is a key element in waste disposal sites and soils with high plasticity, such as weighing can absorb too much water.

The objective of this study was to estimate Swcc by fitting models of Tani, expotential, Russo, Fredlund and Xing Five Parameters (FX5), van Genuchten (VG) and to determine parameters of them using Matlab Software and toselect the best model and also investigate soil behavior as liner.

## Materials and Methods

Soils used in the study were obtained from the area around Jurghan road (5 km of roads Tehran).

Soil samples were obtained from depths of 0–30. Particle size distribution (PSD) was determined using hydrometer method, based on Stokes' Law (ASTM D422) and then Texture AutoLookup (TAL) software for windows (Version 4.2) was used to determine the soil texture class based on United States Department of

Agriculture Textural Classification System and Soil Texture Triangle (USDA). Soil characterization data are

presented in Table 1.

## **Plasticity Index**

Soil plasticity index was obtained according to standard ASTM D4318-98, 2000. Soil characterization data are presented in Table 1.

Calculate the plasticity index as follows:

PI = LL - PL

where LL=liquid limit, PL=plastic limit and PI=plasticity index.

(1)

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	Soil type	Clay
Dentiale size enclose	Clay%	70.35
Particle size analysis	Silt%	13.4
	Sand%	16.25
Attack and limits	LL	37.12
Atterberg mints	PI	20.79

#### Table 1. Soil Characterization (%)

#### Compaction

Compaction test was performed in the form of volume 944 cubic centimeters and by weight of 5.2 kg that was dropped from height of 30 cm. For the standard compaction, the hammer was dropped on the soil in the mold 25 times on each of three soil layers (ASTM D1557). The reduced compaction was similar to standard compaction with one exception; 15 blows/layer were used instead of 25 blows/layer (Daniel & Benson, 1990). The reduced effort was used to simulate poor quality compaction procedures in the field. The modified compaction, the heavier hammer was also dropped 25 times on each of five soil layers (ASTM D698). Then compaction tests were performed over a range of soil moisture contents. The results were then plotted as dry density versus moisture contents. The maximum dry unit weight occurs at a water content calling the optimum water content. The maximum dry unit weights and the corresponding optimum water contents were estimated. Compaction characteristics of the soils are presented in Table 2.

#### Table 2. Compaction Characteristics of Soil Samples

Soil	Clay		
Compaction effort	Modified	Standard	Reduced
Maximum unit weight(KN/m <sup>3</sup> )	14.57	13.91	13.08
Optimum water content%	12.46	16.39	22.48

After calculation the optimum water content, once again, soil samples were compacted. Then, soil samples were prepared at three compaction effort under three water content conditions included 2% dry of optimum, optimum and 2% wet of optimum water content. Nine samples were prepared.

#### **Determination of Swcc**

The Swcc was measured in the laboratory using volumetric pressure plate extractor for matric potentials of 33, 100, 300, 500 and 1000 kPa (Lin & Cerato, 2012).

Various equations have been proposed to represent Swcc. In this stady, five models are used: Tani, Expotential, Russo, Fredlund and Xing five parameters and van Genuchten equations.

#### **Evaluation procedures**

In this research, optimization parameters (SSR) and performance evaluation parameters such as RMSE and  $R^2$  were obtained by curve fitting in Matlab. Where the sum of the squared residuals (SSR) is defined as follows:

$$SSR = \sum_{i=1}^{n} w_i \left( \theta_{wi} - \theta_{ci} \right)^2 \tag{1}$$

#### **Discussion and Results**

The  $R^2$  and RMSE calculated for the clay soil are close to 1 and 0, respectively (Table 4). Mean values of the RMSE for the five models: VG, FX5, Russo, Expotential and Tani are, 0.01872, 0.0189, 0.07755, 0.2323 and 0.04106 cm<sup>3</sup>cm<sup>-3</sup>, respectively.

In witness sample, SSR in models of FX5 and VG is less than 10<sup>-3</sup>, while in modified compaction, all models except models of Tani and Russo in modified compaction-optimum, models of Expotential and FX5 in standard compaction and also VG model in standard compaction-dry, FX5 model in reduced compaction-dry and wet is less than 10<sup>-3</sup>. The standard compaction-optimum, SSR in any model is not less than 10<sup>-3</sup>, which is within the range of SSR values obtained by Leong and Rahardjo (1997) and Miller et al. (2002) in similar studies.

Therefore, in all models, amounts of both SSR,  $R^2$  and RMSE were able to estimate the moisture curve. All models provide the best performance in clay soil but the FX5 and Tani models provide the better and weakest performance compared to the other methods, respectively.

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Table 4. SSR parameter, R <sup>+</sup> and RMSE of evaluation of the fitting models for clay soil							
Parameter/M	odel		Tani	Expotential	Russo	VG	FX5
Witness		SSR	0.02077	7.7×10 <sup>-3</sup>	0.0139	7.7×10 <sup>-4</sup>	7.5×10 <sup>-4</sup>
		$\mathbf{R}^2$	0.815	0.932	0.69	0.993	0.993
		RMSE	0.0832	0.0507	0.084	0.028	0.194
Modified	Dry	SSR	2.9×10 <sup>-4</sup>	2.6×10 <sup>-4</sup>	2.4×10 <sup>-4</sup>	9.4×10 <sup>-4</sup>	4.7×10 <sup>-4</sup>
compaction		$\mathbf{R}^2$	0.984	0.986	0.987	0.949	0.975
		RMSE	0.0099	0.0092	0.011	0.031	0.015
	Optimum	SSR	8.1×10 <sup>-4</sup>	2.5×10 <sup>-4</sup>	4.3×10 <sup>-4</sup>	1.65×10 <sup>-4</sup>	5.1×10 <sup>-4</sup>
		$\mathbf{R}^2$	0.97	0.991	0.985	0.994	0.982
		RMSE	0.0165	0.0092	0.015	0.013	0.0131
	Wet	SSR	$1.9 \times 10^{-3}$	$4.8 \times 10^{-4}$	$1 \times 10^{-3}$	6.99×10 <sup>-5</sup>	$5.1 \times 10^{-4}$
		$\mathbf{R}^2$	0.95	0.988	0.974	0.998	0.987
		RMSE	0.022	0.013	0.022	0.0084	0.0159
Standard	Dry	SSR	$3.25 \times 10^{-3}$	$1.1 \times 10^{-4}$	$1.9 \times 10^{-3}$	9.75×10 <sup>-5</sup>	$1.1 \times 10^{-3}$
compaction		$\mathbf{R}^2$	0.927	0.973	0.955	0.998	0.977
		RMSE	0.029	0.0199	0.032	0.0099	0.022
	Optimum	SSR	4.9×10 <sup>-3</sup>	1.7×10 <sup>-3</sup>	3×10 <sup>-3</sup>	8.88×10 <sup>-5</sup>	1.1×10 <sup>-3</sup>
		$\mathbf{R}^2$	0.91	0.969	0.945	0.998	0.982
		RMSE	0.035	0.0239	0.0389	0.0094	0.022
	Wet	SSR	7.2×10 <sup>-3</sup>	2.34×10 <sup>-4</sup>	$4.4 \times 10^{-4}$	9.6×10 <sup>-5</sup>	$9.5 \times 10^{-4}$
		$\mathbf{R}^2$	0.89	0.965	0.935	0.9986	0.986
		RMSE	0.042	0.0023	0.047	0.0098	0.0218
Reduced	Dry	SSR	9.4×10 <sup>-3</sup>	3.59×10 <sup>-3</sup>	6.1×10 <sup>-3</sup>	5.16×10 <sup>-4</sup>	1.5×10 <sup>-3</sup>
compaction		$\mathbf{R}^2$	0.87	0.951	0.918	0.9931	0.979
		RMSE	0.056	0.036	0.055	0.0227	0.0278
	Optimum	SSR	0.011	3.5×10 <sup>-3</sup>	6.6×10 <sup>-3</sup>	2.5×10 <sup>-3</sup>	1.8×10 <sup>-3</sup>
		$\mathbf{R}^2$	0.88	0.959	0.923	0.9699	0.979
		RMSE	0.051	0.034	0.0575	0.051	0.03
	Wet	SSR	0.0133	3.7×10 <sup>-3</sup>	8.04×10 <sup>-3</sup>	3.37×10 <sup>-5</sup>	$1.6 \times 10^{-3}$
		$\mathbf{R}^2$	0.867	0.963	0.919	0.9997	0.984
		RMSE	0.66	0.035	0.063	0.0058	0.028

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## Conclusions

In this study, using the field data and laboratory analysis of Swcc models were evaluated. The results of this study can be summarized as follows:

- 1. Increasing compaction, increased amount of water held in potential more than 33 Kpa and resulting in reduced leakage and environmental pollution.
- 2. Among the fitting models to experimental models by Matlab, FX5 and VG models provided the best performance compared to other models and Thani model presented the weakest performance.
- 3. There is poor correlation between the measured and predicted values of  $\theta_r$  and  $\theta_s$  in models FX5 and VG.
- The amount of  $\alpha$  by increasing compaction and also moisture have increasing trend and in high 4. compaction with increasing moisture is a constant value.

Keywords: Clay Soil, Compaction, Moisture, Pressure Plate apparatus, Fixed Parameters

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## Comparison of linear and hybrid models in predicting the distribution of heavy metals using remote sensing and spatial analysis in East of Zanjan city

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Received: February, 2016 Accepted: May, 2017

## **Expanded Abstract**

## Introduction

Accumulation of heavy metals in soil has been considered as an important global environmental issue during past decades. Many efforts have been done to prevent its detrimental effects on ecosystem cycles. Conventional methods for assessing the spatial distribution of soil heavy metals require many soil sampling and laboratory analyses make it very time consuming and costly. Furthermore, a quick and reliable monitoring of heavy metals concentration is crucial for a close to real time management of polluted regions. Remote sensing and satellite imagery have the potential to provide a quick, non-destructive and low cost tools for predicting and mapping the distribution of soil heavy metals. The aims of this study were to evaluation of a linear model and hybrid algorithms considering the spatial distribution of soil heavy metals concentrations and to study its responsible factors, using remote sensing. The local Moran index applied to classify the spatial distribution of lead, zinc, cadmium and copper in east of Zanjan city. One of the most important cases in mismanagement and quality reducing of soils and also decreasing in optimum conditions of plant growth is accumulation of pollutants in unnatural doses. The accumulation of these elements disrupts organism's life cycles in soils and puts human health and living organisms in risk. Human activities such as mining, transportation, disposal of industrial wastes, inappropriate waste disposal systems and application of chemical fertilizers and pesticides are the major threats of soil health. These problems, as the main environmental threats components, have been investigated in the past two decades. Accumulation of heavy metals in soil has been considered as an important global environmental issue during past decades and many efforts have been done to prevent their detrimental effects on ecosystem cycles. Conventional methods for assessing the spatial distribution of soil heavy metals require many soil sampling and laboratory analyses making it very time consuming and costly. Furthermore, a quick and reliable monitoring of heavy metals concentration is crucial for a close to real time management of polluted regions. Remote sensing and satellite imagery have the potential to provide a quick, non-destructive and low cost tools for predicting and mapping the distribution of soil heavy metals. Recently, for remote sensing modeling by satellite images, and application of these models to the ambient environment, smart models like artificial neural networks and genetic algorithms have shown good capabilities. The aims of this study were to evaluation of a linear model and hybrid algorithms consider the spatial distribution of soil heavy metals concentrations and to study its responsible factors, using remote sensing. The local Moran index applied for classifying the spatial distribution of lead, zinc, cadmium and copper in east of Zanjan city.

## **Materials and Methods**

The rich lead and zinc mining areas in Angouran region, Zanjan province, which are unique in the Middle East, are led to the accumulation lead and zinc industries in the province. One of the main manufacturers is Iranian national lead company, which is located at 13 km of the east of Zanjan, in Dizajabad region. The major activities of this company are the processing and extraction of lead and zinc in soils and stone powder containing these elements. The soil samples (n=300) were collected at 0 to 5 cm soil depths based on a 250 m grid in industrial and agricultural regions and a 500m grid in bare lands. The soil samples air dried and 2 mm-sieved. Total (t) forms of zinc, lead, cadmium and copper were determined for each sample. In each sampling point, the mean value of digital numbers was calculated by averaging image pixel's values within a 30 m radius in MATLAB. To observe the quantitative relationships between spectral parameter values and metal levels in the studied area,

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stepwise linear regression and back propagation artificial neural network-genetic algorithm were applied. After providing descriptive statistics and data normalization, data modeling of heavy metals concentrations, Zn, Pb, Cd and Cu was conducted using stepwise multivariate linear regression models and neural-network model combined genetic algorithm. Modeling by neural network-genetic algorithms was done using feed-forward multilayer perceptron neural networks with sigmoid transfer function. Seven neurons, including satellite and network output to a neuron contains concentrations of heavy metals, formed the input layers of the artificial neural network. Spatial autocorrelation analysis was used to evaluate the heavy metal source identification and finding their hotspots. Autocorrelation analysis describes the spatial properties of a variable in a region and is a reflection of the space mean differences between all space cells and their neighboring cells. To investigate the spatial autocorrelation analysis the local Moran I was employed to identify the presence of clusters: Local Moran I:

$$I_i = x_i \sum_{j=1}^N w_{ij} x_i$$

N is number of spatial observation pixel, xi is standardized observed value of pixel I, xj is standardized observed value of pixel j, and wij is the standardized spatial weighting value. The validation of models was done by Root mean square error and coefficient of determination ( $R^2$ ) statistics. The prediction maps were provided by most models with lowers root mean square error and highest  $R^2$ . Analysis of satellite images, drawing of heavy metals maps was conducted using ArcGIS software version 10.2.

#### **Discussion and Results**

Descriptive statistics obtained from chemical analysis of heavy metals concentrations in soil of the study area. The results indicated that average concentrations of Pb (t) Zn (t), Cd (t) and Cu (t) were 354.98, 501.10, 1.92 and 12.69 mgkg<sup>-1</sup>, respectively. According to the standards of the Department of Environment of Iran, mean concentrations of lead and zinc were classified in risky level, and the average value of Cd and Cu was classified in the no risky level. Statistical analysis of multivariate stepwise linear regression model and artificial neural network-genetic algorithm model showed root mean square error of training data with neural network-genetic algorithm model for Pb, Zn, Cd and Cu were 0.067, 0.087, 0.17 and 0.21, respectively, and with the multivariate stepwise linear regression model were 0.45, 0.32, 0.48 and 0.54, respectively. The results of the models test also had similar trends. Models coefficient of determination of artificial neural network-genetic algorithm model for Pb, Zn, Cd and Cu were 0.88, 0.80, 0.75 and 0.45 and of multivariate stepwise linear regression model were 0.53, 0.43, 0.43 and 0.44, respectively. The obtained training and test error values of neural network-genetic algorithm hybrid model were less than corresponding values of multivariate stepwise linear regression. On contrary, the values of coefficient of determination in of artificial neural network-genetic algorithm hybrid model were higher than corresponding values of multivariate stepwise linear regression. These results indicated that prediction ability of heavy metals especially in high concentrations by artificial neural network-genetic algorithm hybrid model was higher than linear models. The neural network-genetic algorithm model had acceptable accuracy to estimate the amount of heavy metals in soil using satellite imagery data in this study and were used to produce predict distribution maps of heavy metals in the area. According to the predicted maps, the area of highly risk region for Pb, Cd, Zn and Cu were 50.00, 2.00, 0.02 and 0.04 percentage of study area, respectively. After monitoring heavy metals, it is very important to find certain relationship among dispersed concentrations, and to identify source of the pollutions. Spatial autocorrelation analysis is contained appropriate information of phenomena which have spatial distribution. The spatial autocorrelation results can be used as a strategy for source identification and finding disturbing agents of heavy metals. After taking a confidence level of Moran values, the levels that were significantly greater than zero are indicated positive correlation between clusters of cells. Moran levels that were significantly smaller than zero, are indicated a negative correlation between adjacent cells. If the values were closer to 1, there was very little difference between the cells and if these values were closer to -1, there were large space differences. Spatial autocorrelation of Moran index indicated the strong hotspots concentration of Pb and Cd around industrial zones in the study area. The pattern showed that Pb concentrations were affected by dominant wind, and the Zn distribution maps showed the concentration of these elements around industrial installations and streams. This indicated that industrial activities effect on heavy metals distributions strongly and might result in surface and ground water contamination.

#### Conclusion

This study defined the artificial neural network-genetic algorithm and multivariate stepwise linear regression models to predict the heavy metal distribution in different land-use by Landsat image. Root mean square errors of training data with artificial neural network-genetic algorithm model for studied heavy metals were lower than the linear model. Models coefficient of determination of artificial neural network-genetic algorithm training and testing hybrid model showed higher values than the linear model. The results showed the success of the artificial neural network-genetic algorithm model in prediction of the heavy metals distribution, using remote sensing

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techniques. The remarkable ability of hybrid models in the estimation of heavy metals in high concentrations was also observed. The concentrations of Cd, Cu, Pb and Zn showed a decreasing trend with increasing distance from the industrial installations. Moreover, the distributions of regional hotspots of Cu and Cd were similar and close to factories. In addition, the Pb concentrations were affected by wind direction and streams had effect the Zn transport in the studied area.

Keywords: Dizajabad, landsat, local Moran, soil pollution, spatial variability

The pollution effects of nitrate and ...

Sepideh Omrani and Mohammad Ali Dorri

# The pollution effects of nitrate and phosphate on eutrophication status in Gomishan international wetland

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Received: June, 2016 Accepted: May, 2017

## **Extended** abstract

## Introduction

Nitrate and phosphate can be considered as nutrient limiting of primary production and affecting on eutrophication in surface water. Even momentary increase in the nutrient can stimulate tremendous growth and productivity. Phosphorus limitation dominates in tropical terrestrial (because of effects of soil age) and marine ecosystems (because of effects of sequestration in calcareous sediments), while nitrogen limitation is raised in primary production and eutrophication in many estuarine areas. Although the effects of nutrient loading have been less studied in wetland ecosystems, they can stronglybe affected, byeutrophication. Thecoastalwetland of CaspianSea (Gomishan) duetothe expansion of drainage systems and urbanization, wastewater and aquaculture was the eutrophication occurrenceincoast, andrarely been studied. Furthermore, the residence time and climate change affect the eutrophication patterns in different coastal ecosystems. Based on these issues, the necessity of this study was obvious in order to determine role limiting of nitrate and phosphate in Gomishan international wetland. In this paper, the relationship between Chlorophyll concentrations, phosphate, nitrate and turbidity and some environmental factors such as water temp, salinity, pH, hasbeen studied.

## **Matherials and Methods**

Gomishan international wetland is located in the north of Iran. The west of wetland by a very narrow sandy strip separated from sea. Therefore, almost all its water is supplied through sea communication channels. Sampling in this study was done during May to September and in six stations along the Gomishan wetland were sensitive to loading nutrient, includingestuarine of

Gorgan rud River (St2), drain a gechannel of Gomishan City (St3), overflow channel of Alago linternational the state of the state of

wetland(St4), input (St6) and output (St5) channels of shrimp site and border area of Magtymguly(St7), also, one station of Caspian Sea.

Some physical-environmental factors, like salinity, pH, turbidity andwater temperature, were measured bymultiparameterportablesystem. In the laboratory, then utrients were measured by a spectrophotometer (Hach Company). Furthermore, 0.5 L phytoplankton sample water of stations was filtered using the vacuum pump (0.45  $\mu$  filter paper) in the laboratory. Finally, extracts absorption was read at the wavelengths of chlorophylla(Chla) pigments by a spectrophotometer and also calculated using trichromatic method. The linear regression and Pearson's correlation between the nutrients and Chla were determined by SPSS.

## **Discussion of results**

The physico-chemical parameters are the major factors that control the dynamics and structure of the phytoplankton of aquatic ecosystem. Seasonal variations in these parameters have an important role in the distribution, periodicity and quantitative and qualitative composition of the species livingthere. According to the results of physico-chemical parameters in this study, non algal turbidity was high in the Gorganroud estuarine(S2) and the border area of Magtymguly(S7), in addition to Caspian Sea (S1)(Figs. 1and2a).So,by reducing it during the study period, the availability rate of orthophosphate was increased (Figs. 1and2c). Non algal turbidity can produce low algal chlorophyll-to-nutrient ratios and cause a lack of relationship between

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chlorophyll and phosphorus in some regions. Effluent of industrial parks and human wastewater was the main reasons of high turbidity in S2.

Furthermore, in thesestations, in September compared to August, between increasing the concentration of Chla and nitrateand decreasing inorthophosphate there was a positive correlation. Because the nitrogen availability may boost non-nitrogen-fixing *cyanobacteria*, nitrogen played more the limitationrole. S2andS7respectively were the southernmost and northernmost stations of Gomishanwetland.

Changes of hydrological parameters during the study period at some stations



In other studied stations, including drainage channel of Gomishan (S3), overflow channel of Alagol(S4) and input(S5) and output(S6) of shrimpsite, between the increase of turbidity, Chla and orthophosphate, there was a positive relationship. As a result, phosphorus played the limiting role in these stations. Furthermore, inS3 and S4, being central stations of wetland, in September compared to August, nitrate concentration was low and orthophosphate was high (Figs. 3 and 4d,c). This issue showed in the nitrogen resource constraints, as soon as obtaining a small amount of phosphate resources, N/P decreased and cyanobacteria level blooms increased in September (Figs. 3 and 4 b).

The significant increase of nutrients especially phosphate indicatives the development process of urbanization and wastewater, non-normative increase of aquaculture and farming activities being effective on hydrologic drought of wetland. Furthermore, the results of Pearson correlation and Linear regression showed a significant correlation of orthophosphate with log Chla (P<0.01). This correlation between orthophosphate and turbidity was significant at level P<0.05.

According to the results, the coastal wetlands such as Gomishanwhereentered freshwater inputs and wastwater, the role of phosphorus was more effective than nitrate. Low depth of wetland was also affected on phosphate loading and leading to eutrophication especially in S3 and St4. The impact of global warming process in climate conditions of Caspian area, along with increasing human and agriculture activities in Caspian Sea catchment of reasons in the shallow was of Gomishanwetland in recent years.



Changes of hydrological parameters during the study period at some stations

In continuation the process of shoal Gomishan international wetland based on mentioned reasons, the possibility of dystrophycould be expected in this area that dangerous consequences of environmental and its climate at local and global level is obvious for experts. The occurrence possible of dust storms and salt dust

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isespecially in Golestanprovince and in the most omportant adjacent areas. So, it seems restoring of Gomishan wetland acting as a buffer between land and sea, is essential to create a dynamic ecological balance. According to Table 1 and the mean of hydrologic parameters, salinity was recorded 31.2 ppt in Gomishanwetland. Therefore, it can be considered as the salty systems. Although, the wetland water comes mainly of Caspian Sea, due to the shallow depth and dry and semi-dry condition of Turkmen Sahra plain led increased the surface evaporation, salty geological formations (Clay) and also urban drainage channels the amounts solutes observed of wetland was high compared to Caspian Sea especiallyin summer. According to the measurement of Chla concentration during May-September (Table1), Gomishan wetland showed the eutrophiclevel.

Table1 The mean of		مسط المثمام مشمما و		Constation and loss d
radier. The mean of	physicochemical	and biological	parameters in the	Gomisnan wetiand

DO mg/l	Water temperature $C^{\circ}$	PH	Salinity ppt	Turbidity NTU	Chlorophyll <i>a</i> µg/l	Nitrate mg/l	phosphateOrtho mg/l
6.15	29.7	8.1	31.2	46.5	43.97	1.5	0.07

## Conclusions

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The changes of the eutrophication status which are cause wetland water quality degradation may be predicted based on timely sampling and analysis of key water quality parameters especially phosphate. Also, for controlling runoff, prevention of development open drainage channels is essential which have abundantly been seen around the wetland.Furthermore, interpretation of observed chl*a* concentration is not limited to the inputs or sediment composition in local scale, because the climate changes were also effective.

Keywords: chlorophylla, Gomishaninternational wetland, loading, nitrate, ortophosphate.

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# Environmental assessment of urban water and wastewater systems from greenhouse gasses production point of view (Case study: City of Sari)

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Received: July, 2016

Accepted: May, 2017

## **Extended abstract**

## Introduction

Urban water and wastewater systems should be constructed and designed within the framework of sustainable development. Therefore, the assessment of environmental impacts of these systems' construction and operation is an essential issue. One of the environmental impacts is the global warming in which the equivalent carbon dioxide has the most important role. The equipments, energy and chemical materials used in drinking water cycle (including the phases such as withdrawal water from its resources, water treatment, water distribution, wastewater collection and treatment) have environmental impacts such as the intensification of global warming due to the increase in greenhouse gasses emission.

There are various tools for sustainability assessment of water and wastewater systems. Life Cycle Assessment (LCA) is one of these tools. Unlike the three decade records of applying the LCA in the world, this method has been rarely employed in Iran to resolve the problems of real water and wastewater systems. In this study, the LCA of drinking water system has been implemented in order to estimate its impact on global warming and to examine different cases with minimum environmental impacts. Determination of the water cycle phases with the maximum impact on global warming has been also aimed. In this regard, released equivalent carbon dioxide in life cycle of drinking water was estimated by means of SiamPro software. Sari, a city (in north of Iran) in which drinking water is supplied from wells, has been selected as the case study. Three different scenarios for replacing groundwater resources by a reservoir dam (Shahid Rajaee) were studied.

## **Materials and Methods**

In the present research, Sari city is selected as the case study (Fig. 1). Population of the city is about 350,000 in which 57,000 inhabitants profit by the wastewater collection and treatment system. Drinking water cycle is divided into four phases including water withdrawal from its resources, water distribution, wastewater collection and wastewater treatment in which the electricity is supplied from thermal power plant.

Because of the nonexistence of required infrastructures, drinking water in Sari city was supplied from underground water resources before July 2015. In other words, drinking water in Sari city was supplied from 28 wells with discharge of 1180 l/s. 18% of this amount was lost due to the leakage. On the other hand, underground water resources have been exposed to pollution due to the usage of farming fertilizers and operating cesspools. Therefore, replacing underground water resources by Shahid Rajaee dam has been mooted. In this regard, water will be transferred from Shahid Rajaee dam to Kiasar water treatment plant. Then the treated water will be transferred to Sari city. Wastewater treatment plant of Sari has been designed in four modules. The first module which has been operated since 2010, serves about 105,000 people. The average and the maximum input discharges of this module are 269 and 546 l/s, respectively.

Three scenarios have been considered for replacing underground water resources by Shahid Rajaee dam. These scenarios are: (1) Supplying a part of Sari drinking water demand from Shahid Rajaee dam; (2) Supplying the total drinking water demand from Shahid Rajaee dam; and (3) Supplying the total drinking water demand from Shahid Rajaee dam and using hydroelectricity. It should be noted that the environmental impacts of dam construction has not been considered in these Scenarios. SimaPro is one of the common software for assessing the life cycle. In this study, SimaPro 5.1 is employed for calculating the greenhouse gasses produced in water and wastewater systems.

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Fig. 1. Map of the studied area

#### **Discussion of results**

Total amount of the equivalent carbon dioxide produced in drinking water life cycle in Sari city is presented in Figure 2. According to this figure, total amount of the equivalent carbon dioxide produced in drinking water cycle is  $0.392 \text{ kg } \text{CO}_2/\text{m}^3$  water in which the phase of withdrawal water from its resources has the greatest part (about 60% of the total equivalent carbon dioxide) in producing the greenhouse gasses. Water distribution network, wastewater treatment plant and wastewater collection network have portions of about 20%, 12% and 8% respectively, in producing the greenhouse gasses.



Fig.e 2. The equivalent carbon dioxide produced in drinking water life cycle in Sari

According to the obtained results, water supplying from the Shahid Rajaee dam will reduce the environmental impact to a great extent. Scenarios 1 and 2 with common electricity production (in which 500 and 1500 l/s water was respectively supplied from Shahid Rajaee dam and was treated in Kiasar water treatment plant) reduce 84% and 86% of greenhouse gasses production in the water withdrawal phase, in addition to supply water with higher quality. In scenario 3 with hydroelectricity, 89% of greenhouse gasses produced in the water withdrawal phase are reduced (Fig. 3). The equivalent carbon dioxide produced by various agents in introduced scenarios is shown in Figure 4.

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Fig. 3. The equivalent carbon dioxide produced in the present situation and various scenarios



Fig. 4. The equivalent carbon dioxide relevant to various agents in scenarios 1-3

#### Conclusions

It can be concluded that operation of Shahid Rajaee dam and Kiasar water treatment plant and using hydroelectricity would lead to a great reduction in electricity consumption and producing greenhouse gasses. Another result is that the biggest share among the factors producing carbon dioxide is associated to electricity.

**Keywords:** drinking water life cycle, greenhouse gasses, life cycle assessment, SimaPro software, urban water and wastewater systems.

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# Removal of hexavalent chromium from water by functionalized magnetic nano porous graphene (NPG / Fe<sub>3</sub>O<sub>4</sub> @ COOH).

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Received: September, 2016

Accepted: May, 2017

#### **Extended abstract**

#### Introduction

We used Chemical Vapor Deposition (CVD) technique to synthesize Nano-Porous Graphene (NPG) on transition metals. Magnetic Nano-Particles (MNPs) prepared for synthesis of NPG/Fe3O4 as an adsorbent for the economic and efficient removal of  $Cr^{+6}$  ions from aqueous solution. Modification of graphene with different materials can produce various adsorbents to improve their adsorption capacity. The purpose of this work was the synthesis NPG by CVD method and magnetite with MNPs (NPG/Fe<sub>3</sub>O<sub>4</sub>) for economic separation from water then functionalized with the carboxyl group to provide different nano-composite (COOH@NPG/Fe<sub>3</sub>O<sub>4</sub>) as an adsorbent for the removal of  $Cr^{+6}$  ions from aqueous solutions. The characterization of COOH@NPG/Fe<sub>3</sub>O<sub>4</sub> as an adsorbent for the removal of  $Cr^{+6}$  ions from aqueous solutions. The characterization of parameters such as pH of solution, contact time, temperature, initial ion concentrations and adsorbent dosage were studied. In addition, the adsorption experiments were conducted under varying conditions to investigate the equilibrium isotherms, kinetic models and thermodynamics.

#### **Materials and Methods**

Anhydrous iron (III/II) chloride, (99.9%) ammonia solution, potassium dichromate and (28%) hydrazine hydrate were purchased from Merck, Co, Germany. A hand magnet was also prepared to separate adsorbents from solution. NPG was synthesized by CVD technique which is a highly effective and low-cost method. NPG/Fe<sub>3</sub>O<sub>4</sub> nano-composite was synthesized according to method reported in the previous studies (Juang et al., 2010) with some modifications. NPG was functionalized by carboxyl. About 1 gr of graphene was treated in 25 ml of nitric acid and 75 ml of sulfuric acid for 3 h at 60°C. The mixture was kept in an ultrasonic bath and then washed by distilled water until reaching to the natural pH.

Scanning Electron Microscope (SEM, model MIRA3, Tescan, Czech Republic) was used to measure surface morphology, size and distribution of synthesized adsorbents. The morphological and shape of the adsorbent were recorded by a transmission electron microscope (TEM, model PHILIPS, EM 208 S). In addition, the surface functional groups were characterized by fourier transforms infrared spectroscopy (FTIR).

Parameters such as pH of solution (2-10), contact time (5-120 min), adsorbent dose (20, 35, 50, 100, 150 and 200 mg/L), temperature (283, 298, 303 and 323 K) and different concentrations of  $Cr^{+6}$  (25, 50, 100,150 and 200 mg/L) on the adsorption efficiency was investigated. The Langmuir and Freundlich isotherm models were used to evaluate  $Cr^{+6}$  adsorption onto the adsorbent. The adsorption kinetic models of  $Cr^{+6}$  on COOH@NPG/Fe<sub>3</sub>O<sub>4</sub> adsorbents along with their corresponding regression coefficients are calculated. The thermodynamic diagram of  $Cr^{+6}$  adsorption is demonstrated.

#### **Discussion and Results**

The FTIR spectra of synthesized composite of COOH@NPG/Fe<sub>3</sub>O<sub>4</sub>+ $Cr^{+6}$  and NPG/Fe<sub>3</sub>O<sub>4</sub>+ $Cr^{+6}$  characterized the functional groups on the adsorbent surfaces can play an important role in the adsorption mechanism. The other

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groups that have emerged in the wavelength of 1421.86 cm<sup>-1</sup> and 3312 cm<sup>-1</sup> can be assigned to represents aromatic C=C bonds and OH stretching vibrations of the carboxylic acid group, respectively. Finally, alkoxy CO bond is defined at 1029 cm<sup>-1</sup> indicates the graphene structure of NPG. The peak around 1700 cm<sup>-1</sup> appears in the spectra of COOH@NPG/Fe<sub>3</sub>O<sub>4</sub>+Cr<sup>+6</sup>.

In addition, Figure 1e represents the morphology, size and surface area of the NPG being analyzed by SEM in high magnification. It can be see good porosity and high adsorption capacity. By TEM technique, it could be pointed out that a high density of  $Fe_3O_4$  nanoparticles is noticed on the NPG layers (Fig. 1f) low-magnification (Fig. 1g) and high-magnification.

#### The effect of various parameters

The amount of  $Cr^{+6}$  removal in various ranges of pH between two adsorbents is shown in Figure 2a. According to a similar study, the adsorption of  $Cr^{+6}$  on COOH@NPG/Fe3O4 was significant at acidic conditions. The contact time is one of the most essential parameters in designing a batch system affecting the adsorption of contaminants (Fig. 2b). The effect of the optimal absorbent concentration (20, 35, 50, 100, 150 and 200 mg/L) on the 100 mg/L Cr (VI) removal under optimal is shown in Figure 3a. The effect of various chromium concentrations (25, 50, 100, 150 and 200 mg/L) under optimum conditions (pH=3, time=60, 200 rpm, m<sub>0</sub>=0.2 g/L) is shown in Figure 3b.

#### Kinetic, thermodynamic and adsorption isotherm models

The adsorption kinetic models of  $Cr^{+6}$  on adsorbent along with their corresponding regression coefficients are given in Table 3. These are further verified by the diagrams presented in Figure 7. According to the regression coefficient ( $R^2$ ) in Table 3, the adsorption kinetic data was well-fitted by the pseudo second-order model. The thermodynamic diagram of  $Cr^{+6}$  adsorption is demonstrated. The results were obtained by the curve where the values of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  can be achieved from the slope and intercept of the plot of lnK° against 1/T. Equilibrium adsorption isotherm models are used for better explanation of adsorption capacity between adsorbent and adsorbate which is an important factor in optimizing the application of adsorbents. The obtained values based on both Langmuir and Freundlich models for  $Cr^{+6}$  sorption on COOH@NPG/Fe<sub>3</sub>O<sub>4</sub> at ambient temperature and optimum conditions are shown.

#### Conclusions

In this study, NPG was synthesized by CVD method then magnetized by  $Fe_3O_4$  and  $Fe_2O_3$  powder for both rapid and economic separation by external magnetic field, due to its magnetism contributed from  $Fe_3O_4$  instead of older method. The NPG/Fe<sub>3</sub>O<sub>4</sub> was also functionalized with carboxyl (COOH@NPG/Fe<sub>3</sub>O<sub>4</sub>) for using as an adsorbent for removal of  $Cr^{+6}$  from aqueous solution. The structural, functional and morphological properties of synthesized adsorbent were characterized using SEM, TEM, and FTIR, techniques. The optimum experimental conditions of  $Cr^{+6}$  removal was investigated in batch adsorption experiments. The adsorption efficiency of  $Cr^{+6}$ was increased with decreasing the pH of solution and initial  $Cr^{+6}$  concentrations. But, an increasing trend was happened in  $Cr^{+6}$  adsorption efficiency with increasing the adsorbent dosage and contact time until 60 min. In addition, the adsorption data was best fitted to Langmuir isotherm model. The Langmuir model indicated that it is monolayer adsorption of  $Cr^{+6}$  on the adsorbent surface. Kinetic data of adsorption can be best described by a pseudo second-order model. The sorption reaction onto adsorbent was an endothermic and spontaneous process. It should be noted that the synthesized adsorbent has promising potential in wastewater treatment which can easily be separated by an external magnet.

Keywords: adsorption, heavy metal, isotherm, thermodynamic.

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## Investigation of heavy metals concentration in surface sediments of Choghakhor wetland

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Received: August, 2016

Accepted: May, 2017

## **Extended abstract**

## Introduction

Inorganic contaminants, such as heavy metals enter into terrestrial and aquatic ecosystems from different paths such as erosion and weathering of rock, agricultural and industrial activities, automobile exhaust, sewage and atmospheric subsidence. These heavy metals have bioaccumulation potential, toxicity, ubiquitous, and resistance degradation and can be a serious threat to ecological systems and human health. According to Amin et al. (2009), more than 90% of heavy metals loading in aquatic ecosystems found in sediments; so, the quality of sediments can be a good indicator of water pollution. In these ecosystems, sediments play an important role as a sink for organic and inorganic contaminants (heavy metals) and provide a history of human-origin emission of pollutants and environmental changes.

To address the sediment contamination by heavy metals, different approaches such as hazard quotients, crop uptake and transformation, concentrations of weakly extractable metal and total heavy metal concentration can be used.

Considering the total heavy metal concentration approach, sediment contamination is often assessed by comparing heavy metal concentrations with the relevant environmental references or by quantifying an accumulation factor in comparison to the related background concentrations. Up to now, numerous different indices such as the index of geoaccumulation (Igeo), the enrichment factor, the pollution index (PI) and the integrated pollution index (IPI), the individual element polluted index, the contamination factor and degree of contamination, the contamination factor (CF), the pollution load index (PLI) and the total contamination index (Zs) hasve introduced to estimate the degree of heavy metal contamination. To calculate the size of the polluted area from sediment samples, two methods including the proportion of contaminated samples and calculation of the polluted area from an interpolation map of sediment heavy metals can be used.

Up to now, numerous studies have documented the distribution, origin and extent of heavy metals contamination in sediments of various wetlands. However, wetland sediment contamination has sparsely been investigated in Iran in general and no information is available for the Choghakhor wetland. Choghakhor wetland is one of the most important wetland for waterfowl in Iran which has been exposed to different non-point pollution sources and different contaminants such as heavy metals due to surrounding agricultural and recreational activities and discharge of domestic effluents without treatment. Therefore, the aim of this study was to quantify the concentrations of Ni, Zn, Cu and Fe in surface sediments of Choghakhor wetland. Also, assessment of heavy metals contamination using different contamination indices was another purpose of this study.

## Materials & Methods

## Study area

Choghakhor wetland and its margins located in the form of a small valley among mountains in the north slopes of Mount Kelar, in 61 km south of Shahrekord. Study area has an area of over 6,184 hectares which lake with an area of 1,428 hectares is located in its center (Fig. 1).

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Fig. 1. Location of Choghakhor wetland in Iran and sediment sampling points

## **Materials and Methods**

A total of 52 surface sediment samples were collected randomly from different parts of the Choghakhor wetland; then the samples were placed in clean plastic bags and were transferred to the laboratory for further analysis. 1 gr of sieved sediment sample was digested by using the combination of the three acids: HF, HNO<sub>3</sub> and HClO<sub>4</sub> whit the ratio of 3:5:7. After cooling the samples, 2 ml of boric acid 7% was added to remove the fluoride residual and with distilled water was reached to volume of 25 cc. The concentration of metals in sediments was measured by flame atomic absorption. For quality control and assurance, standard reference materials and blank samples were used.

Various types of direct (Earth Chemical) and indirect methods (statistical) are commonly used to calculate the contamination of heavy metals in the environment. However, statistical methods are more common than chemical methods because the earth is not alone useful for determining the concentration of background samples, also statistical methods have lower lab work and cost. In this study, a statistical method introduced by Ismailia et al. (2014) was used for calculating of the background concentrations. Contamination assessment was carried out using several different indices including Enrichment factor (EF), Geo-accumulation index (Igeo), Contamination factor (CF) and pollution load index (PLI).

Sediment quality assessment guidelines (SQGs) can be very useful in determining the amount of sediment pollution compared with the corresponding guides. In this paper, two sets of guidelines including National Oceanic and Atmospheric Administration USA (NOAA) and the Interim Sediment Quality Guidelines Canada (ISQG) were used. These guidelines express the quality level and degree of contamination of sediments which may have an adverse effect on aquatic organisms. The Correlation and PCA analysis were used to determine the source of heavy metals in sediment samples. Inverse distance weighting method was used for mapping of heavy metals distribution in surface sediments of wetland.

## **Discussion of results**

The mean total concentrations of Cu, Fe, Mn, Ni and Zn in surface sediments in the whole study area were 15.75, 6076.86, 297.74, 30.07 and 29.87 mg/kg, respectively (Table 1). Average metal concentrations followed the order Fe> Mn> Ni> Zn> Cu. With the exception of Fe, the concentrations of other heavy metals in the surface sediments of Choghakhor wetland were all lower than the background values.

Table 1. Descriptive statistics of heavy	w metal concentrations in wetland sediments	(52 samples) (µg/g dry weight)
		(

Metals	Min.	Avg.	Max.	Std. dev.	background
Ni	15.75	30.07	67.82	18.95	62.72
Cu	4.35	15.75	36.80	6.55	24.03
Zn	2.02	29.87	61.64	12.90	50.15
Mn	101.47	297.74	742.23	128.40	433.97
Fe	170.77	6076.86	14296.50	4170.91	1240.86

Mean EF, Igeo and CF values of analyzed metals with respect to the average background concentrations are presented in Table 2. Mean EF values of heavy metals followed the order: Ni> Zn> Cu> Mn. Average EF values for Ni, Cu, Zn and Mn wereas 1.34, 2.47, 1.75 and 2.54, respectively suggesting a minor enrichment of these metals. Considering background values, enrichment of heavy metals in this study showed that heavy metals

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concentrations in sediment samples were mostly controlled by natural and partly anthropogenic sources. Average Igeo values for Ni, Cu, Zn, Mn and Fe were 0.014, 0.032, 0.018, 0.005 and 0.0001, respectively indicating no pollution in wetland sediment samples. However, Igeo is not readily comparable to the other indices of metal contamination due to the nature of the Igeo calculation involving a log function, and a background multiplication of 1.5. Mean CF values for Ni, Cu, Zn, Mn and Fe were 0.48, 0.65, 0.59, 0.68 and 0.48, respectively indicating low contamination of heavy metals in wetland sediment samples.

Table 2. Enrichment factor, geo-accumulation index and contamination factor values of heavy metals in Choghakho	r
wetland	

Metals	EF	$I_{geo}$	CF	
Ni	1.34	0.014	0.48	
Cu	2.47	0.032	0.65	
Zn	1.75	0.018	0.59	
Mn	2.54	0.005	0.68	
Fe	-	0.0001	0.48	

Results of correlation analysis showed that the heavy metals concentrations of sediment samples were significantly correlated with each other at level 1%. From this, it could be said that their source was almost the same and which may be derived from the natural sources. Considering PCA analysis, all the heavy metals were well represented by the first principal component, which accounted for over 64.79% of the total variance. The results of PCA agreed well with that of the correlation analysis. As mentioned before, the concentrations of the most heavy metals were lower than the background values. Therefore, it could be said that the distribution of heavy metals in sediment samples was mainly controlled by natural sources.

In this study, we analyzed the spatial distributions of heavy metals in the whole area of Choghakhor wetland. The spatial distribution patterns of the most of heavy metals, especially Cu, Fe and Ni were generally similar, with increasing concentrations from the north of the wetland to the south nearby villages and residential areas. In other words, the high concentrations or hotspots for the three heavy metals mainly existed in southern parts of the area under study. In addition, the spatial distribution of Mn and Zn concentrations showed decreasing trends from the west of the area to the east.

Therefore, from the above discussion can be concluded that although entire wetland is non-polluted and the heavy metals concentrations in sediment were mostly controlled by geomorphological sources but high concentrations of heavy metals in specific areas or hot spots could be related to human activities especially agricultural activity. In particular, these hot spots are located in environmental guard station, tourist area and residential areas especially villages of Kheder Abad, Saki Abad, Seyf Abad and Khani Abad in the vicinity of wetland.

## Conclusions

Results indicated that the average concentrations of heavy metals were all lower than background values. According to the results of contamination factor, geoaccumulation index and enrichment factor, considerable and intense contamination of heavy metals in sediments of study area was not observed. Based on the sediments quality guidelines, the concentration of Ni at whole study area has frequently adverse biological effect on aquatic organisms. Although, the results of the PCA revealed that all heavy metals were mainly originated from natural sources, their spatial distribution maps showed that there were several hotspots located in different parts of the area under study. In general, wetland showed a little contamination but management and control of rural and agricultural waste and reduce the consumption of chemical fertilizers to prevent and avoid damage to wetland biodiversity is essential.

Keywords: Choghakhor wetland, sediment, soil pollution index, toxic metal, zoning.

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# Determination of the optimal water release of dam with considering quantitative and qualitative demands

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Received: October, 2015

Accepted: May, 2017

## **Extended** abstract

## Introduction

Utilization of common water resources has caused conflicts between the stakeholders due to various constraints. For numerous reasons, the stakeholders prefer short-term self-interest over the public interest and want to take more share of the ideal volume of the public water resources. This is likely to damage the environment and even in the long-term causes loss for stakeholders' benefits. On the other hand, economic and social developments in the river basin reduced river flows and increased the amount of pollutant concentrations discharged into the rivers.

Considering the limited amount of available water resources to supply different purposes such as domestic, industrial and agricultural requirements, environmental flow and by increasing the risk of contamination in surface water, determine river flow is necessary to meet these purposes. The release of dam's water capacity can supply to these purposes. However, due to existing limitations, determining the amount of the release led to conflict among river's stakeholders. The release of dam mainly is determined based on short-term purposes and that's why there is not enough attention at environment flow. Thus, to determine the release of the dam, considering all purposes are necessary and purposes should be prioritized based on their importance.

The environmental and pollution control purposes in reservior-river systems have been less attentive than domestic, industrial and agricultural purposes. But, because domestic, industrial, agricultural, environmental flow and pollution control are connected together, studying of them should be done at the same time. The optimal dam release that is determined by taking acount all of purposes, could supply more requierments of all existing purposes.

So, in this study, to determine the release of dam operation considering the traditional and environmental purposes and pollution control is discussed. To do this, at first the range of environmental flows for the river is determined. In the following, qualitative simulation of river for the entire range of environmental flows is done. The purposes of the case study is using the result of simulations defined and calculated. Finally, using the conflict resolution theory, the optimal release is determined. In applying the conflict resolution theory, it is necessary to address each of the relative weight to be given.

## 2. Materials & Methods

## 2.1. Environmental flow calculation

To calculate the environmental flow of rivers, many different methods have been proposed. These methods can be classified into four main categories (hydraulic, hydrologic, simulation settlement and comprehensive methods). In this study due to lack of sufficient data, hydrological methods used to determine the environmental flow, because the hydrological methods are simpler than other methods.

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## 2.2.Purposes

In this study, five purposes in determining the optimal release are intended. As mentioned earlier, one of the main purposes of this study is supply environmental flows. Therefore the first target is the environmental flows supplement. Gotvand dam has been constructed to meet the water requirements of hydropower generation purposes, flood control, agricultural water management and create tourist attractions. Therefore, one of the aspects needed to be considered in determining the optimal release is to meet these purposes. It is necessary to define the second objective as reliability to determine the optimal release streams while dams purposes are also considered. Taking account the purpose of reliability among the other purposes of the dam causes the supply of water needs for all purposes (hydropower generation purposes, flood control, agricultural water management and creating tourist attractions) in determining the optimal release.

Another important target related to this issue is supplying of high-quality water in downstream regions. Given that the drinking water in the downstream regions including the Ahwaz city, it is supplied from the Karun river and given the importance of providing high-quality drinking water. So, it is necessary to put a purpose to supply a high-quality water. Therefore, another purpose as supply downstream water demands has defined to provide high-quality water for downstream regions.

Surface water pollution is an important phenomenon that is threatened humans health, animals and the environment. Thus, in addition to the environmental flow, it is also necessary to consider a purpose to manage and control river pollution constantration.

There are two river pollution targets due to behavior of the release flow. The two conflicting targets are "average concentration" and "length polluted". To calculate the average concentration of greater than 1 ppm, concentrations are averaged and the average value is considered as the concentration of BOD indicator for release flow. Concentrations less than 1 mgr/l are not accounted because the water in which concentrations of BOD indicator is smaller than 1 mgr/l is considered pure. The mathematical definition of the average concentration is illustrated:

$$C_{0,i} = \begin{cases} C_i - 1 & \text{if } C_i \ge 1\\ 0 & \text{else} \end{cases}$$
$$C_{mean} = \frac{\sum_{i=1}^{nt} C'_i}{nt}$$

## 2.3. Conflict resolution model

If there is more than one stakeholder in the decision-making process, due to the different aims and different priorities of the views of stakeholders, decision-making process will have not made such as lack of agreement. In such matters, it is the decision in such a way that all views of all stakeholders are taken into account, and the rights of all stakeholders are met. One way to solve this kind of problem is using models of conflict resolution. One of the common conflict resolution methods is Nash.

## 3. Case study

One of the main aims of this study was to determine the environmental flow in the Gotvand dam location to downstream of Shoshtar city. Karun is the most important river of Iran and it has the largest discharge of water among the Iran's rivers. The length of this river is 800 km and long-term average annual flow of the river is 453  $m^3$ /s and average. For the purposes of this study, all data were collected from the study area. This data includes the release of dam, river hydraulic details and characteristics are sources of pollutants.

## 4. Discussion of Results & Conclusions

In this part, the results will be discussed. At the first, by using the QUAL-2K model, water quality simulations is done and then the simulation results to calculate purposes and average concentrations and length polluted are used. Finally, by using the theory of Nash conflict resolution, the optimal release under three scenarios relative weights is determined.

## 4.1. Environmental flow calculation

Environmenta flow of Karun River in the study area was calculated by using flow-based Tennant (1976) and Aquatic Base Flow methods. The range environmental flow was 45 to 272 ( $m^3/s$ ).

## 4.2. Simulation BOD in the range of dam release

Qualitative simulations for releases from the dam flows of the range of 13 to 458 have been done by using the QUAL-2K.



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## 4.3. Calculation of average concentrations and length polluted

Once, the river's qualitative simulation is finished. BOD indicator concentrations along the river is obtained for each discharge flow releases from the dam. Using the obtained concentrations, the average concentration and length of contact with the river can be calculated. Therefore, the mean concentrations were calculated for different values of release flow from the dam.

By increasing the release rate, due to increased volume of water and dilution of contamination concentrations, the average concentration decreases and vice versa. But as the flow rate increases, due to increased flow velocities, unallowable concentrations run longer in the river and increase the length of the contact, and vice versa. This issue is of great importance in determining the proper locations for the water extraction from the river. This is especially important in downstream areas that are used to supply drinking water to riverside water. Downstream of the study area contains many cities and villages such as Ahwaz. Therefore, it is necessary to determine the release rate in such a way that the concentration of water pollution of the river before reaching the water extraction points has fallen to the standard limits.

#### 4.4. Determining the optimal release

One scenario has been defined to evaluate impact of relative weights that was determined according to the different qualitative and changes various conditions. Normalization of data to assess the importance of purposes is necessary in conflict resolutions methods. According to Nash conflict resolution model, before running the optimization model of conflict resolution, it is necessary to set out the minimum acceptable level for each of the purposes. The minimum acceptable level for each of the five purposes listed in the previous section were defined After normalization of the data of the purposes and determining their minimum acceptable level, for each of these purposes, relative weights should be determined according to their importance. But relative weights depend on many conditions including economic, social, climate (wet or drought), and so on. Therefore, these conditions may always change at any time, and the relative weights of purposes should be changed. Relative weights are used to indicate the importance of each purpose on determining the release rate of the dam. In the present study, the relative weight of purposes has been determined based on the authors' experiences. Therefore, in order to apply the results of this research, it is necessary to determine the relative weights of each purpose according to the time conditions and existing expectations. In this study, one scenario of relative weights is defined. In this scenario, relative weights for all purposes are equal to one.

At last, by using Nash conflict solution method, optimal flow releases from the dam under one relative weights of purposes was determined. The amount of released flow from the dam to the scenario was  $184 \text{ m}^3/\text{s}$ .

Keywords: conflict resolution, environmental flow, flow release, Karun river and Gotvand dam, water quality.

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