

ORIGINAL RESEARCH PAPER

## Removal of heavy metals from Tehran south agricultural water by Zeolite N.P./PEG/GO nano-composite

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### ABSTRACT

The zeolite N.P./PEG/GO composite was synthesized by the hydrothermal assisted sol-gel method to be used as Pb<sup>2+</sup> and Cd<sup>2+</sup> ions nano-adsorbent from the agricultural water. The FT-IR spectrum confirmed the expected microstructure of synthesized adsorbent. The SEM revealed the formation of zeolite nanoparticles and the layer structure of graphene. The existence of expected elements and crystalline structures were confirmed by EDS and XRD analysis, respectively. The pH, contact time, temperature and adsorption amount was optimized in the removal process of lead (II) and cadmium ions. The results were 6, 20 min, 25 °C and 0.005g for Pb<sup>2+</sup> and 4, 20 min, 25 °C and 0.005g for Cd<sup>2+</sup> respectively. The adsorption capacity of Lead (II) and cadmium ions were 49.6 and 50.2 mg.g<sup>-1</sup> of adsorbent, respectively. Interference ions don't show any considerable effects on the efficiency of adsorption for both ions. The equilibrium data can well be fixed using both Langmuir and Freundlich equations.

**Keywords:** Adsorption; Cadmium; Graphene Oxide; Lead (II); Zeolite Nanoparticles

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## INTRODUCTION

Heavy metal ions such as lead, chromium, zinc, and nickel are known as toxic pollutants of water sources [1-7]. The industrial revolution increases these pollutants in the soil and crops [1,4]. Many industrial activities including battery manufacturing, screens, combustion of fossil fuels, metals production, alloys, ceramics, and glasses contaminate the aqueous medium by lead (II) and cadmium ions [8]. According to World Health Organization (WHO), the maximum concentration of cadmium ion in water is 0.003 mg/L [9] and more concentrations may be carcinogenic. The US Environmental protection Agency (USEPA) guideline states that the maximum contamination level for Pb<sup>2+</sup> ion in drinking water is 0.015 mg/L [10].

Variety methods such as adsorption [8, 11-12], chemical precipitation [13], ion exchange [14-

16], ultra-filtration [17], reverse osmosis [18], oxidation [17] and extraction [19] have been developed to remove heavy metals from aquatic media. The adsorption process has also considered as an efficient and economical method for chemical removing of heavy metals [20]. Many heavy metal adsorbents such as activated carbon [21], zeolite [22], bentonite [23], synthetic and biopolymers [24], clay and chitosan [25] have been applied in processing wastewater [26]. The high surface area of zeolite nano-particles (zeolite N.P.) with interlinked tetrahedral of alumina (Al<sub>2</sub>O<sub>3</sub>) and silica (SiO<sub>2</sub>) structures introduce them as suitable candidates for adsorption of heavy metals from wastewater [27]. The agglomeration of zeolite N.P. during the removal process is a major challenge. Making nanocomposite of suitable compounds can overcome this problem. On the other hand, the layer structure of graphene oxide with high surface

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area is important factors in the adsorption process [17]. According to the recent reports, graphene oxide (GO), chemically functionalized graphene, reduced graphene oxide (rGO) and graphene nano-composites have received much attention to the elimination of environmental pollutants [28-29]. Furthermore, polyethylene glycol (PEG) is a compound that can contribute to a composite including GO. As a polymer, PEG has a high oxygen content that can adsorb heavy metals [30].

In this work, the zeolite N.P./PEG/GO composite was synthesized via the hydrothermal assisted sol-gel method for the first time and used to remove  $Pb^{2+}$  and  $Cd^{2+}$  ions from aqueous media. The nanocomposite was made of natural compounds that may be retrieved after usage. The compounds are environmentally friendly and don't create any new pollutant. The effective factors of the adsorption process were investigated and optimized.

## EXPERIMENTAL

### Materials

All reagents were selected of analytical grade and used without further purification. Graphite powder,  $H_2SO_4$ ,  $HNO_3$ ,  $KClO_3$ , NaOH, fumed silica, PEG and sodium aluminate were purchased from Merck and Sigma-Aldrich.

### Synthesis of zeolite nanoparticle/PEG/GO composite

Graphene oxide was synthesized by Staudenmaier method [30]. Briefly, 1g of graphite was mixed with 18mL of  $H_2SO_4$  under constant stirring. After 10min, 2mL of  $HNO_3$  was added gradually to the prepared solution then 11g of  $KClO_3$  was added slowly to it. The temperature was kept less than 25 °C and the solution stirred for 10 days. The resulting mixture was washed with distilled water to reach pH=7 and dried at 80 °C to obtain graphite oxide. 0.1g of

graphite oxide was added to 100mL of distilled water and imposed to an ultrasound wave for 2h to get GO sheets.

As the final synthesis stage, 0.01g of GO sheets was added into 35mL of distilled water and mixed with 3.43g  $SiO_2$  and 2.42g sodium aluminate. Then the NaOH solution was added to it at vigorous stirring and transferred into Teflon of autoclave and kept at 60°C for 4 days. The obtained crystalline sediment was imposed to microwave for 4h at 100°C. The precipitate was washed with distilled water and dried to obtain the zeolite N.P./GO composite. At last, 18g of PEG was dissolved in the ethanol and added to the precipitate and stirred for 4h, and dried to get zeolite N.P./PEG/GO composite.

### Characterization

The structure and phase composition of the sample was characterized using a powder X-ray diffractometer (XRD: GNR XRD, Npb3000, Italy). Surface morphology of the samples was monitored by scanning electron microscope (SEM) and energy dispersive X-ray (EDS) spectrum was obtained with a Mira3-XMU (Germany) microscope. Fourier transform infrared spectra (FT-IR) of nano-composite was collected using Tensor 27 Bruker spectrophotometer in the range of 400-4000  $cm^{-1}$ . Atomic absorption spectrometer (AAS) (pH-827, UK) was employed to determine the concentration of lead (II) and cadmium ions.

## RESULTS AND DISCUSSION

### Characterization of the nanocomposite

The morphology of GO and zeolite N.P./PEG/GO composite were studied using SEM. The layered structure of GO (Fig. 1a) was detected with an average thickness of about 70nm. Fig. 1b shows that GO sheets are homogeneously covered by

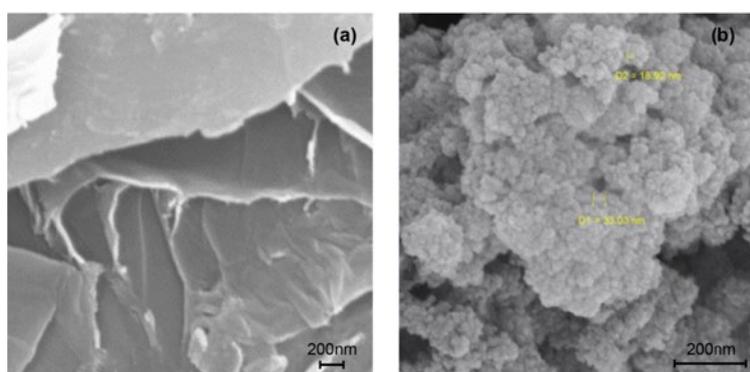


Fig. 1. SEM images of (a) GO and (b) zeolite N.P./PEG/GO nano-composite

nanoparticles that can be referred to as zeolite N.P. Increasing the thickness of graphene layers may be devoted to covering by PEG.

The EDS spectrums of GO and zeolite N.P./PEG/GO composite given in the Figs. 2a and 2b respectively, show the peaks of oxygen, sodium, aluminum, and silicon elements. The oxygen content of nano-composite, (51.45%), plays an important role in the metal ions adsorption. Covering the GO by the zeolite N.P. and increasing its thickness, prevent the layers to be seen in Fig. 1b.

The FT-IR spectra of synthesized nano-composite before and after adsorption processes of  $Pb^{2+}$  and  $Cd^{2+}$  ions are shown in Fig. 3. The band around  $1025\text{cm}^{-1}$  was assigned to C-O stretching vibration bond of epoxide and  $1654\text{cm}^{-1}$  relates to C=O stretching bond of carbonyl and carboxyl groups. The tertiary C-OH group stretching bond can be seen at  $1463\text{cm}^{-1}$  and O-H stretching vibration bond there is at  $3445\text{cm}^{-1}$ [33]. The peak at  $986.9\text{cm}^{-1}$  can be attributed to the zeolite tetrahedron internal vibration. Peaks at 3442, 1601, 862.04 and  $755.36\text{cm}^{-1}$  correspond to the stretching vibration bond of H-O-H, bending vibration bond

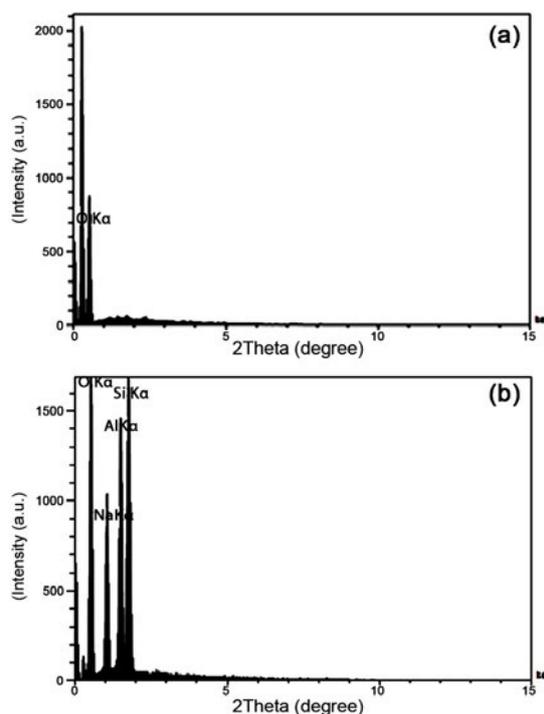


Fig. 2. EDS patterns of (a) GO and (b) zeolite N.P./PEG/GO nanocomposite

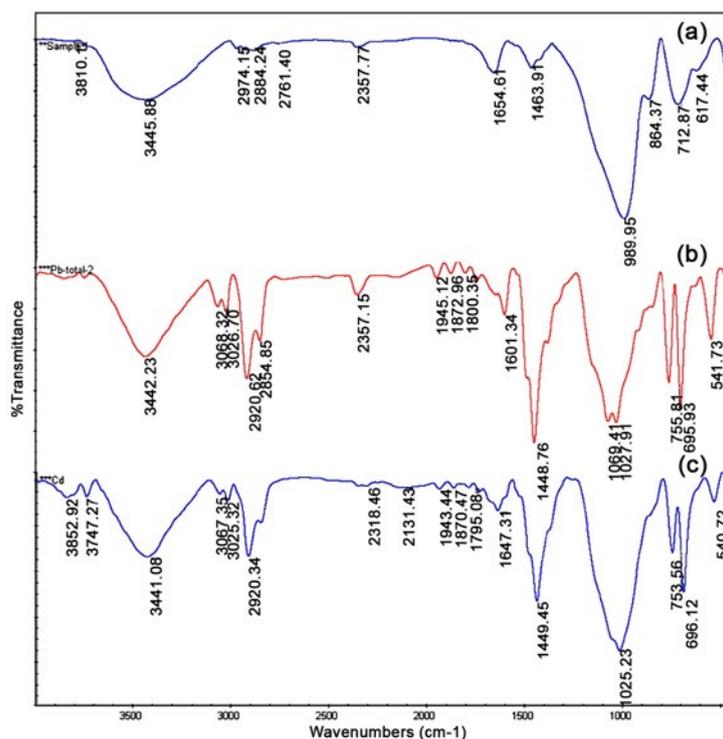


Fig. 3. FT-IR spectra of (a) zeolite N.P./PEG/GO composite, (b) zeolite N.P./PEG/GO composite after adsorbed  $Pb^{2+}$  and (c) zeolite N.P./PEG/GO composite after adsorbed  $Cd^{2+}$  ions

of -OH, the symmetric stretching bond of Si-O-Si or Al-O-Si, and symmetric stretching bond and bending vibration bond of Si(Al)-O, respectively [34]. The peak intensities changed after removal processes shown in the Figs. 3b and 3c that can be confirmed the adsorption of heavy metals by nano-sorbent functional group.

The XRD patterns of GO and zeolite N.P./PEG/GO composite are shown in the Figs. 4a and 4b, respectively. Diffraction peak at  $2\theta=12^\circ$  in Fig. 4a can be indexed as graphene oxide. The major peak of the well-solidified graphene oxide has observed in a 10 to 12 degree in  $2\theta$ . This peak may be changed by the degree of oxidation of the graphene and also changes in the presence of water molecules that are not evaporated between the GO sheets [33]. Fig. 4b shows three peaks at 18 and 39  $2\theta$  value, on the other hand, the broad peaks at around 27 to 30 degree in  $2\theta$  may be included 22, 25, 27 and  $30^\circ$  peaks that are merged. The XRD pattern of synthesized zeolite almost matched with faujasite (FAU) NaX zeolite that reported in the

other researches [34-36] and confirms that it is FAU-NaX zeolite. Decreasing the intensity of GO peak in Fig. 4b may be devoted to the presence of zeolite nanoparticles and polymer on graphene oxide layers.

*Removal study by using zeolite N.P./PEG/GO nano-composite*

*Batch adsorption experiments*

Stock solutions of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions were prepared from  $\text{CdCl}_2$  and  $\text{PbCl}_2$ , respectively. 0.01 g of synthesized nano-composite was added to 50mL of  $\text{Cd}^{2+}$  or  $\text{Pb}^{2+}$  solutions and stirred for 30 minutes. The concentration of ions before and after adsorption were measured by Flame-AAS. Removal efficiency percentages were calculated by

$$\text{Removal}\% = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

In which  $C_0$  and  $C_e$  show the initial and equilibrium concentrations of the solutions in  $\text{mg.L}^{-1}$ , respectively.

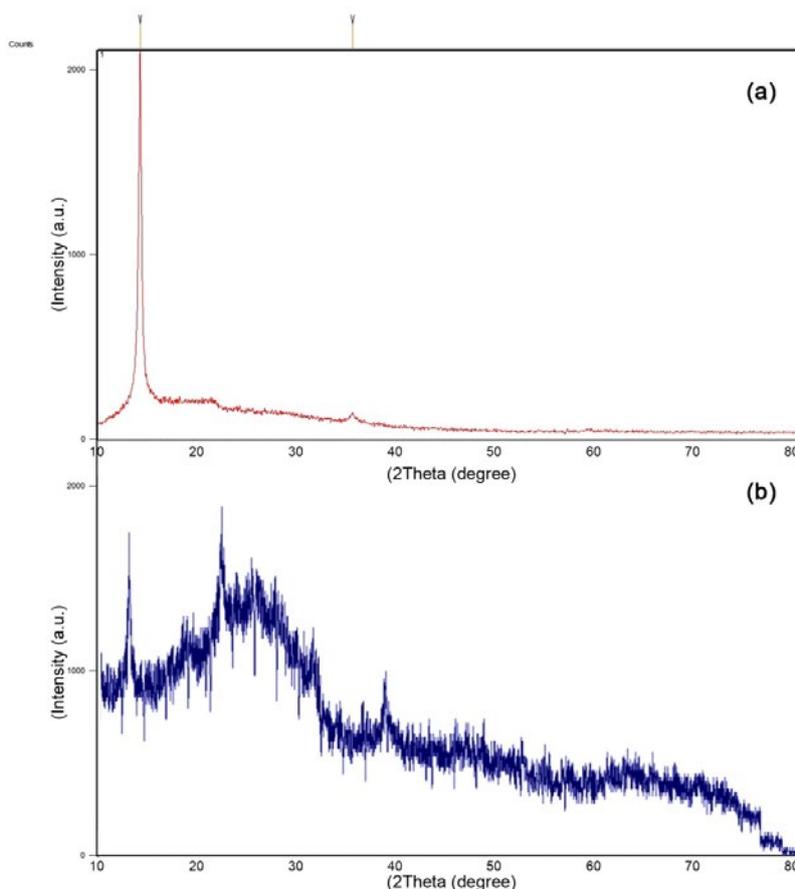


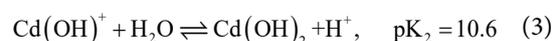
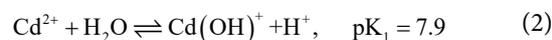
Fig. 4. XRD pattern of (a) Graphene oxide (b) zeolite N.P./PEG/GO nano-composite

### pH Effect

The pH was optimized as the surface charge value relates to it.  $\text{Pb}(\text{OH})_2$  or  $\text{Cd}(\text{OH})_2$  was formed at basic pH, therefore the pH effect was investigated in the 3-7 range. The results showed that pH strongly influences the adsorption process. According to Fig. 5, the best results were obtained at 6 and 4 pH values for  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  ions, respectively. At acidic condition,  $\text{H}_3\text{O}^+$  ion adsorbs on the synthesized nano-composite and occupies the active sites and decrease the removal efficiency. Besides, the adsorbed hydronium ions make the surface charge of nano-sorbent. This prevents surface adsorption of cations due to electrostatic repulsion.

The species of cadmium may be found in the distilled water in the forms  $\text{Cd}^{2+}$ ,  $\text{Cd}(\text{OH}^+)$ ,  $\text{Cd}(\text{OH})_2$ ,  $\text{Cd}(\text{OH})_{2(s)}$ , etc. The value of hydrolyzed cadmium relates to its concentration and the pH solution. It was found that the ion form of  $\text{Cd}^{2+}$  occurs in  $\text{pH} < 6.0$ . The dominant species at  $\text{pH} > 8.0$

is  $\text{Cd}(\text{OH})_2$  and at  $\text{pH} < 8.0$  are  $\text{Cd}^{2+}$  and  $\text{Cd}(\text{OH}^+)$  [37, 38]. The following equations help us to calculate the probability of hydrolyzing  $\text{Cd}^{2+}$  ion.



The equilibrium constants show that in  $\text{pH} < 6$  there are  $\text{Cd}^{2+}$  ions [38].

It is considered that changing pH in 4 to 7 has no significant effects on the removal efficiency of  $\text{Cd}^{2+}$  ion, considerably. This may be related to the selectivity of nano-sorbent to this ion. On the other hand, more removal efficiency of  $\text{Cd}^{2+}$  ion compared to  $\text{Pb}^{2+}$  ion in all of the experiments may be devoted to the selectivity of nano-adsorbent to cadmium ion.

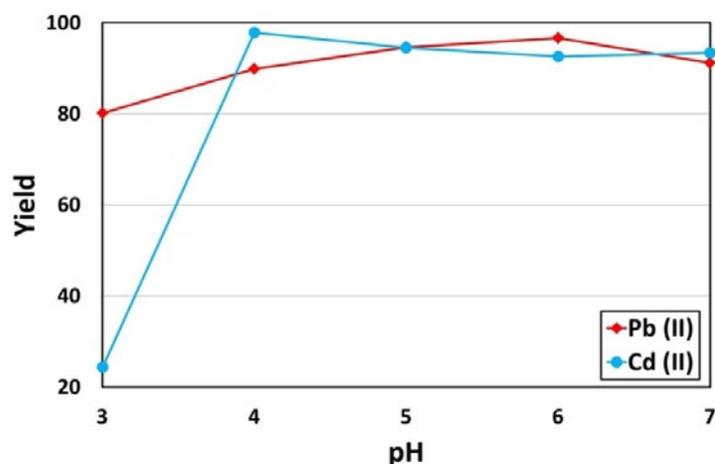


Fig. 5. Effect of pH on the removal of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  ions

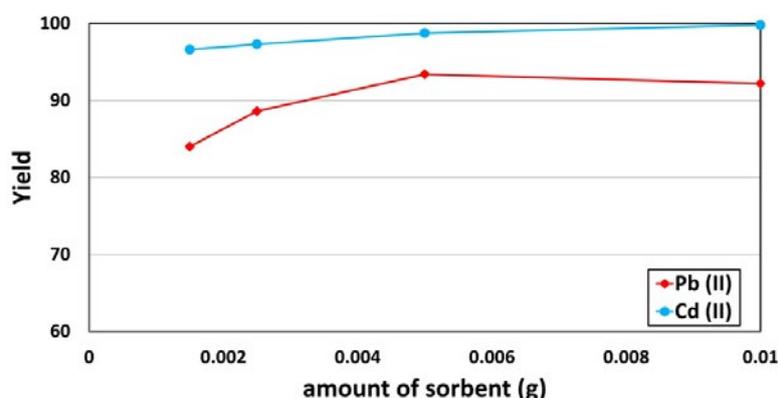


Fig. 6. Effect of sorbent dosage on the removal of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  ions

### Sorbent dosage Effect

The amount of adsorbent may be considered as the most essential parameter in the removing process of heavy metals. Therefore by keeping the test conditions in an optimal pH, this parameter was studied at different amounts of nano-sorbent including 0.0015, 0.0025, 0.005 and 0.01g. The removal efficiency for  $Pb^{2+}$  and  $Cd^{2+}$  ions were 93.4% and 98.78%, respectively, for 0.005g of the nano-sorbent. These values were changed to 92.2% and 99.8% when the nano-sorbent changed to 0.01g. The minor changes in the removal efficiency may be devoted to the random error of the AAS instrument, so, the 0.005g was considered as the optimum value of nano-sorbent for both ions. When all ions adsorbed on the active sites, the removal efficiency will not be affected by further nano-sorbent.

### Contact time Effect

The adsorption efficiency of  $Pb^{2+}$  and  $Cd^{2+}$  ions on the nano-composite was measured in 10, 20,

30, 40 and 50 minutes, while all other parameters were kept constant. Fig. 7 shows the increase of removal efficiency by contact time. The maximum removal was observed at 20 min for both ions. As time goes by, the adsorption capacity of nano-sorbent tends to a constant value, asymptotically. This can be devoted to the strong bond of the sorbent active sites with  $Cd^{2+}$  ions. The adsorption capacity of  $Pb^{2+}$  ion decreases by the time that can be attributed to a weak bond between  $Pb^{2+}$  ion and nano-composite.

### Temperature Effect

The removal process was reported at 10, 20, 25 and 30 °C to investigate the effect of temperature. According to Fig. 8, the removal efficiency improves up to 25°C, providing primary activation energy. Further increasing of temperature, minor reduces the removal efficiency so it can be inferred that the reaction is exothermal. In this way, the optimal temperature considered to be 25°C. Adsorption capacities of  $Pb^{2+}$  and  $Cd^{2+}$  ions were 49.6 and 50.2

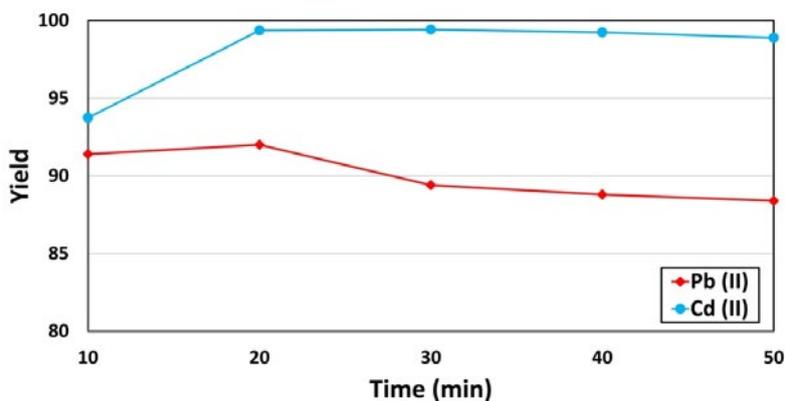


Fig. 7. Effect of contact time on the removal of  $Pb^{2+}$  and  $Cd^{2+}$  ions

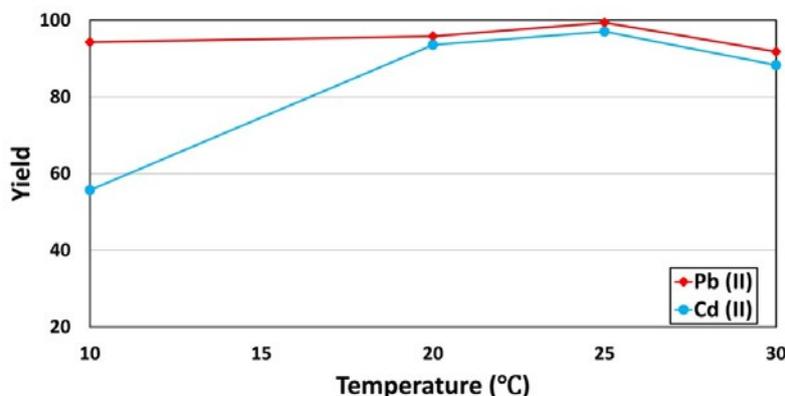


Fig. 8. Effect of temperature on the removal of  $Pb^{2+}$  and  $Cd^{2+}$  ions

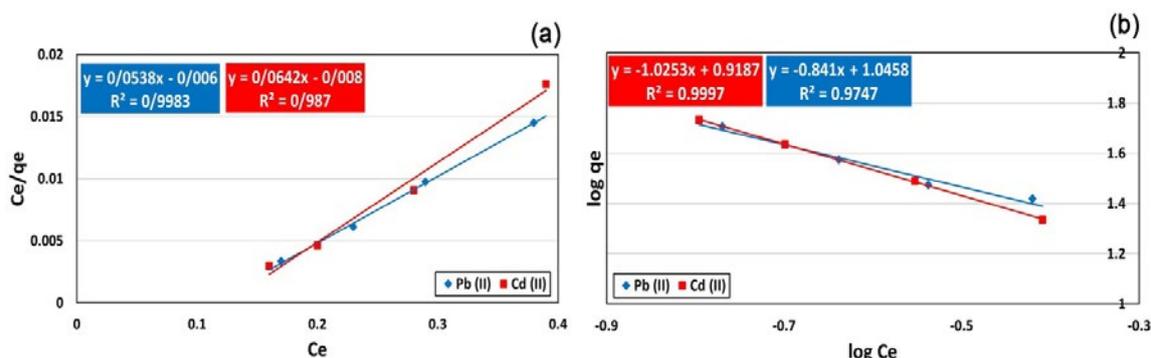


Fig. 9. (a) Langmuir and (b) Freundlich models of Pb<sup>2+</sup> and Cd<sup>2+</sup> adsorption with zeolite N.P./PEG/GO nano-composite

mg.g<sup>-1</sup> adsorbent, respectively, according to the experimental data.

*Adsorption isotherms*

An adsorption isotherm shows the interaction mechanism of sample and sorbent. Among the various developed isotherms, the Langmuir and Freundlich models were considered in this study. The monolayers adsorption capacity in constant temperature is given by the Langmuir model [31]

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \tag{5}$$

where q<sub>e</sub> and q<sub>max</sub> are the equilibrium and maximum adsorbed capacities (mg.g<sup>-1</sup>), respectively. K<sub>L</sub> is the Langmuir constant that relates to the free energy of adsorption (L.mg<sup>-1</sup>) and C<sub>e</sub> is the equilibrium concentration of adsorbed ion (mg.L<sup>-1</sup>). The dimensionless coefficient

$$R_L = \frac{1}{(1+bC_0)} \tag{6}$$

shows the nature of adsorption. If R<sub>L</sub> < 1, the adsorption process is favorable but for R<sub>L</sub> > 1, the adsorption evaluates as unfavorable and R<sub>L</sub> = 1 confirms the linear adsorption and for irreversible adsorption, R<sub>L</sub> equals zero [32].

Freundlich model is an experimental equation, which usually applies to describe the adsorption data. The Freundlich equation commonly gives by [32]

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{7}$$

where K<sub>F</sub> is the Freundlich constant, and 1/n is the adsorption intensity. The adsorption is suitable when n is smaller than one [23].

In the present removal study, the equilibrium adsorption capacity (q<sub>e</sub>) was calculated by the equation

$$q_e = \frac{(C_0 - C_e) \times V}{M} \tag{8}$$

where V is the volume of wastewater (Liter) and M is the nano-composite mass (g). C<sub>0</sub> and C<sub>e</sub> are the concentrations of ions before and after the adsorption process, respectively.

The adsorption isotherm curves are shown in Fig. 9 based on the Langmuir and Freundlich models. The constant parameters of Langmuir and Freundlich isotherms and linear regression coefficient R<sup>2</sup> are given in Table 1. As a result, the adsorption data are consistent with both Langmuir and Freundlich isotherms.

**METHOD PERFORMANCE**

*Interference ions Effect*

As adsorption is a competitive phenomenon, the presence of different ions must change the removal efficiency. Therefore, it was investigated in the presence of interference ions with the molar ratio of 100 to Pb<sup>2+</sup> or Cd<sup>2+</sup> ions. The removal

Table 1. Isotherm constant parameters of Pb<sup>2+</sup> and Cd<sup>2+</sup> adsorption with zeolite N.P./PEG/GO nano-composite

Isotherm	Freundlich			Langmuir			
	n	K <sub>F</sub>	R <sup>2</sup>	q <sub>max</sub>	K <sub>L</sub>	R <sub>L</sub>	R <sup>2</sup>
Pb <sup>2+</sup>	1.189	11.112	0.9747	18.587	8.967	0.0257	0.9983
Cd <sup>2+</sup>	0.975	8.292	0.9997	15.576	8.025	0.0287	0.987



Table 2. The removal percentages of Cd<sup>2+</sup> and Pb<sup>2+</sup> ions in the presence of potassium, sodium, copper (II) and iron (III)

Interfering ion	R%±RSD%([Pb <sup>2+</sup> ])	R%±RSD% ([Cd <sup>2+</sup> ])
K <sup>+</sup>	99±0.2	93±2
Na <sup>+</sup>	99.4±0.6	91±4
Cu <sup>2+</sup>	93.8±5	99.5±4.5
Fe <sup>3+</sup>	95.8±3.8	97±2

R%: Removal efficiency percent

Table 3. Results of Pb<sup>2+</sup> and Cd<sup>2+</sup> ions removal by zeolite N.P./PEG/GO nano-composite in the actual samples

Sample	Pb <sup>2+</sup>		Cd <sup>2+</sup>	
	Remaining Amount of ion (µg)	%Removal	Remaining Amount of ion (µg)	%Removal
Gol-HesarShahr-e-Rey region	12.07±1.2	78.72	7.8±0.7	87
Hassanabad region	1.08±0.7	98.2	4.1±0.9	93.1
Beheshtzahra region	1.73±0.2	97.12	5.24±1.1	91.27

Table 4. Comparison of adsorption capacity (qe) and removal experimental parameters for Pb(II) and Cd(II) ions

Adsorbent	pH	Sorption capacity (mg g <sup>-1</sup> )		Contact time (min)	Ref.
		Pb (II)	Cd (II)		
Biochar-alginate	6	-	9.7	240	[39]
NFRGO	4	18.4	-	83	[40]
P(MMA-HEMA)	6	31.4	-	120	[41]
Biochar	5/5	47.3	46.8	1440/1440	[42]
Magnetic graphene	5.5	6	-	-	[43]
zeolite N.P./PEG/GO	6/4	49.6	50.2	20/20	In this work

percentages of Cd<sup>2+</sup> and Pb<sup>2+</sup> ions in the presence of four selected interfering ions under optimized condition are given in Table 2. There is no evidence of interference according to R% amounts.

#### Reproducibility of the method

By considering all optimized conditions, reproducibility of the proposed method was assessed for each ion using 10 repetitions. The amount of RSD percentage was calculated 2.345% and 1.007% for Pb<sup>2+</sup> and Cd<sup>2+</sup> ions, respectively.

To investigate the nano-composite ability to remove ions in a complex matrix, the process was examined for three kinds of agricultural water. Each sample was individually added by 60µg of Pb<sup>2+</sup> or Cd<sup>2+</sup> ion and the removal process was done in optimum conditions. The results are given in Table 3 that shows the appropriate and acceptable ability of synthesized nano-composite in such a way that it may be used to purify the agricultural waters.

According to some reports of Pb<sup>2+</sup> and Cd<sup>2+</sup> ions given in Table 4, the adsorption capacity of zeolite N.P./PEG/GO nano-composite most of the listed adsorbent. The comparative data signifying the advantage of zeolite N.P./PEG/GO composite over other materials concerning the adsorption capacity.

#### CONCLUSION

The zeolite N.P./PEG/GO nano-composite was successfully synthesized by hydrothermal assisted sol-gel method and characterized by the FT-IR, XRD, SEM, and EDS. The nano-composite used to remove Pb<sup>2+</sup> and Cd<sup>2+</sup> ions from different samples of water. The pH, contact time, dosage and temperature were optimized as effective factors of the adsorption process.

The results showed that the existence of interference ions don't change the removal percentage of Pb<sup>2+</sup> and Cd<sup>2+</sup> ions by zeolite N.P./PEG/GO composite, considerably. The adsorbent capacity of Pb<sup>2+</sup> and Cd<sup>2+</sup> ions was obtained 49.6 and 50.2 mg ion per gram adsorbent, respectively. The adsorption process of lead (II) and cadmium ions was consistent to both Langmuir and Freundlich isotherms.

#### CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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