

ORIGINAL RESEARCH PAPER

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

Susan Samadi^{1,*}, Mostafa Mirzaie Shalmani², Seyed Amirabbas Zakaria¹

¹ Department of Chemistry, College of Basic Science, Yadegar-e-Imam Khomeini (RAH) Shahr-e-Rey Branch, Islamic Azad University, Tehran, Iran

² Department of Chemistry, Science and research branch, Islamic Azad University, Tehran, Iran

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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 Pb²⁺ and Cd²⁺ 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 Pb²⁺ and 4, 20 min, 25 °C and 0.005g for Cd²⁺ respectively. The adsorption capacity of Lead (II) and cadmium ions were 49.6 and 50.2 mg.g⁻¹ 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 Pb²⁺ 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 (Al₂O₃) and silica (SiO₂) 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

* Corresponding Author Email: susansamadi@iausr.ac.ir



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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

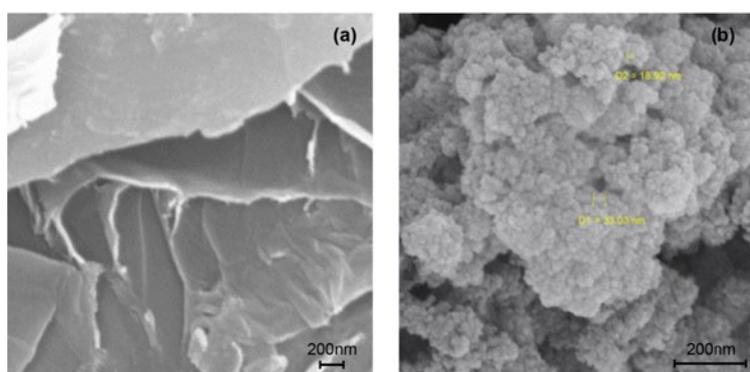


Fig. 1. SEM images of (a) GO and (b) zeolite N.P./PEG/GO nano-composite

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 1025cm^{-1} was assigned to C-O stretching vibration bond of epoxide and 1654cm^{-1} relates to C=O stretching bond of carbonyl and carboxyl groups. The tertiary C-OH group stretching bond can be seen at 1463cm^{-1} and O-H stretching vibration bond there is at 3445cm^{-1} [33]. The peak at 986.9cm^{-1} can be attributed to the zeolite tetrahedron internal vibration. Peaks at 3442, 1601, 862.04 and 755.36cm^{-1} correspond to the stretching vibration bond of H-O-H, bending vibration bond

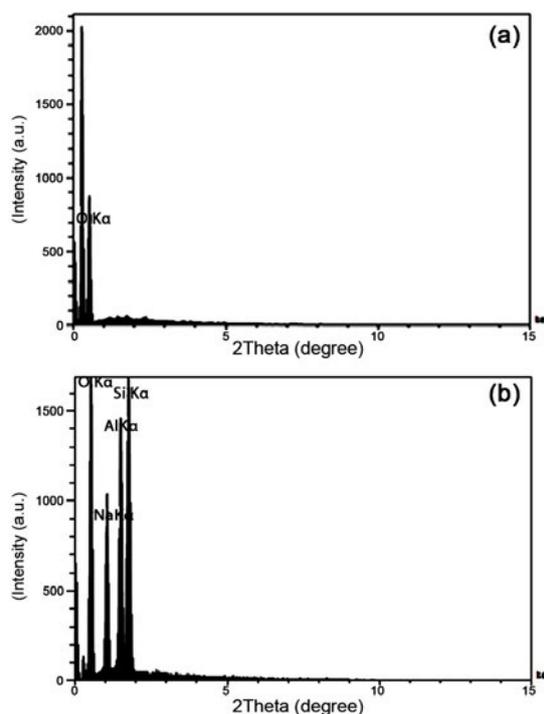


Fig. 2. EDS patterns of (a) GO and (b) zeolite N.P./PEG/GO nanocomposite

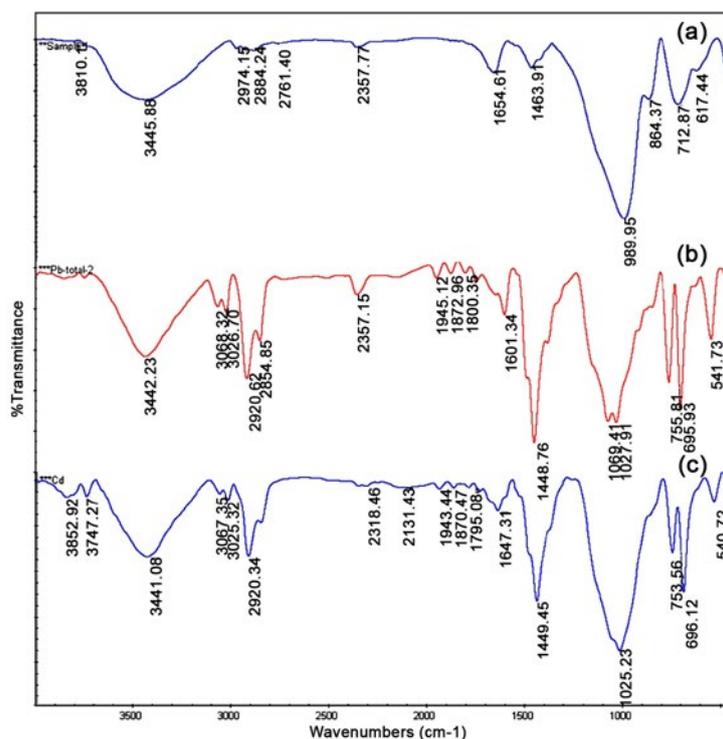


Fig. 3. FT-IR spectra of (a) zeolite N.P./PEG/GO composite, (b) zeolite N.P./PEG/GO composite after adsorbed Pb^{2+} and (c) zeolite N.P./PEG/GO composite after adsorbed Cd^{2+} ions

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 2θ . 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 2θ value, on the other hand, the broad peaks at around 27 to 30 degree in 2θ may be included 22, 25, 27 and 30° 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 Cd^{2+} and Pb^{2+} ions were prepared from CdCl_2 and PbCl_2 , respectively. 0.01 g of synthesized nano-composite was added to 50mL of Cd^{2+} or 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 mg.L^{-1} , respectively.

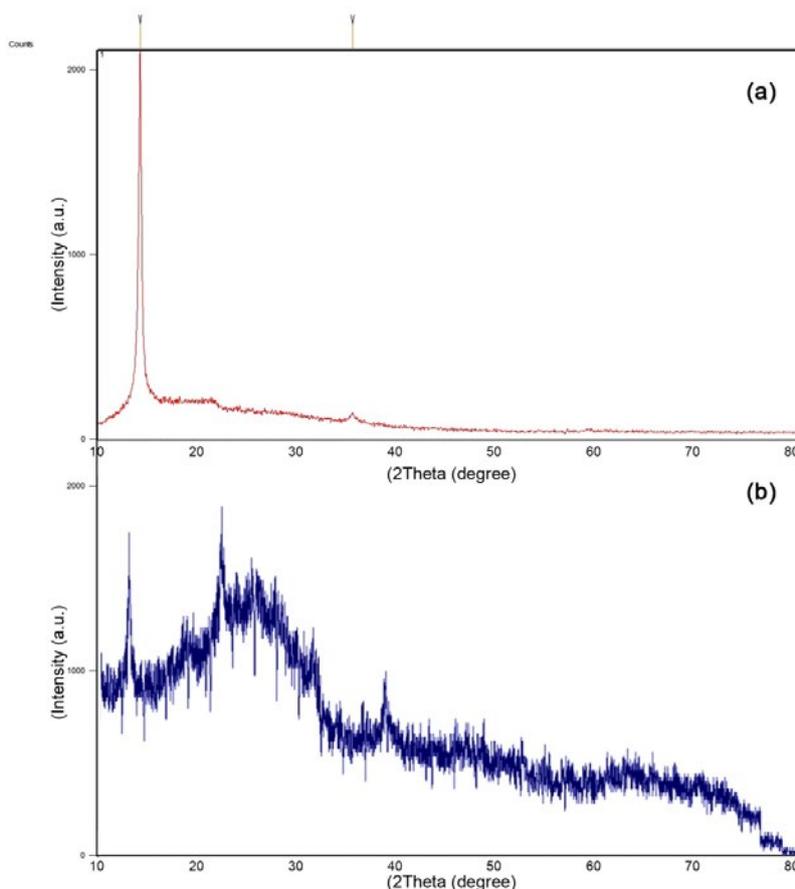


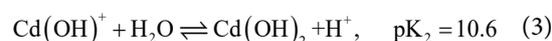
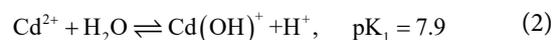
Fig. 4. XRD pattern of (a) Graphene oxide (b) zeolite N.P./PEG/GO nano-composite

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 Pb^{2+} and Cd^{2+} ions, respectively. At acidic condition, H_3O^+ 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 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 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 Cd^{2+} and $\text{Cd}(\text{OH}^+)$ [37, 38]. The following equations help us to calculate the probability of hydrolyzing Cd^{2+} ion.



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

It is considered that changing pH in 4 to 7 has no significant effects on the removal efficiency of 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 Cd^{2+} ion compared to Pb^{2+} ion in all of the experiments may be devoted to the selectivity of nano-adsorbent to cadmium ion.

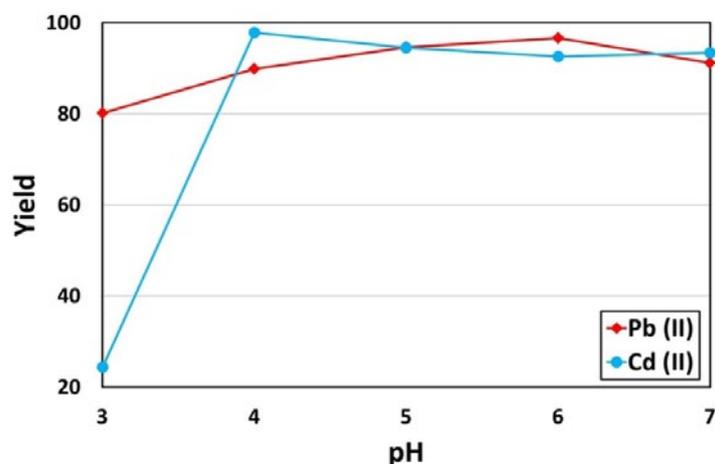


Fig. 5. Effect of pH on the removal of Pb^{2+} and Cd^{2+} ions

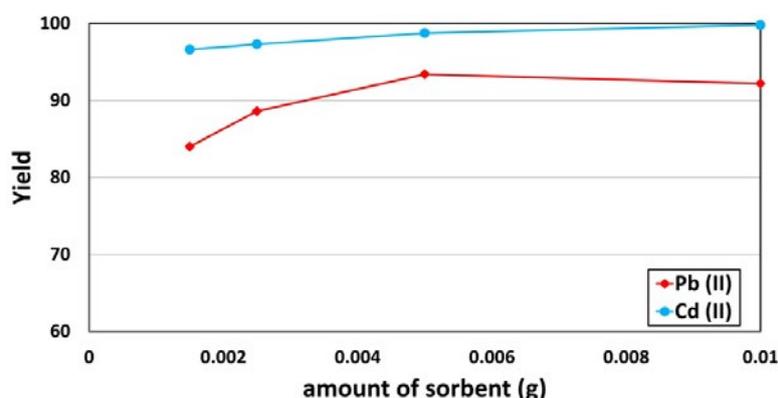


Fig. 6. Effect of sorbent dosage on the removal of Pb^{2+} and Cd^{2+} ions

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

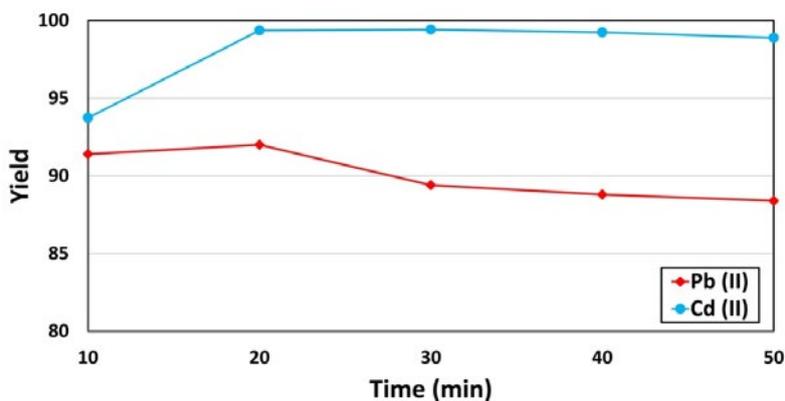


Fig. 7. Effect of contact time on the removal of Pb^{2+} and Cd^{2+} ions

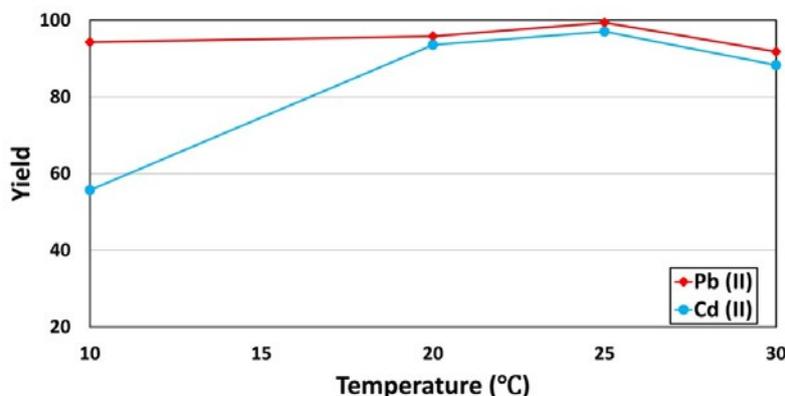


Fig. 8. Effect of temperature on the removal of Pb^{2+} and Cd^{2+} ions

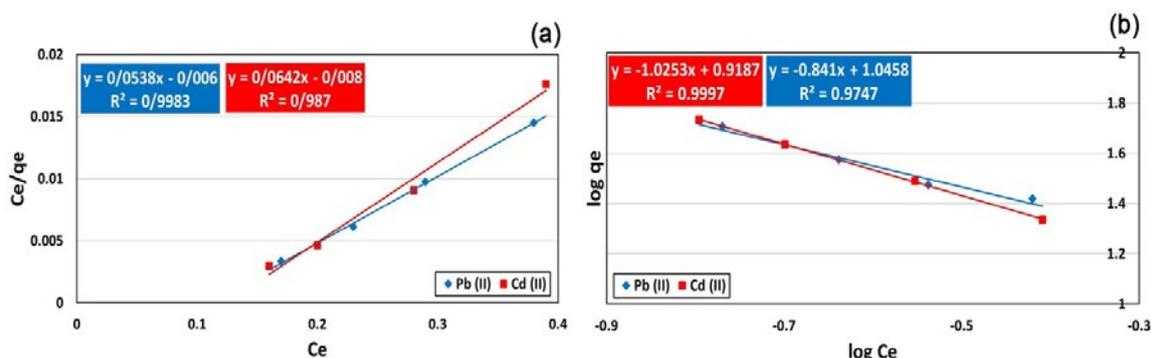


Fig. 9. (a) Langmuir and (b) Freundlich models of Pb²⁺ and Cd²⁺ adsorption with zeolite N.P./PEG/GO nano-composite

mg.g⁻¹ 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_e and q_{max} are the equilibrium and maximum adsorbed capacities (mg.g⁻¹), respectively. K_L is the Langmuir constant that relates to the free energy of adsorption (L.mg⁻¹) and C_e is the equilibrium concentration of adsorbed ion (mg.L⁻¹). The dimensionless coefficient

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

shows the nature of adsorption. If R_L < 1, the adsorption process is favorable but for R_L > 1, the adsorption evaluates as unfavorable and R_L = 1 confirms the linear adsorption and for irreversible adsorption, R_L 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_F 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_e) 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). C₀ and C_e 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 R² 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 Pb²⁺ or Cd²⁺ ions. The removal

Table 1. Isotherm constant parameters of Pb²⁺ and Cd²⁺ adsorption with zeolite N.P./PEG/GO nano-composite

Isotherm	Freundlich			Langmuir			
	n	K _F	R ²	q _{max}	K _L	R _L	R ²
Pb ²⁺	1.189	11.112	0.9747	18.587	8.967	0.0257	0.9983
Cd ²⁺	0.975	8.292	0.9997	15.576	8.025	0.0287	0.987



Table 2. The removal percentages of Cd²⁺ and Pb²⁺ ions in the presence of potassium, sodium, copper (II) and iron (III)

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

R%: Removal efficiency percent

Table 3. Results of Pb²⁺ and Cd²⁺ ions removal by zeolite N.P./PEG/GO nano-composite in the actual samples

Sample	Pb ²⁺		Cd ²⁺	
	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 ⁻¹)		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 Cd²⁺ and Pb²⁺ 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 Pb²⁺ and Cd²⁺ 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 Pb²⁺ or Cd²⁺ 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 Pb²⁺ and Cd²⁺ 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 Pb²⁺ and Cd²⁺ 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 Pb²⁺ and Cd²⁺ ions by zeolite N.P./PEG/GO composite, considerably. The adsorbent capacity of Pb²⁺ and Cd²⁺ 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.

REFERENCES

1. Ab Razak NH, Praveena SM, Aris AZ, Hashim Z. Drinking water studies: A review on heavy metal, application of biomarker and health risk assessment (a special focus in

- Malaysia). *Journal of Epidemiology and Global Health*. 2015;5(4):297-310.
2. Yousefi, T., H.R. Moazami, H.R. Mahmudian, M. Torab-Mostaedi and M.A. Moosavian, 2018. Modification of natural zeolite for effective removal of Cd(II) from wastewater. *Journal of Water and Environmental Nanotechnology*, 3(2): 150-156.
 3. Simeonidis K, Mourdikoudis S, Kaprara E, Mitrakas M, Polavarapu L. Inorganic engineered nanoparticles in drinking water treatment: a critical review. *Environmental Science: Water Research & Technology*. 2016;2(1):43-70.
 4. Lu F, Astruc D. Nanomaterials for removal of toxic elements from water. *Coordination Chemistry Reviews*. 2018;356:147-64.
 5. Yousefi, T., M.A. Mohsen, H.R. Mahmudian, M. Torab-Mostaedi, M.A. Moosavian and H. Aghayan, 2018. Removal of Pb(II) by Modified Natural Adsorbent; Thermodynamics and Kinetics Studies. *Journal of Water and Environmental Nanotechnology*, 3(3): 265-272.
 6. Tanzifi, M., M. Kolbadi Nezhad and K. Karimipour, 2017. Kinetic and Isotherm Studies of Cadmium Adsorption on Polypyrrole/Titanium dioxide Nanocomposite, *Journal of Water and Environmental Nanotechnology*, 2(4): 265-277.
 7. Shannon MA, Bohn PW, Elimelech M, Georgiadis JG, Mariñas BJ, Mayes AM. Science and technology for water purification in the coming decades. *Nature*. 2008;452(7185):301-10.
 8. Dubey S, Banerjee S, Upadhyay SN, Sharma YC. Application of common nano-materials for removal of selected metallic species from water and wastewaters: A critical review. *Journal of Molecular Liquids*. 2017;240:656-77.
 9. WHO, 2008. Guidelines for Drinking Water Quality: Recommendations. 3(1), World Health Organization, Geneva.
 10. USEPA Nutrient Criteria Technical Guidance Manual, Lakes and Reservoirs, United States Environmental Protection Agency (USEPA), Washington, DC, 1999 (April, Document EPA 822-D-99-001).
 11. Srivastava V, Weng CH, Singh VK, Sharma YC. Adsorption of Nickel Ions from Aqueous Solutions by Nano Alumina: Kinetic, Mass Transfer, and Equilibrium Studies. *Journal of Chemical & Engineering Data*. 2011;56(4):1414-22.
 12. Yousefi, T., M. Torab-Mostaedi, A. Charkhi and A. Aghaei, 2016. Cd(II) Sorption on Iranian Nano Zeolites: Kinetic and Thermodynamic Studies. *Journal of Water and Environmental Nanotechnology*, 1(2): 75-83.
 13. Wang LK, Vaccari DA, Li Y, Shammass NK. Chemical Precipitation. *Physicochemical Treatment Processes: Humana Press*; 2005. p. 141-97.
 14. Ostroski IC, Barros MASD, Silva EA, Dantas JH, Arroyo PA, Lima OCM. A comparative study for the ion exchange of Fe(III) and Zn(II) on zeolite NaY. *Journal of Hazardous Materials*. 2009;161(2-3):1404-12.
 15. Taffarel SR, Rubio J. On the removal of Mn²⁺ ions by adsorption onto natural and activated Chilean zeolites. *Minerals Engineering*. 2009;22(4):336-43.
 16. Xing Y, Chen X, Wang D. Electrically Regenerated Ion Exchange for Removal and Recovery of Cr(VI) from Wastewater. *Environmental Science & Technology*. 2007;41(4):1439-43.
 17. Gupta K, Khatri OP. Reduced graphene oxide as an effective adsorbent for removal of malachite green dye: Plausible adsorption pathways. *Journal of Colloid and Interface Science*. 2017;501:11-21.
 18. Bódalo-Santoyo A, Gómez-Carrasco JL, Gómez-Gómez E, Máximo-Martín F, Hidalgo-Montesinos AM. Application of reverse osmosis to reduce pollutants present in industrial wastewater. *Desalination*. 2003;155(2):101-8.
 19. Rykowska I, Wasiak W, Byra J. Extraction of copper ions using silica gel with chemically modified surface. *Chemical Papers*. 2008;62(3).
 20. Zanin E, Scapinello J, de Oliveira M, Rambo CL, Francescon F, Freitas L, et al. Adsorption of heavy metals from wastewater graphic industry using clinoptilolite zeolite as adsorbent. *Process Safety and Environmental Protection*. 2017;105:194-200.
 21. Guo X, Du B, Wei Q, Yang J, Hu L, Yan L, et al. Synthesis of amino functionalized magnetic graphenes composite material and its application to remove Cr(VI), Pb(II), Hg(II), Cd(II) and Ni(II) from contaminated water. *Journal of Hazardous Materials*. 2014;278:211-20.
 22. Huang Y, Zeng X, Guo L, Lan J, Zhang L, Cao D. Heavy metal ion removal of wastewater by zeolite-imidazolate frameworks. *Separation and Purification Technology*. 2018;194:462-9.
 23. Hamid SA, Shahadat M, Ismail S. Development of cost effective bentonite adsorbent coating for the removal of organic pollutant. *Applied Clay Science*. 2017;149:79-86.
 24. Ho S-H, Chen Y-d, Yang Z-k, Nagarajan D, Chang J-S, Ren N-q. High-efficiency removal of lead from wastewater by biochar derived from anaerobic digestion sludge. *Bioresource Technology*. 2017;246:142-9.
 25. Sun S, Wang L, Wang A. Adsorption properties of crosslinked carboxymethyl-chitosan resin with Pb(II) as template ions. *Journal of Hazardous Materials*. 2006;136(3):930-7.
 26. Meng Q, Chen H, Lin J, Lin Z, Sun J. Zeolite A synthesized from alkaline assisted pre-activated halloysite for efficient heavy metal removal in polluted river water and industrial wastewater. *Journal of Environmental Sciences*. 2017;56:254-62.
 27. Choi H-J, Yu S-W, Kim KH. Efficient use of Mg-modified zeolite in the treatment of aqueous solution contaminated with heavy metal toxic ions. *Journal of the Taiwan Institute of Chemical Engineers*. 2016;63:482-9.
 28. Chowdhury S, Balasubramanian R. Recent advances in the use of graphene-family nanoadsorbents for removal of toxic pollutants from wastewater. *Advances in Colloid and Interface Science*. 2014;204:35-56.
 29. Yusuf M, Elfgi FM, Zaidi SA, Abdullah EC, Khan MA. Applications of graphene and its derivatives as an adsorbent for heavy metal and dye removal: a systematic and comprehensive overview. *RSC Advances*. 2015;5(62):50392-420.
 30. Samadi S, Mirseyfard SMH, Assari M, Hassannejad M. Effect of hydroxypropyl cellulose (HPC), polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) on Nd-TiO₂ / graphene oxide nanocomposite for removal of lead(II) and copper(II) from aquatic media. *Water Science and Technology*. 2017;76(1):15-27.
 31. Serag, E., A. El-Nemr and A. El-Maghraby, 2017. Synthesis of Highly Effective Novel Graphene Oxide-Polyethylene Glycol-Polyvinyl Alcohol Nanocomposite Hydrogel for Copper Removal. *Journal of Water and Environmental Nanotechnology*, 2(4): 223-234.
 32. Wawrzekiewicz M, Wiśniewska M, Wołowicz A, Gun'ko VM, Zarko VI. Mixed silica-alumina oxide as sorbent for dyes and metal ions removal from aqueous solutions and

- wastewaters. Microporous and Mesoporous Materials. 2017;250:128-47.
33. Sheshmani, S. and M. Arab Fashapoyeh, 2013. Suitable Chemical Methods for Preparation of Graphene Oxide, Graphene and Surface Functionalized Graphene Nanosheets. *Acta Chimica Slovenica*, 60: 813–825.
 34. Samarghandi MR, Al-Musawi TJ, Mohseni-Bandpi A, Zarrabi M. Adsorption of cephalexin from aqueous solution using natural zeolite and zeolite coated with manganese oxide nanoparticles. *Journal of Molecular Liquids*. 2015;211:431-41.
 35. Yurekli Y. Removal of heavy metals in wastewater by using zeolite nano-particles impregnated polysulfone membranes. *Journal of Hazardous Materials*. 2016;309:53-64.
 36. Mirfendereski M, Mohammadi T. Effects of Synthesis Parameters on the Characteristics of NaA Type Zeolite Nanoparticles. *Proceedings of the World Congress on Recent Advances in Nanotechnology*; 2016/04: Avestia Publishing; 2016.
 37. Mobasherpour I, Salahi E, Pazouki M. Removal of divalent cadmium cations by means of synthetic nano crystallite hydroxyapatite. *Desalination*. 2011;266(1-3):142-8.
 38. Srivastava VC, Mall ID, Mishra IM. Equilibrium modelling of single and binary adsorption of cadmium and nickel onto bagasse fly ash. *Chemical Engineering Journal*. 2006;117(1):79-91.
 39. Roh H, Yu M-R, Yakkala K, Koduru JR, Yang J-K, Chang Y-Y. Removal studies of Cd(II) and explosive compounds using buffalo weed biochar-alginate beads. *Journal of Industrial and Engineering Chemistry*. 2015;26:226-33.
 40. Lingamdinne LP, Koduru JR, Chang Y-Y, Karri RR. Process optimization and adsorption modeling of Pb(II) on nickel ferrite-reduced graphene oxide nano-composite. *Journal of Molecular Liquids*. 2018;250:202-11.
 41. Moradi O, Aghaie M, Zare K, Monajjemi M, Aghaie H. The study of adsorption characteristics Cu²⁺ and Pb²⁺ ions onto PHEMA and P(MMA-HEMA) surfaces from aqueous single solution. *Journal of Hazardous Materials*. 2009;170(2-3):673-9.
 42. Ding Y, Liu Y, Liu S, Li Z, Tan X, Huang X, et al. Competitive removal of Cd(II) and Pb(II) by biochars produced from water hyacinths: performance and mechanism. *RSC Advances*. 2016;6(7):5223-32.
 43. Drweesh SA, Fathy NA, Wahba MA, Hanna AA, Akarish AIM, Elzahany EAM, et al. Equilibrium, kinetic and thermodynamic studies of Pb(II) adsorption from aqueous solutions on HCl-treated Egyptian kaolin. *Journal of Environmental Chemical Engineering*. 2016;4(2):1674-84.