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Synthesized chitosan/ iron oxide nanocomposite and shrimp shell in removal of nickel, cadmium and lead from aqueous solution

M. Keshvardoostchokami^{1,2}, L. Babaei¹, A.A. Zamani^{1,*}, A.H. Parizanganeh¹, F. Piri²

¹Environmental Science Research Laboratory, Department of Environmental Science, Faculty of Science, University of Zanjan, Zanjan, Iran

²Organic Chemistry Research Laboratory, Department of Chemistry, Faculty of Science, University of Zanjan, Zanjan, Iran

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ABSTRACT: In this study, an easy synthesized method for preparation of chitosan/iron oxide nanocomposite as a bio-sorbent has been applied. Analytical techniques such as Fourier transform infrared spectroscopy, X-ray diffraction, Field emission scanning electron microscopy and transmission electron microscopy were utilized to survey of morphological structure and the functional groups characterization. The histogram of frequency of particle size confirmed that medium size of the synthesized nanoparticles was 50 nm. Beside the obtained nanocomposite, application of chitosan as the precursor and shrimp shell as natural chitin and a natural polymer were assessed as adsorbents for decontamination of Ni²⁺, Cd²⁺ and Pb²⁺ as examples of heavy metals from drinking water. Batch studies were done for adsorption experiments by changing variables such as pH, contact time and adsorbent dose. Based on the experimental sorption capacities, 58, 202 and 12 mg of Ni, Cd and Pb per g of Chitosan-FeO nanocomposite as adsorbent respectively, confirm that combination of Fe₂O₃ nanoparticles with chitosan makes a more efficient adsorbent than chitosan and chitin. Adsorbents in uptake of the mentioned heavy metals are in the order of Chitosan-FeO nanocomposite > chitosan > chitin. In addition, the kinetics and isotherm investigations were surveyed. Moreover, it has been shown that the synthesized nanocomposite significantly reduces the amount of the mentioned ions from the real wastewater sample.

KEYWORDS: *Adsorbent; Chitosan iron oxide; Heavy metals; Nanocomposite; Water treatment.*

INTRODUCTION

Development of modern life and industries have been caused production huge amount of different type effluents that pollutes the environment. Discharging of effluents containing toxic compounds in soil and water sources, even in low concentrations, has created serious diseases and this story continues. Wastewaters from industries mainly contain highly toxic heavy metals like chromium, cobalt, nickel, copper, zinc, cadmium, mercury, and lead. Among

the heavy metals, nickel, cadmium and lead specially, affect the human health (Bernard *et al.*, 2013). Human cell culture studies have confirmed nickel as a possible carcinogen. Different metal crafts such as electroplating, extraction of non-ferrous metal such as zinc production and other mineral processing and battery manufacturing specially Ni-Cd batteries are the main anthropogenic sources for Ni pollution (Pandey *et al.*, 2007). Cadmium as metal is named in the red list of department of environment in the United Kingdom (UK) and black list of Environment European Commission (EEC) and group carcinogen of US Environment Protection Agency (USEP) (Jain

*Corresponding Author Email: zamani@znu.ac.ir

Tel.: +98 24 3305 4046 Fax: +98 24 3305 4046

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et al., 2015). Metal plating, smelting, alloy industries, pigments, phosphate fertilizers, stabilizers are the main and famous sources for cadmium (Gupta and Nayak, 2012). Moreover, such as nickel, it penetrates to environment compartments from various origins specially Ni-Cd batteries (Jain et al., 2015; Zamani et al., 2013). Even very low amount of lead metal can be dangerous for children from the point of view of mental and physical growth. Therefore, Anaemia, hypertension, stomach and kidney diseases, muscle debility, brain damage and eventually death are some consequences of high level of lead in children bodies (Gupta et al., 2011). The age of an exposed person and amount of lead can change lead poisoning effects (Zamani et al., 2013). Due to increasing the heavy metal concentration in water, soils, crops, food and subsequently in human body, these pollutions must be removed from industrial wastewater before discharge or intake to environment. Thus, an access to economic method for removing even low levels of heavy metals from waste stream is important and mandatory (Sunil and Jayant, 2013; Sonali et al., 2013).

Adsorption procedure has been shown to be a feasible treatment process with advantages such as economical price and favourable efficiency to remove heavy metals from water and wastewater (Bailey et al., 1999; Jain et al., 2016; Park et al., 2016; Gupta et al., 1998; Gupta et al., 2012; Gupta and Saleh, 2013). For this reason, different natural materials combine for achieving impressive adsorbents which their capacity and applicability are dependent on ingredients (Wang et al., 2016a; Nodeh et al., 2016; Ali et al., 2016). Adaptation to the environment is another important characteristic of the synthesized adsorbents that should be considered. Chitosan as a natural biopolymer captures from chitin. After cellulose, chitin is the most plentiful and natural polymer in environment. Due to environmental considerations and having different functional groups, it is highly regarded (Ariff et al., 2016; Yamani et al., 2016; Dehghani et al., 2016). The presence of various oxygen and nitrogen in structure of functional groups on chitosan surface causes forming negative charges. For this reason, the chitosan adsorbent frequently used in decontamination of heavy metals and other pollutants with positive charge (Ali et al., 2016; Ariff et al., 2016; Dehghani et al., 2016; Ren et al., 2008; Saber-Samandari et al., 2014; Cho et al., 2016; Wang et al., 2016b; Mallakpour and Madani, 2016; Hossein Beyki et al., 2016).

In the current study after fabrication and characterization of inexpensive and environmentally friendly chitosan/iron oxide nanocomposite (CH-FeO nanocomposite), abilities and properties of the adsorbent were evaluated for uptake of Ni^{2+} , Cd^{2+} and Pb^{2+} ions from water solutions, which their importance in removal from drinking water can be proved by maximum concentration limit (MCL). World health organization (WHO) and Institute of standards and industrial research of Iran (ISIRI) announced the MCL values for studied heavy metals (Ni: 0.070, Cd: 0.003, Pb: 0.010 mg/dm^3) (Zamani et al., 2012). This article compares adsorption characteristics of CH-FeO nanocomposite, chitosan and chitin in uptake Ni^{2+} , Cd^{2+} and Pb^{2+} ions from polluted water. Fabrication method of CH-FeO nanocomposite have low price and is an easy method. The synthesized CH-FeO nanocomposite, chitosan, and chitin used for removal important heavy metal ions that entrance in water sources and create a serious menace for health. Also in given data a selective separation method can be seen for separation of Ni from Cd and lead ions. Besides study of variables effect on removal procedure, kinetics and isotherm parameters were evaluated. Finally, applicability of the synthesised adsorbent was assessed in a real wastewater sample. This study was carried out in environmental science research laboratory of University of Zanjan in Iran in 2015.

MATERIALS AND METHODS

Chitin

In this Research, in the first step shrimp shell was used as a natural adsorbent in order to remove of nickel, cadmium and lead ions from polluted waters. Shrimp shell was collected from Zanjan fishing shopping. Achieved shrimp shell was washed, air-dried, and applied as a natural bio-adsorbent for heavy metal uptake from water solutions. Nickel (1122770250, Merck), Cadmium (1020010250, Merck) and lead (1120671000, Merck) powders were used in order to make solutions with 1000 mg/dm^3 concentration as stock solutions. After weighting (by Electronic Balance FX 400) enough amounts of the powder metals, a little volume of concentrated nitric acid (1004411000, Merck) with analytical grade was used to dissolve nickel, cadmium and lead powder. Then extra amount of nitric acid was removed by heating after dissolution and volume set was done with using deionized water. The pH of the made solution controlled by adding diluted solutions of HCl (100317, Merck) and NaOH (106498, Merck) by

pH meter instrument model 827 Metrohm. For removal experiments, 0.15 g of chitin was weighted and added to 20 dm³ of aqueous solution content of Ni, Cd and Pb ions with concentration of 20 mg/dm³. The prepared mixture stirred with IKA KS 260 BASIC stirrer and in the final step of adsorption experiment, the adsorbent was collected by centrifuge model universal 320.

Chitosan

Medium molecular weight chitosan with a de-acetylated degree 75-85% was obtained from Sigma–Aldrich Chemical and was used in synthesise of chitosan-iron oxide nanocomposite (CH-FeO) as adsorbent.

Chitosan-iron oxide nanocomposite

Chitosan-iron oxide nanocomposite as adsorbent synthesized through our previous reported method (Keshvardoostchokami *et al.*, 2017). In step one, 50 dm³ of acidic solution (acetic acid with concentration 1% v/v) was prepared, and then 0.4 g of chitosan compound was dissolved in this solution, in continuous 0.1g of FeCl₃ salt (Merck) was added in ultrasonic bath (Bandelin DT102H). In step two 20 dm³ NaOH solution (8 M) was added and sonication continued for 600 seconds. The precipitants as product were washed repeatedly with deionized and distilled water and then the slurry mixture was centrifuged (Universal 320 bench-top centrifuge) at speed of 33 revolutions per second (rps) and then air-dried. With the aim of applicability of CH-FeO nanocomposite as adsorbent, 0.05 g of CH-FeO was added to 20 dm³ solution content nickel, cadmium and lead ions with initial concentration 10 mg/dm³ in an Erlenmeyer flask. The mixture was stirred (on a shaker IKA KS 260) at 300 rpm speed for 1800 seconds at room temperature (298 ± 2 K). Before of beginning the test, the pH of aqueous studied solutions was controlled in desired value by the addition of diluted solution of HCl or NaOH. Phase separation was performed by centrifuge at 33 rps. Determination of the studied ion concentration was carried out by using Flame atomic absorption spectrophotometer (FAAS).

Point of Zero Charge (pH_{pzc}) of CH-FeO nanocomposite

The pH_{pzc} define as the pH that the whole number of positive and negative charges on the surface of used adsorbent becomes equal. To gain pH_{pzc} for CH-FeO nanocomposite, pH of experimental NaCl solutions (NaCl as electrolyte with concentration 0.005 mol/dm³) was fixed between 2-12. 0.05 g of the adsorbent was added to 50 dm³ of any prepared solutions and they shaken at 298±5 K for two day. After the pH stabilization, the final pH was registered. The diagram of final pH of solution against initial pH was drawn. Drawn figure was applied in determination of points at which the initial and final pH amount were identical (Vijayakumar *et al.*, 2012).

Determination of heavy metal concentration in solution

Flame atomic absorption spectrophotometer Varian 220 was used to determine the remaining of heavy metal concentration in solution. The residue of studied heavy metals was calculated using Eq. 1.

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

Where, q_e shows the amount of adsorbed heavy metal in mg on the surface of adsorbent in g in equilibrium time; C₀ and C_e in mg/ dm³ are the initial and equilibrium concentrations of the heavy metals in solution, respectively; V means the volume of the used solution in dm³ and M_s in gram is the mass of the adsorbent. All results are the means of triplicate experiments that were performed.

Several different sets of Ni, Cd and Pb standard ion solutions in creating the calibration curve were used prior to employing AAS instrument to assessment of the heavy metal ions amount. Standard solutions were made by diluting the stock solutions that these prepared by dissolve 1.000 g of nickel, cadmium and lead nitrate in a minimum volume of (1+1) HNO₃, then diluted to 1 dm³ with 1% (v/v) HNO₃. Atomic absorption conditions in determination and calibration curves in determination of studied ions are given in Table 1.

Table 1: Atomic absorption conditions in determination of heavy metal ions

Element	Wavelength (nm)	Linear range in mg/dm ³	Flame (oxidant-fuel)	Calibration curve equation
Ni	232.0	0.1-20	Air-acetylene	A = -0.0014C ² + 0.0753C + 0.0113 R ² = 0.998
Cd	228.8	0.02-3	Air-acetylene	A=0.3263C+0.0001 R ² =0.999
Pb	217.0	0.1- 30	Air-acetylene	A = -0.0014C ² + 0.0753C + 0.0113 R ² = 0.9983

A: Absorbance; C: Concentration

RESULTS AND DISCUSSION

Characterization of synthesized CH-FeO

One of the methods for characterization and functional groups detection of nanocomposites surface is Fourier transform infrared spectroscopy (FT-IR) spectra. Following peaks reported in FTIR spectra for chitosan: 3456 1/cm for bond stretching O-H and N-H, 1423 1/cm ascribes to -C-O stretching of primary alcoholic group, 1077 1/cm and 1030 1/cm for C-OH stretching bond (Huang *et al.*, 2009). Most studies have reported that magnetic chitosan show a peak in ~580 1/cm (Fig. 1) for the Fe-O group due to pure Fe₂O₃ (Yuwei and Jianlong, 2011). As shown in Fig.1 Shifting of O-H and N-H bonds from 3456 1/cm to 3445 1/cm, C=O of -NH=C=O stretching bond (amide I) from 1657 1/cm to 1606 1/cm and N-H bending modes (amide II) from 1600 1/cm to 1592 1/cm indicates that Fe and chitosan were combined successfully. X-ray powder diffraction (XRD) pattern of Chitosan-Fe₂O₃ nanocomposite is illustrated in Fig. 2. Obvious diffraction peaks at $2\theta = 30.26$, 35.64, 43.34, 53.84, 57.36 and 62.96, are assigned to (2 2 0),

(3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) lattice planes of Fe₂O₃ (Huang *et al.*, 2009) (based on card numbers (00-039-0238 and 00-019-0615 for Fe₂O₃). The amorphous peak at $2\theta = 20^\circ$ reveals chitosan structure in the synthesized composite (Huang *et al.*, 2009). So based on the XRD pattern, Fe₂O₃ nanoparticles have been introduced into chitosan films.

Field emission scanning electron microscopy (FE-SEM) image of CH-FeO nanocomposite is given in Fig. 3a. The average particle size of Fe₂O₃ on adsorbent surface is measured by using Scherer evaluation (Tran *et al.*, 2010) and Transmission electron microscopy (TEM) image at 22 nm and 50 nm (Fig. 3b.), respectively.

Study adsorption behavior versus pH change

The change of aqueous pH value at adsorption of heavy metals was examined by adding 0.15 g Chitin, 0.2 chitosan and 0.05 g CH-FeO nanocomposites to 20 dm³ polluted solution (10 mg/dm³) which shaken for 1800 s at room temperature. The results are given in Fig. 4. This study shows that increasing in

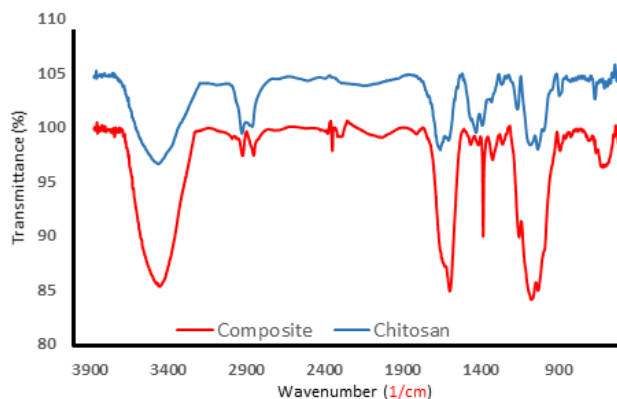


Fig. 1. FT-IR-spectra of CH and CH-FeO

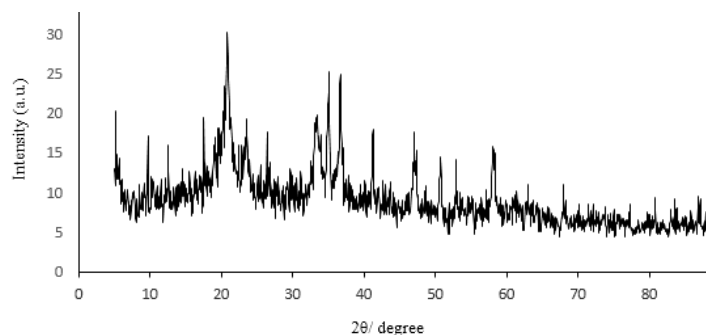


Fig. 2. XRD analysis of CH-FeO nanocomposite

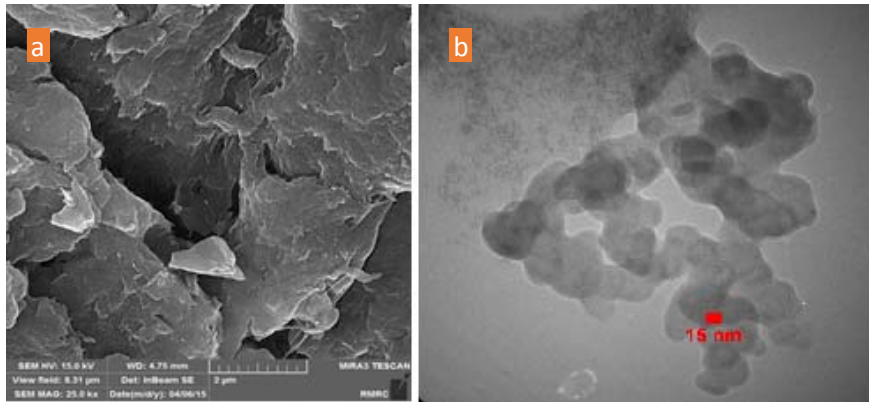


Fig. 3. a) FE-SEM and b) TEM images of CH-FeO nanocomposite

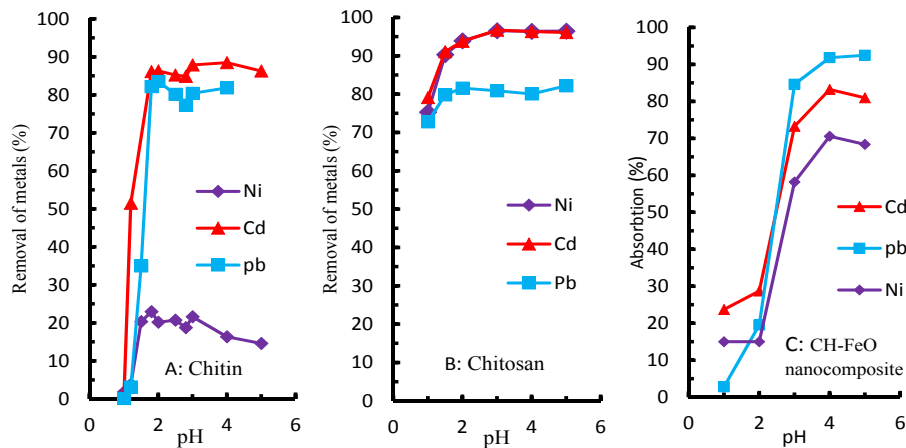


Fig. 4. Heavy metal adsorption versus changing pH with A) Chitin 0.15 g, B) Chitosan 0.2 g and C) CH-FeO nanocomposite 0.05 g. The experiment conditions: 20 dm³ solution, initial ion concentrations 10 mg/dm³, the mixing speed 5 rps, mixing time 1800 s, room temperature.

pH, increases removal of the studied heavy metals by CH-FeO nanocomposites. The uptake of heavy metal enhances with pH values which reveals a cation exchange mechanism exists for the adsorption process. As shown in Fig. 5, charge of surface is being negative via enhancing pH values therefore; sorption of studied cation ions was increased. For all used adsorbents, surface charge is positive in pH lower 2 so the uptake of positive heavy metals is low on the positive surface. With alkaline pH in aqueous solution surface charge on adsorbent is neutral until pH 5 and then becomes negative. Because of these changes, uptake of positive ions on the neutral surface increased until pH 5 then decreased. From data in Fig. 5, it seems that surface charge on chitin and CH-FeO nanocomposites are the same but different with chitosan.

It can be confirmed that the order of removal efficiency by chitin and CH-FeO nanocomposites as

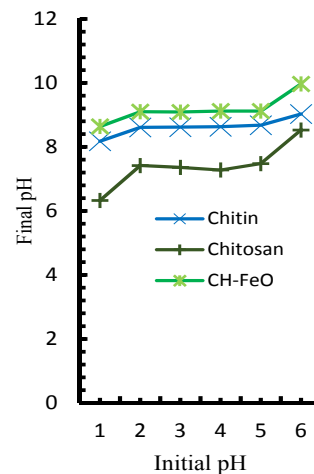


Fig. 5. Determination of charge zero pH of Chitin, Chitosan and CH-FeO nanocomposite. The experiment conditions: 20 dm³ solution, initial ion concentrations 10 mg/dm³, the mixing speed 5 rps, mixing time 1800 s, room temperature

adsorbent from multi heavy-metal solutions at the given experimental conditions is as follows: Pb (II) \approx Cd (II) > Ni (II). Comparison between crystal ionic radius for studied heavy metal ions of Pb (0.119 nm) > Cd (0.095 nm) > Ni (0.069 nm) and hydrated ionic radius of Pb (0.45 nm) < Cd (0.5 nm) < Ni (0.6 nm) concluded that the experimentally obtained order is highly dependent to hydrated ionic radii. In aqueous solutions, ions normally form hydrates complexes with water thus enlarging the ionic size. Therefore, the smaller hydrated radius ions transport to the particle surface and diffuse inside the particle through the porous channels. The same result was reported in using natural Zeolite for uptake lead, cadmium and nickel from aqueous solutions (Al-Haj-Ali and Al-Hunaidi, 2007). Therefore, chitosan show a different behavior against studied heavy metal ions. Amine functional groups on the surface of chitosan are further than chitin and CH-FeO nanocomposites that it makes further interaction between heavy metal ions and adsorbent. Perhaps due to more interaction, adsorption selectivity is reduced when chitosan was used. The comparison between electronegativity of used ions show the nickel (1.91) has high electronegativity than lead (1.87) and cadmium (1.69) ions (Cai et al., 2014). It can be concluded that for adsorption on chitosan electronegativity is more effective between lead and nickel than hydrated ionic radii.

These experiments help us in treatment polluted water to lead, cadmium and nickel. On one hand we can use chitin or CH-FeO nanocomposites in selective separation Cd and Pb ions from Ni with controlling

pH of solution. On the other hand, complete removal of studied ions is possible by using alone chitosan in one time or using several times of chitin or CH-FeO nanocomposites in $\text{pH} > 3$.

Changing the adsorbent dose

Fig. 6 shows achieved result in changing studied adsorbent dose in the uptake of nickel, cadmium and lead ions from simulated polluted water media. Different amount of the adsorbents were added separately to 20 dm³ solution with initial ion concentrations 10 mg/dm³, pH=3 at 298 K. The given results show that with application of low amount of CH-FeO nanocomposite, heavy metals can be removed from waters quantitatively. In addition, Chitin has selective behaviour versus the Ni²⁺, Cd²⁺ and Pb²⁺ ions. It can't uptake Ni²⁺ ions from polluted waters. This adsorption behaviour is good for selective separation of these ions. The separation of Ni from Cd from the spent of nickel-cadmium battery is important. The Ni-Cd battery is a type of rechargeable batteries using nickel oxide hydroxide and metallic cadmium as electrodes. This novel procedure is an efficient methodology to separate the nickel and cadmium from Ni-Cd batteries with studied adsorbent that is prepared with recyclable and biodegradable compounds.

Time dependency

In order to investigate the contact time among the adsorbent and adsorbate in adsorption value, 0.15, 0.15 and 0.05 g of chitin, chitosan and CH-

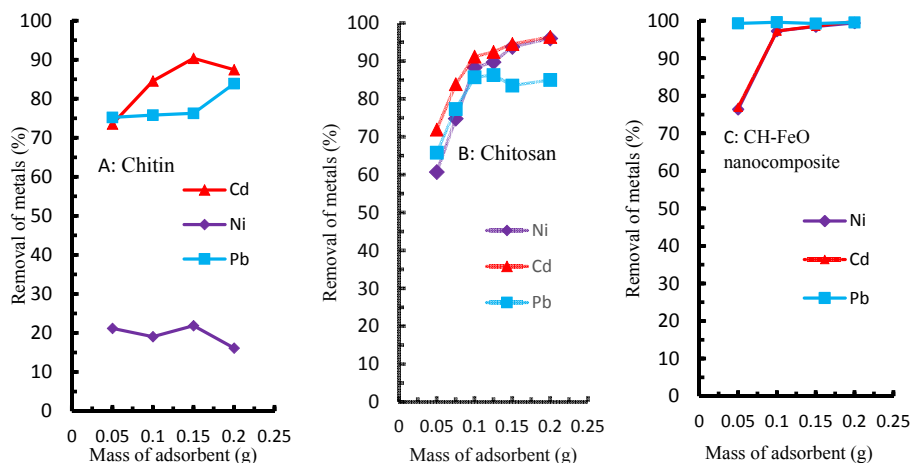


Fig. 6: Heavy metal adsorption versus changing dose of A) Chitin, B) Chitosan and C) CH-FeO nanocomposite. The experiment conditions: 20 dm³ solution, initial ion concentrations 10 mg/dm³, The mixing speed 5 rps, mixing time 1800 s, pH=3, room temperature

FeO nanocomposite added to 20 dm³ (initial ion concentrations 10 mg/dm³) pH=3 at room temperature and shaken at various time. The result reveals with increasing the time of contact the effectiveness surface of interactions was increased. This phenomena is more evident in the case that Chitin and CH-FeO nanocomposite were used. In addition, the selective adsorption Cd and Pb versus Ni ions is seen for Chitin. Besides, the data displayed that the uptake of lead ions on CH-FeO nanocomposite was relatively faster than Ni and Cd ions. In using CH-FeO nanocomposite for removal of Ni and Cd ions, the equilibrium was reached after 30 min. While for chitin, removal of Cd and Pb ions are faster than Ni. The results show that Ni removal isn't dependent on time for this adsorbent. It should be mentioned that amount of CH-FeO nanocomposite is lower than other used adsorbents. Therefore, the rates of studied adsorbents in Fig. 7 cannot be compared with. However, it may be estimated that adsorption rate with CH-FeO nanocomposite is faster than two other adsorbents for uptake of Pb ions.

Adsorption isotherms

Between the different models to explain adsorption isotherms, Langmuir, Freundlich and Temkin models are famous. The Eqs. 2, 3 and 4 were applied to the studied adsorption equilibrium at different adsorbent, respectively.

$$\frac{C_e}{q_e} = \frac{1}{Q_{max}b} + \frac{C_e}{Q_{max}} \tag{2}$$

$$\log q_e = \frac{1}{n} \log C_e + \log F \tag{3}$$

$$q_e = \frac{RT}{d} \ln(a' C_e) \tag{4}$$

Where, "C" shows the concentration of studied ions (mg/ dm³); "q" is the amount of used heavy metal ions that adsorbed by 1 g of adsorbent at equilibrium (mg/g); subscripts "e" and "max" represent time of equilibrium and the maximum capacity of the adsorbent; "b" is the constant for showing the energy amount of formed bond between the adsorbent and adsorbate. "F" and "n" are two constants in Freundlich model and are dependent indexes for noted to adsorption capacity and adsorption intensity, respectively. A favourable adsorption condition is gained when n > 1. In Temkin model, "d" is the Temkin constant for adsorption temperature (kN.m/ mol); "R" defines the gas constant (0.0083 kN.m /K. mol); "a' " is the isotherm constant for Temkin model (dm³/g); and "T" is the temperature in Kelvin (K). Correlation coefficients (R²) as are shown in Table 2, for Ni²⁺ removal by all three adsorbents and Cd²⁺ removal by chitosan and CH-FeO nanocomposite are well fitted to Langmuir model whereas for Cd²⁺ by chitin obeys Temkin model. Removal of Pb²⁺ by chitin and chitosan is fitted to Freundlich and Temkin respectively.

Adsorption Kinetics

Power function, simple Elovich, pseudo-first order and pseudo-second-order kinetics are usually applied to investigate controlling mechanism of the adsorption processes. These kinetic models equations are given in Eqs. 5, 6, 7 and 8.

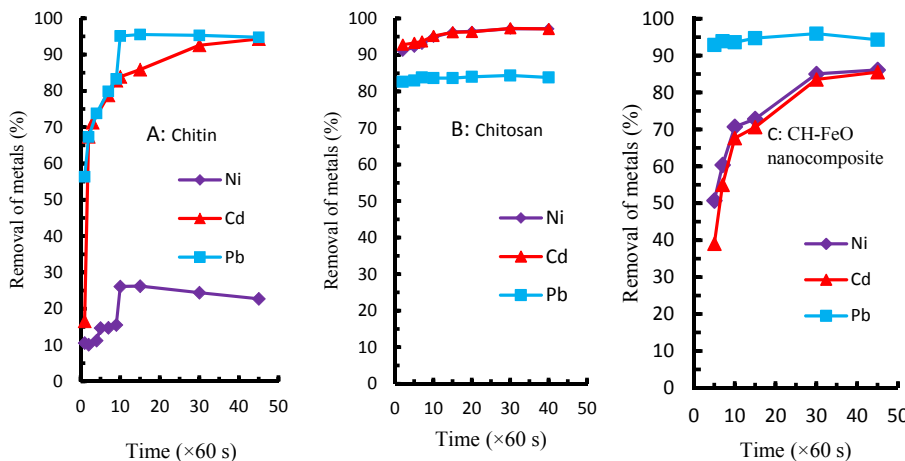


Fig. 7: Heavy metal adsorption versus changing contact time of A) Chitin 0.15 g, B) Chitosan 0.15 g and C) CH-FeO nanocomposite 0.05. The experiment conditions: 20 dm³ solution, initial ion concentrations 10 mg/dm³, the mixing speed 5 rps, pH=3, room temperature.

$$\log q_t = \log k_p + v \log t \tag{5}$$

$$q_t = a + 2.303b' \log t \tag{6}$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{7}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

where “t” noted to the contact time (s) and “ k_p ” (mg/g.s) and “v” are adjustment parameters for power function kinetic model. The parameter “a” (mg /g. s) indicates the speed of chemisorption at zero coverage. “b” (g/mg) in simple Elovich model is the desorption constant that is affiliated to the value of surface coverage and the activation energy for the adsorption. The parameters “a” and “b” are both constant. In the pseudo-first-order model “ k_1 ” denotes rate constant (1/s) also “ k_2 ” in the pseudo-second-order is rate constant (in g/mg.s).

The introduced parameters were assessed based on the used kinetics models for the uptake of Ni, Cd and Pb on chitin, chitosan and CH-FeO nanocomposite (Table 3). The given constants and regression coefficients (R^2) of the studied models show that

three models power function, pseudo-first-order and Simple Elovich kinetic do not appropriately exhibit the experimental adsorption results. Although, the Pseudo-second order kinetic model has high agreement and the significant correlation for the description of the mentioned heavy metals adsorption on the surface of the used adsorbents as Eq. 9.

$$h_0 = k_2 q_e^2 \tag{9}$$

Where, “ h_0 ” denotes the initial rate of sorption (mg/g.s). The results of Table 3 show that CH-FeO nanocomposite has initial quickly rate in removal of lead ions than the raw materials.

Comparison of different adsorbents in removal of studied heavy metal ions

The maximum capacities of adsorption (q_{max}) for our applied adsorbents and some other recently used adsorbents with chitosan framework listed in Table 4. Langmuir isotherm model is applied to assess the maximum adsorption capacity of any adsorbents that it is the appropriate parameter to be considered. Therefore, in other methods the adsorption capacity for used adsorbents in experimental method was determined by

Table 2: The R^2 values in study adsorption isotherms

Studied ions	Adsorbent	Temkin	Freundlich	Langmuir
Ni ²⁺	Chitin	0.41	0.65	0.79
	Chitosan	0.97	0.95	0.98
	CH-FeO nanobiocomposite	0.97	0.95	0.99
Cd ²⁺	Chitin	0.87	0.77	0.36
	Chitosan	0.98	0.97	0.98
	CH-FeO nanobiocomposite	0.91	0.94	0.99
Pb ²⁺	Chitin	0.33	0.43	0.34
	Chitosan	0.71	0.57	0.01
	CH-FeO nanobiocomposite	0.13	0.10	0.09

The experiment conditions: 20 dm³ solution, initial ion concentrations 10 mg/dm³, the mixing speed 5 rps, mixing time 1800 s, pH=3, room temperature

Table 3: The R^2 values in study adsorption kinetic

Ions	Adsorbent	Power function	Simple Elovich	Pseudo-first order	Pseudo-second order			
		R^2	R^2	R^2	$k_2 \times 60$ g/mg.s	q_e mg/g	$h_0 \times 60$ mg /g.s	
Ni ²⁺	Chitin	0.86	0.85	0.81	0.96	1.970	0.254	0.127
	Chitosan	0.93	0.94	0.00	0.99	3.713	0.978	3.557
	CH-FeO nanocomposite	0.90	0.94	0.00	0.99	0.067	3.772	0.963
Cd ²⁺	Chitin	0.59	0.75	0.02	0.98	0.332	1.337	0.593
	Chitosan	0.92	0.91	0.00	0.99	4.354	0.978	4.165
	CH-FeO nanocomposite	0.85	0.92	0.18	0.99	0.037	4.106	0.621
Pb ²⁺	Chitin	0.94	0.92	0.01	0.98	0.078	1.292	1.295
	Chitosan	0.75	0.74	0.00	0.99	29.946	0.841	21.186
	CH-FeO nanocomposite	0.53	0.52	0.00	0.99	5.555	3.795	80.000

The experiment conditions: 20 dm³ solution, initial ion concentrations 10 mg/dm³, the mixing speed 5 rps, pH=3, room temperature

adding 0.05g of adsorbent to 50 dm³ of polluted solution content of studied heavy metals. The concentration range for Ni²⁺, Cd²⁺ and Pb²⁺ ions was 0-500 mg/dm³ and contact time was 7200s. With drawing adsorption capacity versus adsorbed ions in equilibrium, q_{max} of adsorbent was computed. Based on the results obtained from experimental tests, the synthesised CH-FeO nanocomposite efficiently removed Cd²⁺ in comparison of Chitosan/ Sulfhydrylfunctionalized graphene oxide composites (CS/GO-SH) polyaniline grafted chitosan (PGC), chitosan/poly (ethylene oxide) nanofibrous (Chitosan/PEO) and chitosan-xylan-TiO₂ hybrid (CXTH), while raw chitosan and chitin are not such successful as natural adsorbents. Therefore, we can conclude that inserting of Fe₂O₃ nanoparticles to chitosan and fabricating chitosan-Fe₂O₃ nanocomposite, is an effective strategy for constructing high proficiency metal sorbents. More significantly we should consider that, the uptake occur in multi-metal systems. It means Cd²⁺ can be detached from Ni²⁺ and Pb²⁺ selectively. Nevertheless, based on the results calculated from Langmuir model, the synthesised CH-FeO nanocomposite efficiently removed studied ions in comparison of raw chitosan and chitin. In addition, the results confirm improvement of surface CH-FeO nanocomposite and its adsorption behaviour. A low amount of q_{max} calculated from the Langmuir equation of used adsorbents is the main disadvantage of this adsorption procedure in comparison with values

from experiment and reported adsorbents. It should be noted that when isotherms do not have the right shape and only low concentration data is used, calculated adsorption maxima from the Langmuir equation are in error by 50% or more (Athappan and Sattler 2013; Karbassi and Heidari, 2015; Abdel-Ghani *et al.*, 2016).

Applicability of the proposed method in treatment real samples

To investigate the efficiency of the synthesized nanocomposite, it was used for the uptake of lead, cadmium and nickel from spent batteries (Panasonic, Sony, Philips). Leaching experiments of metals from solid materials of spent batteries were carried out under reported methods (Huang *et al.*, 2009). Subsequently 2 g of solid materials dissolved in 20 dm³ of mixture HNO₃/HCl solution (1:1) for two day. Then, it agitated for 3 hours under 323 K. The resulted solution filtered and 20 dm³ of it used for investigation of 0.05 g of the nanocomposite, 0.15 g of chitin and 0.2 g of chitosan under pH=3, room temperature and mixing speed 300 rpm. The results exhibited in Table 5. As indicated from the Table 5, the synthesized composite significantly reduces the amount of the heavy metal ions in the sample. Utilization of chitin and CH-FeO nanocomposite is successful in separation of nickel from cadmium and lead ions same as prepared experimental solution. Nevertheless, ability of chitosan in real sample was changed. It can be

Table 4: Comparison of the studied adsorbents and other different adsorbents for removal of Ni²⁺, Cd²⁺ and Pb²⁺ ions

Ions	Adsorbent	q _{max} (mg/g)		Isotherm model	Kinetic model	Reference
		exp.	theo.			
Ni ²⁺	Chitin	0.01	0.01	Langmuir		The current study
	Chitosan	8.97	1.27	Langmuir		The current study
	CH-FeO nanocomposite	57.86	3.29	Langmuir	Pseudo-second order	The current study
	EDTA-Chitosan	-	71.00	Intraparticle diffusion		(Repoet <i>et al.</i> , 2010)
	DTPA-Chitosan	-	53.1	Intraparticle diffusion		(Repo <i>et al.</i> , 2010)
	CXTH	52.1	113	Langmuir		(Wu <i>et al.</i> , 2014)
Cd ²⁺	Chitin	0.79	1.39	Temkin		The current study
	Chitosan	8.62	1.29	Langmuir		The current study
	CH-FeO nanocomposite	201.84	3.26	Langmuir	Pseudo-second order	The current study
	CS/GO-SH	177.00	-	Freundlich		(Li <i>et al.</i> , 2015)
	PGC	12.87	-	Freundlich		(Karthik and Meenakshi, 2015)
	CXTH	40.7	122.8	Langmuir		(Wu <i>et al.</i> , 2014)
Pb ²⁺	Chitin	0.07	0.32	Freundlich		The current study
	Chitosan	0.92	1.13	Temkin		The current study
	CH-FeO nanocomposite	11.69	3.13	-	Pseudo-second order	The current study
	CS/GO-SH	447.00	-	Freundlich		(Li <i>et al.</i> , 2015)
	PGC	13.23	-	Freundlich		(Karthik and Meenakshi, 2015)
	Chitosan/PEO	16.03	89.54	Freundlich		(Islam <i>et al.</i> , 2017)

q_{max, exp.}: Maximum capacity calculated from experiment; q_{max, theo.}: Maximum capacity calculated from Langmuir model

Table 5: Removal of Ni²⁺, Cd²⁺ and Pb²⁺ from real sample with studied adsorbents

Adsorbent	Uptake (%)		
	Ni ²⁺	Cd ²⁺	Pb ²⁺
Chitin	6.59	95.71	98.73
Chitosan	71.99	95.20	98.51
CH-FeO nanocomposite	21.73	99.91	99.95

The experiment conditions: 0.05 g CH-FeO, 0.15 g chitin and 0.2 g chitosan in 20 dm³ solution, the mixing speed 5 rps, pH=3, room temperature, mixing time 1800 s.

because of existence of other ions in real matrix or high concentration of ions in used real solution.

CONCLUSION

The present investigation showed that chitin (shrimp shell) and chitosan-Fe₂O₃ nanocomposite are efficient adsorbents for treatment of polluted waters with Ni, Cd and Pb ions. The selectivity and applicability of the process are profoundly dependent on the used adsorbents, the aqueous phase pH and the contact time. The shrimp shell adsorbent has great ability in removing Cd ions. This ability for Cd ions was shown to be better in comparison with Ni ion using shrimp shell sorbent. Adsorption procedure was strongly affiliated to pH, and with increasing the ion concentration, more adsorbent is needed. The three used adsorbents in the removal of cadmium and lead are better than nickel ions from spent Ni-Cd batteries and have operation that is more successful. Our studies in real sample show that, this adsorbent can be used efficiently in separation Cd and Ni ions. In addition, these adsorbents could be applied for removal of relatively higher metal ion concentrations from wastewater. It is a simple and low cost removing methodology for heavy metals. This ability was studied for chitosan and chitosan-Fe₂O₃ nanocomposite adsorbents as well. Importantly, this work introduces an environmentally friendly recycling bioadsorbent for diminishing the waste Ni-Cd batteries, which have negative impacts on environmental and human health.

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CONFLICT OF INTEREST

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

ABBREVIATIONS

<i>A</i>	Absorbance
<i>a</i>	Speed of chemisorptions at zero coverage
<i>a'</i>	Isotherm constant for Temkin model (dm ³ /g)
<i>b</i>	Constant for showing the energy amount of formed bond between the adsorbent and adsorbate
<i>b'</i>	Elovich model is the desorption constant that is affiliated to the value of surface coverage and the activation energy for the adsorption
<i>C</i>	Concentration in mg/dm ³
<i>C_e</i>	Equilibrium concentrations of the heavy metals in solution in mg/dm ³
<i>CH-FeO</i>	Chitosan/iron oxide
<i>Chitosan/PEO</i>	Chitosan/poly (ethylene oxide) nanofibrous
<i>C_o</i>	Initial concentrations of the heavy metals in solution in mg/dm ³
<i>CS/GO-SH</i>	Chitosan/ Sulfhydrylfunctionalized graphene oxide composites
<i>CXTH</i>	Chitosan-xylan-TiO ₂ hybrid
<i>d</i>	Temkin constant for adsorption temperature (kJ.m/mol)
<i>dm³</i>	Cubic decimeter
<i>DTPA-Chitosan</i>	Diethylenetriaminepentaacetic acid-Chitosan
<i>EDTA-Chitosan</i>	Ethylenediaminetetraacetic acid -Chitosan
<i>EEC</i>	Environment European commission
<i>Eq</i>	Equation
<i>F</i>	Constant in Freundlich isotherm model that show adsorption intensity
<i>FAAS</i>	Flame atomic absorption spectrometer
<i>FE-SEM</i>	Field emission scanning electron microscopy
<i>FT-IR</i>	Fourier transform infrared spectroscopy
<i>g</i>	Gram
<i>ISIRI</i>	Institute of standards and industrial research of Iran
<i>K</i>	Kelvin
<i>k₁</i>	Pseudo-first-order rate constant

k_2	Pseudo-second-order rate constant
$kN.m$	Kilo newton. metre
k_p	Adjustment parameters for power function kinetic model
M	Molar
MCL	Maximum concentration limit
M_s	Mass of the adsorbent in gram
mg/dm^3	Milligram per cubic decimeter
mg/g	Milligram per gram
n	Adsorption intensity in Freundlich isotherm model
PGC	Polyaniline grafted chitosan
pH_{pzc}	Point of zero charge
q_e	Amount of adsorbed in equilibrium time
q_{max}	Maximum capacity of the adsorbent
q_t	Amount of adsorbed heavy metal in mg on the surface of adsorbent in g in any time
R	Defines the gas constant (0.0083 kN.m /K. mol)
rps	Revolutions per second
T	Temperature in Kelvin
t	Contact time
TEM	Transmission electron microscopy
UK	United Kingdom
$USEPA$	US Environment protection agency
V	Volume of the used solution in dm^3
WHO	World health organization
XRD	X-ray powder diffraction
v	Adjustment parameters for power function kinetic model

REFERENCES

- Abdel-Ghani, N.T.; Rawash, E.S.A.; El-Chaghaby, G.A., (2016). Equilibrium and kinetic study for the adsorption of p-nitrophenol from wastewater using olive cake based activated carbon. *Global J. Environ. Sci. Manage.*, 2(1): 11-18 (8 pages).
- Al-Haj-Ali, A.; Al-Hunaidi, T., (2007). Sorption of aqueous heavy metal cations by fixed-beds of natural zeolite. *Mu'tah J. Res. Stud.*, 22(2): 81-100 (20 pages).
- Ali, I.; Al-othmsn, Z.A.; Alharbi, O.M., (2016). Uptake of pantoprazole drug residue from water using novel synthesized composite iron nano adsorbent. *J. Mol. Liq.*, 218: 465-472 (8 pages).
- Ariff, N.F.M.; Hanafiah, M.; Kamal, M. A.; Hussin, Z. M.; Ibrahim, S. C.; Ngah, W. S. W., (2016). Kinetics and isotherm studies on Nd (III) adsorption onto Xanthated chitosan. *Materials Science Forum*, Trans. Tech. Publ., 857: 530-534(5 pages).
- Athappan, A.; Sattler, M. L., (2013). A comparison of Bituminous coal-based and coconut Shell-Based activated carbon for removal of trace hazardous air pollutants in Landfill Gas. *J. Civil Eng. Urban.*, 3(6): 331-337 (7 pages).
- Bailey, S. E.; Olin, T. J.; Bricka, R. M.; Adrian, D. D., (1999). A review of potentially low-cost sorbents for heavy metals. *Water Res.*, 33(11): 2469-2479 (11 pages).
- Bernard, E.; Jimoh, A.; Odigure, J.O., (2013). Heavy metals removal from industrial wastewater by activated carbon prepared from coconut shell. *Res. J. Chem. Sci.*, 3(8): 3-9 (7 pages).
- Cai, W.; Duan, G.; Li, Y., (2014). Hierarchical micro/nanostructured materials fabrication properties and applications, Taylor and Francis group.
- Cho, D.W.; Jeon, B. H.; Jeong, Y.; Nam, I. H.; Choi, U. K.; Kumar, R.; Song, H., (2016). Synthesis of hydrous zirconium oxide-impregnated chitosan beads and their application for removal of fluoride and lead. *Appl. Surf. Sci.*, 372: 13-19 (7 pages).
- Dehghani, M.H.; Ghadermazi, M.; Bhatnagar, A.; Sadighara, P.; Jahed-Khanihi, G.; Heibati, B.; Mckay, G., (2016). Adsorptive removal of endocrine disrupting bisphenol A from aqueous solution using chitosan. *J. Environ. Eng-ASCE*, 4(3): 2647- 2655 (9 pages).
- Gupta, V.K.; Srivastava, S.K.; Mohan, D.; Sharma, S., (1998). Design parameters for fixed bed reactors of activated carbon developed from fertilizer waste for the removal of some heavy metal ions. *Waste Manage.*, 17(8): 517- 522 (6 pages).
- Gupta, V.K.; Agarwal, S.; Saleh, T., (2011). Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal. *J. Hazard. Mater.*, 185: 17-23 (7 pages).
- Gupta, V. K.; Nayak, A., (2012). Cadmium removal and recovery from aqueous solutions by novel adsorbents prepared from orange peel and Fe_2O_3 nanoparticles. *Chem. Eng. J.*, 180:81- 90 (10 pages).
- Gupta, V.K.; Ali, I.; Saleh, T.; Nayak, A.; Agarwal, S., (2012). Chemical treatment technologies for waste-water recycling-an overview. *RSC Advances.*, 2: 6380-6388 (9 pages).
- Gupta, V. K.; Saleh, T., (2013). Sorption of pollutants by porous carbon, carbon nanotubes and fullerene- an overview. *Environ. Sci. Pollut. Res. Int.*, 20(5): 2828- 2843 (16 pages).
- Hossein Beyki, M.; Miri, S.; Shemirani, F.; Bayat, M.; Rashidi Ranjbar, P., (2016). A new derivative of core-shell magnetic chitosan biopolymer: Synthesis, characterization and application for adsorption of lead and copper ions. *Clean*, 44(6): 710-719 (10 pages).
- Huang, G.; Zhang, H.; Shi, J.X.; Langrish, T.A., (2009). Adsorption of chromium (VI) from aqueous solutions using cross-linked magnetic chitosan beads. *Ind. Eng. Chem. Res.*, 48(5): 2646-2651 (6 pages).
- Islam, M.S.; Sharif, S.B.; Lee, J.; Habiba, U.; Ang, B.C.; Afifi, A.M., (2017). Adsorption of divalent heavy metal ion by mesoporous-high surface area chitosan/poly (ethylene oxide) nanofibrous membrane. *Carbohydr. Polym.*, 157: 57-64 (8 pages).
- Jain, M.; Garg, V.; Kadirvelu, K.; Silanpaa, M., (2016). Adsorption of heavy metals from multi-metal aqueous solution by sunflower plant biomass-based carbons. *Int. J. Environ. Sci. Technol.*, 13(2):493-500 (8 pages).
- Jain, M.; Garg, V.K.; Garg, U.K.; Kadirvelu, K.; Silanpaa, M., (2015). Cadmium removal from wastewater using carbonaceous adsorbents prepared from sunflower waste. *Int. J. Environ. Res.*, 9(3):1079-1088 (10 pages).
- Karbassi, A.R.; Heidari, M., (2015). An investigation on role of salinity, pH and DO on heavy metals elimination throughout estuarial mixture. *Global J. Environ. Sci. Manage.*, 1(1): 41-46 (6 pages).
- Karthik, R.; Meenakshi, S., (2015). Removal of Pb(II) and Cd(II) ions from aqueous solution using polyaniline grafted chitosan. *Chem. Eng. J.*, 263:168- 177(10 pages).
- Keshvardoostchokami, M.; Zamani, A.; Piri, F., (2017). One-pot synthesis of chitosan/iron Oxide nanocomposite as an eco-friendly bioadsorbent for water remediation of methylene blue. *Micro. Nano. Lett.*, (In Press).
- Li, X.; Zhou, H.; Wu, W.; Wei, S.; Xu, Y.; Kuang, Y., (2015). Studies of heavy metal ion adsorption on Chitosan/Sulphydrylfunctionalized graphene oxide composites. *J. Colloid Interface Sci.*, 448: 389-397 (9 pages).

- Mallakpour, S.; Madani, M., (2016). Functionalized-MnO₂/chitosan nanocomposites: A promising adsorbent for the removal of lead ions. *Carbohydr. Polym.*, 147:53- 59 (7 pages).
- Nodeh, H.R.; Ibrahim, W.A.W.; Sanagi, M.M.; Aboul-Enein, H.Y., (2016). Magnetic graphene-based cyanopropyltriethoxysilane as an adsorbent for simultaneous determination of polar and non-polar organophosphorus pesticides in cow's milk. *RSC Advances*, 6(30): 24853-24864 (12 pages).
- Pandey, P.K.; Choubey, S.; Verma, Y.; Pandey, M.; Kamal, S.S.K.; Chandrashekar, K., (2007). Biosorptive removal of Ni(II) from wastewater and industrial effluent. *Int. J. Environ. Res. Public Health*, 4(4): 332-339 (8 pages).
- Park, J.H.; Ok, Y.S.; Kim, S.H.; Cho, J.S.; Heo, J.S.; Delaune, R.D.; Seo, D.C., (2016). Competitive adsorption of heavy metals onto sesame straw biochar in aqueous solutions. *Chemosphere*, 142: 77- 83 (7 pages).
- Ren, Y.; Zhang, M.; Zhao, D., (2008). Synthesis and properties of magnetic Cu (II) ion imprinted composite adsorbent for selective removal of copper. *Desalination*, 228(1-3): 135- 149 (15 pages).
- Repo, E.; Warchol, J.K.; Kurniawan, T.A.; Sillanpää, M.E.T., (2010). Adsorption of Co(II) and Ni(II) by EDTA- and/or DTPA-modified chitosan: Kinetic and equilibrium modeling. *Chem. Eng. J.*, 161(1-2): 73- 82 (10 pages).
- Saber-Samandari, S.; Saber-Samandari, S.; Nezafati, N.; Yahya, K., (2014). Efficient removal of lead (II) ions and methylene blue from aqueous solution using chitosan/Fe-hydroxyapatite nanocomposite beads. *J. Environ. Manag.*, 146: 481-490 (10 pages).
- Sonali, R.D.; Jayant, P.K.; Sunil, J.K., (2013). Research for removal of nickel from waste water: A review. *Int. J. Sci. Eng. Technol. Res.*, 2(12): 2162-2166 (5 pages).
- Sunil, J.; Jayant, P.K., (2013). Adsorption for cadmium removal from effluent- A Review. *IJSETR*, 2(10): 1840- 1844 (5 pages).
- Tran, H. V.; Tran, L. D.; Nguyen, T. N., (2010). Preparation of chitosan/magnetite composite beads and their application for removal of Pb(II) and Ni(II) from aqueous solution. *Mater. Sci. Eng., C*, 30(2): 304- 310 (7 pages).
- Vijayakumar, G.; Tamilarasan, R.; Dharmendirakumar, M., (2012). Adsorption, kinetic, equilibrium and thermodynamic studies on the removal of basic dye Rhodamine-B from aqueous solution by the use of natural adsorbent perlite. *J. Mater. Environ. Sci.*, 3(1): 157- 170 (14 pages).
- Wang, Q.; Chen, N.; Yu, Y.; Feng, C.; Ning, Q.; Hu, W., (2016a). Chromium (VI) removal from aqueous solution using a new synthesized adsorbent. *Desalin. Water Treat.*, 57:4537- 4547 (11 pages).
- Wang, Y.; Li, L.; Luo, C.; Wang, X.; Duan, H., (2016b). Removal of Pb²⁺ from water environment using a novel magnetic chitosan/graphene oxide imprinted Pb²⁺. *Int. J. Biol. Macromol.*, 86:505-511 (7 pages).
- Wu, S.; Hu, J.; Wei, L.; Du, Y.; Shi, X.; Deng, H.; Zhang, L., (2014). Construction of porous chitosan-xylan-TiO₂ hybrid with highly efficient sorption capability on heavy metals. *J. Environ. Chem. Eng.*, 2: 1568-1577 (9 pages).
- Yamani, J.S.; Lounsbury, A.W.; Zimmerman, J.B., (2016). Towards a selective adsorbent for arsenate and selenite in the presence of phosphate: Assessment of adsorption efficiency, mechanism, and binary separation factors of the chitosan-copper complex. *Water Res.*, 88: 889-896 (8 pages).
- Yuwei, C.; Jianglong, W., (2011). Preparation and characterization of magnetic chitosan nanoparticles and its application for Cu (II) removal. *Chem. Eng. J.*, 168(1): 286-292 (7 pages).
- Zamani, A.A.; Yafian, M.R.; Parizanganeh, A.H., (2012). Multivariate statistical assessment of heavy metal pollution sources of groundwater around a lead and zinc plant. *Iran. J. Environ. Health Sci. Eng.*, 9(29): 1-10 (10 pages).
- Zamani, A.A.; Shokri R.; Yafian, M.R.; Parizanganeh, A.H., (2013). Adsorption of lead, zinc and cadmium ions from contaminated water onto Peganum Harmala seeds as biosorbent. *Iran. J. Environ. Sci. Technol.*, 10(1): 93-102 (10 pages).

AUTHOR (S) BIOSKETCHES

Keshvardoostchokami, M., Ph.D., Assistant Professor, Environmental Science Research Laboratory, Department of Environmental Science, Faculty of Science, University of Zanjan and Organic Chemistry Research Laboratory, Department of Chemistry, Faculty of Science, University of Zanjan, Zanjan, Iran. Email: keshvardoost@znu.ac.ir

Babaei, L., M.Sc., Environmental Science Research Laboratory, Department of Environmental Science, Faculty of Science, University of Zanjan, Zanjan, Iran. Email: l.babayee@yahoo.com

Zamani, A.A., Ph.D., Assistant Professor, Environmental Science Research Laboratory, Department of Environmental Science, Faculty of Science, University of Zanjan, Zanjan, Iran. Email: zamani@znu.ac.ir

Parizanganeh, A.H., Ph.D., Professor, Environmental Science Research Laboratory, Department of Environmental Science, Faculty of Science, University of Zanjan, Zanjan, Iran. Email: h_zanganeh@znu.ac.ir

Piri, F., Ph.D., Assistant Professor, Organic Chemistry Research Laboratory, Department of Chemistry, Faculty of Science, University of Zanjan, Zanjan, Iran. Email: mohamadimaryam99@yahoo.com

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