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Novel inorganic–organic hybrid polymers to remove heavy metals from aqueous solution

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ABSTRACT

Poly-GPTS was prepared by polymerization of 3-glycidyloxypropyltrimethoxysilane (GPTS) with potassium tert-butoxide (KO^{t}Bu) at 50°C. After this stage, adsorbents poly-GPTS and poly-GPTS/Ti(O)/OH were prepared from hydrolysis of poly-GPTS and mixtures between poly-GPTS and titanium isopropoxide in 1:1 mol ratio. The hydrolysis was carried out in 50 ml of isopropanol with 0.1 M HCl. The characterizations of the adsorbents were performed by elemental analysis, thermogravimetric, and spectroscopic methods. After hydrolysis, it was seen that isopropoxide and methoxide groups were removed from the adsorbents under the studied conditions because of the condensation reactions. Pb^{2+}, Cu^{2+}, and Cd^{2+} ions were removed from the aqueous solution using these hybrid polymers as adsorbents. Influence factors such as the initial pH, adsorption time, the amounts of adsorbent, and solution concentrations on Pb^{2+}, Cu^{2+}, and Cd^{2+} adsorptions were investigated. The study showed that they were very good adsorbents for removing metal ions.

Keywords: AAS; Adsorbents; Aqueous solution; Inorganic–organic hybrid; M^{2+} ions; Synthesis

1. Introduction

Nowadays, heavy metal adsorption processes are a very attractive subject because the heavy metal pollution is the most important environmental problem in the world. The problem has been increased with the rapid development of industries, especially in developing countries [1]. Many heavy metals such as lead, copper, and cadmium are known to be toxic and carcinogenic for living organisms [2]. There are many applications used for the removal of heavy metals from wastewater like chemical precipitation, adsorption, ion-exchange, solid phase extraction, etc. Among these methods, adsorption process is the most used one because of its easy, cheap, and effective applications [3–5]. For adsorption process many natural or synthesized adsorbents such as activated carbon, modified clays, polymeric resins, zeolites, etc. have been used [6–13] and scientists are still investigating new, low-cost, and easily available adsorbents for removal of heavy metal ions from wastewater. In the recent years, researchers have examined the inorganic–organic hybrid materials as adsorbents. Especially metal alkoxide compounds were used as in the synthesis of adsorbents. Addition of water to metal alkoxide complexes leads to hydrolysis of alkoxy groups and condensation reactions resulting in inorganic networks without organic groups or with the small amount of organic groups [14–16]. In this connection,

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it is important to add an organic ligand such as 3-glycidyloxypropyltrimethoxysilane (GPTS) for the formation of organic–inorganic network structures.

One of the most important compounds was the GPTS which was used in functional coatings, optical device, preparations of glasses, ceramics, and adsorbents. This paper includes the use of poly-GPTS instead of GPTS in the preparation of adsorbents. It also deals with the preparation, characterization, and the usage of new adsorbents with functional groups that provide specific activity to adsorb the heavy metals from aqueous solution.

2. Materials and methods

2.1. Chemicals

The standard Pb^{2+}, Cd^{2+}, and Cu^{2+} ion solutions were prepared from their nitrate salts (Merck). For pH adjustment 0.1 M HCl and NaOH solutions were used. Titanium (IV) isopropoxide (98%, Merck), GPTS (97%, Alfa Aesar), and isopropanol (99.5%, Merck) were used as received. All the chemicals were in analytical grade.

2.2. Instrumentation

^1H NMR measurement was carried out with a Bruker 300 MHz Ultra shield TM spectrometer. Infrared spectra of complexes were recorded on a Shimadzu 8201/86601 PC spectrometer (FTIR). The elemental analyses were carried out with a LECO CHNS-932 elemental analyzer. Thermogravimetric measurement was carried out in a Protherm furnace with a heating and cooling rate of 10˚C/min under air. A Perkin-Elmer model Flame AAnalyst 800 Atomic Absorption Spectrometer (AAS) was used for Pb^{2+}, Cu^{2+}, and Cd^{2+} ions quantity analysis. The pH measurements were performed by Hanna pH 211 model pH-meter and several model magnetic stirrers were used for adsorption process.

2.3. Adsorption process

Stock metal ion solutions (1,000 mg/l) of Pb^{2+}, Cu^{2+}, and Cd^{2+} were prepared in deionized water and diluted to desired concentration. Basic and easy batch methods were performed for metal ion adsorption. Two different adsorbents were used to find the maximum adsorption capacities of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions. Adsorption capacity depends on various parameters. Batch conditions; a known amount of adsorbent was stirred with 25,00 ml of the different metal ion concentrations of Pb^{2+}, Cu^{2+}, and Cd^{2+} in 50,00 ml flask at room temperature. After equilibrium time, the adsorbent was filtered with filter paper. Then the filtrate was analyzed by AAS to obtain metal ion concentrations. Controlled experiments were performed and no adsorption was observed on filter paper and glassware. The effect of contact time on adsorption was examined in the range of 5–40 min. The initial pH of the metal ion Pb^{2+}, Cu^{2+}, and Cd^{2+} solutions were studied between 3.0–6.0, 4.0–8.0, and 4.0–8.0, respectively. To find the maximum metal adsorption capacity, the effect of initial metal ion concentration for each metal ion and their concentration ranges for Pb^{2+} (5.0–30 mg/l), Cu^{2+} (1.0–9.0 mg/l), and Cd^{2+} (0.5–4.0 mg/l) were also investigated. For each adsorbent various amount ranging from 1.0 to 10 mg were studied to examine the effect of the adsorbent amount on the metal ion adsorption capacity.

Maximum adsorption capacity was calculated by using the following Eq. (1).

$$q\ (\mathrm{mg/g}) = \frac{(C_\mathrm{i} - C_\mathrm{e}) \times V}{W} \tag{1}$$

where q is adsorption capacity, C_i and C_e are the initial and equilibrium concentrations of adsorbed metal ions (mg/l), V is the volume of the metal ion solution (l), and W is the amount of adsorbent (g).

2.4. Polymerization of GPTS with t-BuOK

Poly-GPTS was prepared and characterized as in literature [17,18]. The catalyst (40 mg, t-BuOK) was taken in a vial and 2.5 ml of GPTS was added under nitrogen. The mixture was stirred at 50˚C for 48 h. The conversion of monomer (GPTS) to polymers was 100%. ^1H-NMR, $CDCl_3$, ppm, δ: 4.28 (CH, broad(br)), 3.74–3.2 (CH, CH_3O, CH_2, $2CH_2O$, br), 1.75 (CH_2, $CH_2CH_2CH_2$, br), 0.72–0.70 (CH_2–Si, br).

2.5. Hydrolysis of poly-GPTS

The poly-GPTS was dissolved in 50 ml of isopropanol and stirred for a few minutes and then hydrolyzed by 0.1 M HCl. 3.0 mol of water per mole of GPTS [$C_6H_{11}O_2$-Si(OCH_3)$_3$] were added dropwise to the solution and stirred for 24 h at room temperature. After 24 h of stirring, the volatile parts of mixture were removed under reduced pressure at 50˚C and beige solid was obtained. FTIR (KBr pellet): 3,448 (OH), 2,941 (C–H, ν_{asym}), 2,883 (C–H, ν_{sym}), 1,460 (CH_2), 1,204 (Si–CH_2) 1,111 (Si–O–Si), 910, 779, 685 cm^{-1}. ^1H NMR spectrum shows that propyl group remains bonded to silicon after hydrolysis.

2.6. Hydrolysis of [poly-GPTS/Ti(O^{i}Pr)$_4$]

The compounds poly-GPTS and titanium isopropoxide were mixed in 1:1 mol ratio in 50 ml of isopropanol and stirred for a few minutes. Then the mixture was hydrolyzed by 0.1 M HCl. 4.0 mol of water per mole of Ti(O^{i}Pr)$_4$ and 3.0 mol of water per mole of GPTS were added dropwise to the solution and stirred for 24 h at room temperature. After 24 h stirring, the volatile parts of mixture were removed under reduced pressure at 50°C and a beige solid was obtained. Elemental analysis, Found: C, 30.41; H, 5.62%. The TGA of the hydrolyzed product showed a weight loss of 37% up to 800°C. FTIR (KBr pellet): 3,438 (OH), 2,931 (CH asym), 2,872 (CH sym), 1,202 (Si–CH$_2$) 1,113 (Si–O–Si), 1,050 (Si–O–Ti) cm^{-1}.

3. Results and discussion

The poly-GPTS was prepared from GPTS monomers and ^{t}BuOK as in literature [17]. It was characterized by ^{1}H-NMR and FTIR spectroscopy before use. Poly-GPTS was hydrolyzed by 0.1 M HCl (3.0 mol of water per mole of GPTS). It is summarized as in Fig. 1.

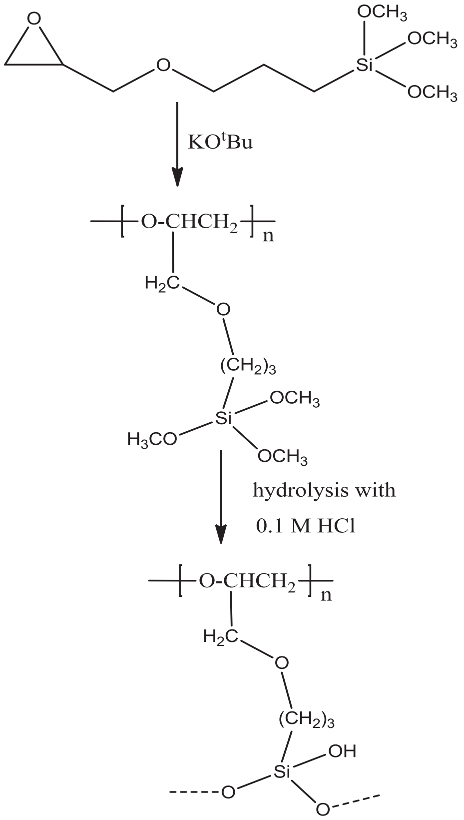

Fig. 1. Silicon containing adsorbent prepared from poly-GPTS.

The adsorbent poly-GPTS/Ti(O)OH was prepared as explained in experimental section.

FTIR studies support the condensation reactions between poly-GPTS and metal alkoxides compounds in the presence of HCl(aq). The poly-GPTS shows characteristic bands at 1,089 cm^{-1} for Si–OCH$_3$ bonds. When poly-GPTS undergoes condensation with metal alkoxides, the peak at 1,089 cm^{-1} disappears in the FTIR spectrum. This disappearance supports the fact that the Si–OCH$_3$ undergoes a condensation reaction. After condensation reaction, new peaks appeared at 1,113 cm^{-1} for Si–O–Si and ~1,050 cm^{-1} for Si–O–Ti bonds, respectively. The presence of the OH groups bounded to silicon and titanium atoms appeared at 3,438 cm^{-1} in the FTIR spectrum. The peak at ~1,202 cm^{-1} in the FTIR spectrum can be attributed to CH$_2$–Si bond (Fig. 2). Elemental analysis measurement also supports the presence of organic groups (CH$_2$CH$_2$CH$_2$Si) with ~36% of C and H.

The synthesis of Si–Ti adsorbent can be summarized as in Fig. 3. The absorbance of the metal ions was followed by the FT-IR spectroscopy in addition to AAS. When Cu^{2+} ion was adsorbed by Si–Ti adsorbent, it gave a peak at 419 cm^{-1} in the FTIR spectrum.

These two adsorbents were used to remove metal (2+) ions from aqueous solution. To investigate the maximum adsorption capacity, optimization studies of several factors were performed. The amounts of adsorption capacities of these experiments were calculated from Eq. (1). The adsorption capacity of Si–Ti adsorbent was better than Si adsorbent. This is very reasonable because of each Ti atom containing four oxygen atoms which adsorb the metal ions. And capacity results obtained from optimization were high for Pb^{2+} compared to Cd^{2+} and Cu^{2+} ions on each new hybrid adsorbent. This can be attributed to the large size of lead ion. The maximum adsorption capacities given in Table 1 which represent optimum condition results.

3.1. Effects of contact time

The results of the contact time were shown below in Fig. 4. All these experiments were carried out separately for each metal ion solution and for each adsorbent. For these experiments, 2.5 mg adsorbents were taken from each adsorbent. The initial metal ion concentrations were 20, 5, and 2 mg/l for Pb^{2+}, Cu^{2+}, and Cd^{2+}, respectively. Equilibrium adsorption time was determined within 10 min for metal ions on the adsorbents. After 10 min, the adsorption capacities got plateau values. After the contact time optimization, the other experiments were performed within 10 min.

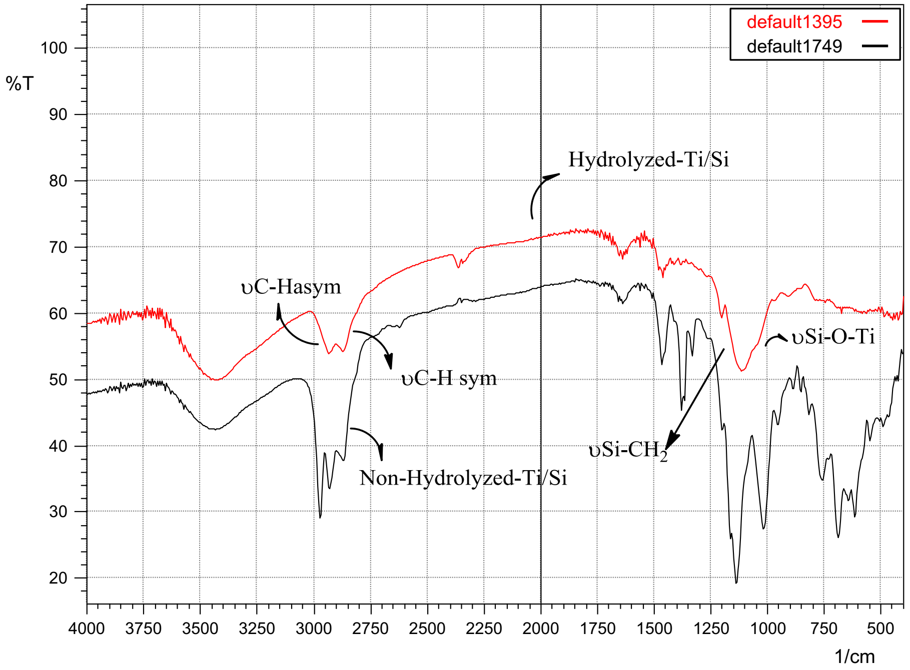

Fig. 2. FTIR spectra of adsorbent poly-GPTS/Ti(O)OH and non-hydrolized compound (poly-GPTS/Ti($O^iPr)_4$).

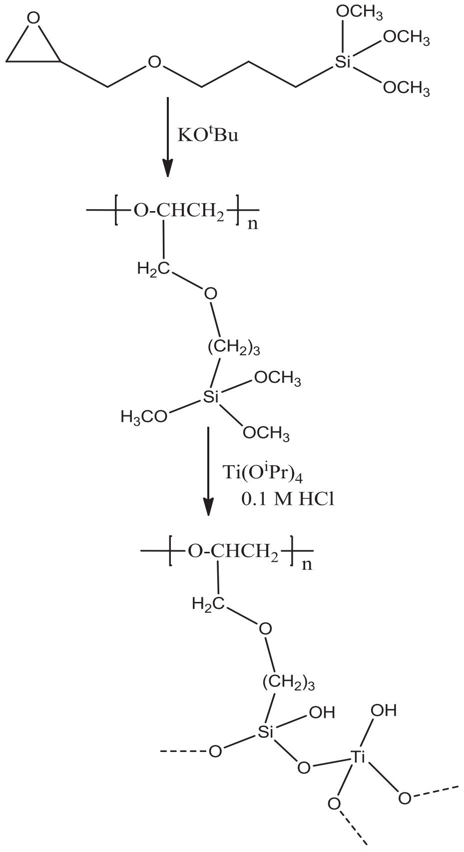

Fig. 3. Silicon and titanium containing adsorbent prepared from poly-GPTS and Ti($O^iPr)_4$.

3.2. Effect of initial pH

The pH is the important parameter in the adsorption process. Fig. 5 shows the effect of initial pH of the metal ion solutions of Pb^{2+}, Cu^{2+}, and Cd^{2+} on adsorption capacity of hybrid compounds. In this work, after pH optimization, as seen from optimization Fig. 5, the adsorption capacities of metal ions were not changed dramatically between pH 5–6. Therefore, all the experiments were carried out at pH ~5.5. The pH from initial time to equilibrium time (10 min) did not change. In other words, there were no changes at the pHs during adsorption process. The other experiment parameters; stirring time was 10 min, metal ions solution volumes were 25 ml, and amounts of adsorbents were 2.5 mg (or 100 mg/l). The initial metal ion solutions pHs were at the pH ranges given in the adsorption process. So there was no need to add NaOH or HCl solution to the adsorption media to arrange the pH values. Also, as can be seen in the figures the adsorption capacities were high at pH ~5.5. Especially for Pb^{2+} ion after pH 6.0, there was apparent precipitation in the metal ion solution. It is known that metal hydroxides form at high pH values [9].

3.3. Effect of initial metal ion concentrations

The maximum adsorption capacity was investigated for each metal with different initial

Table 1
Results of the metal ions adsorption on novel inorganic–organic hybrid compounds

Metal ion	Initial conc. mg/l	Poly-GPTS *q* (mg/g)	Poly-GPTS-Ti *q* (mg/g)	Poly-GPTS % Removal	Poly-GPTS-Ti % Removal
Pb^{2+}	20.0	165.2	199.0	84.40	99.38
Cu^{2+}	5.0	41.28	42.79	82.56	85.58
Cd^{2+}	2.0	32.48	39.41	80.75	98.53

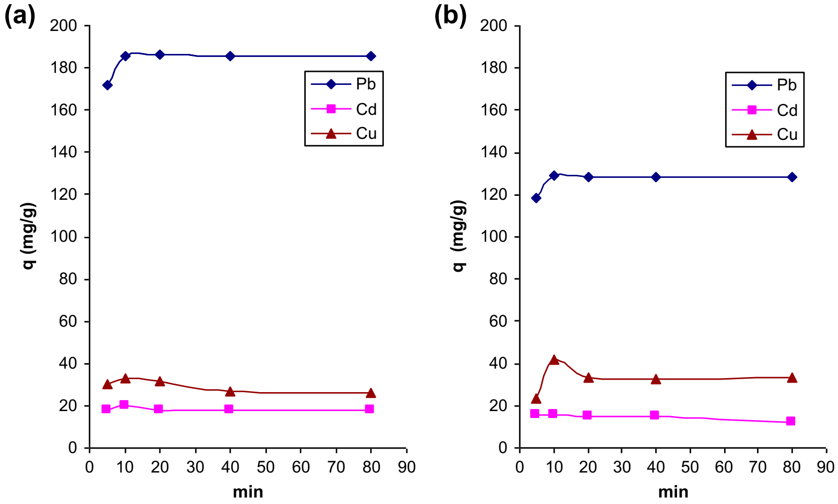

Fig. 4. Effect of contact time on the adsorption of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions on (a) poly-GPTS-Ti and (b) poly-GPTS.

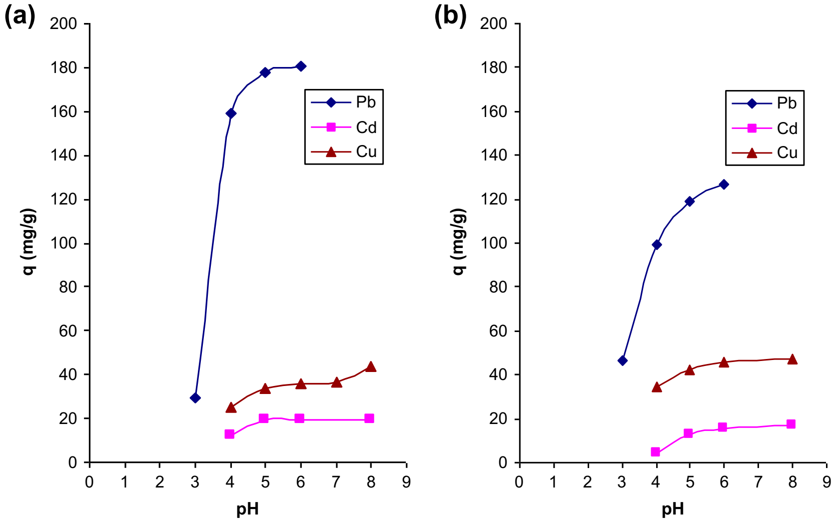

Fig. 5. Effect of initial pH on the adsorption of metal ions on (a) poly-GPTS-Ti and (b) poly-GPTS.

concentration while keeping the time at 10 min and pH ~5.5. When the initial concentration is high, a big concentration difference occurs between bulk solution and adsorption sites. Therefore, the adsorption capacity increases fast [6,9–11]. After the optimum concentration point, the adsorption capacity slightly decreased. It may be saturation of adsorption sites. The maximum amount of adsorption in Fig. 6(a) and

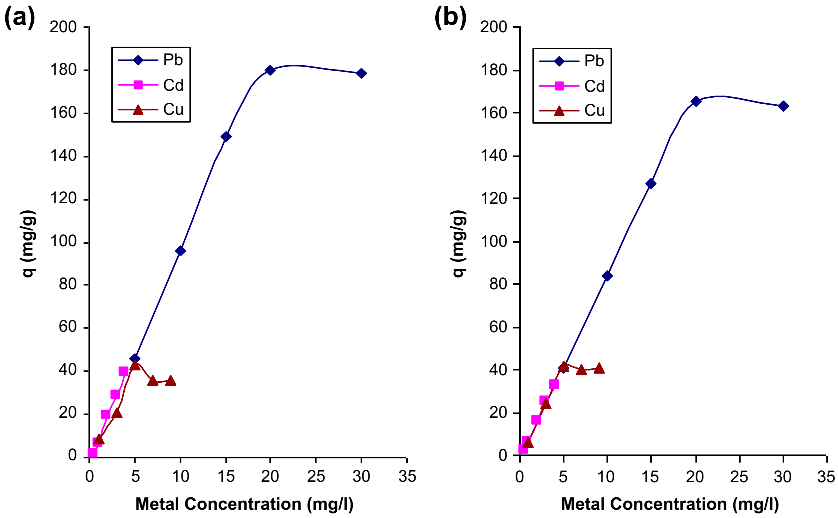

Fig. 6. Effect of initial metal ion concentrations on the adsorptions of metal ions on (a) poly-GPTS-Ti and (b) poly-GPTS.

(b) is consistent with percentage removal of metal ions (as seen in Table 1).

3.4. Effects of the amount of adsorbents

The effects of the amount of adsorbent on the metal adsorption are shown in Fig. 7(a) and (b). When the adsorbent amount is increased, the number of adsorption sites increases. It is obvious that the high adsorption capacity decreases with increasing in the amount of the adsorbent as seen in the Fig. 7(a) and (b). The adsorption capacity was calculated from Eq. (1). Low amount of adsorbents provided high adsorption capacity. In literature, there are many adsorbents which give similar results while metal ions are adsorbed [11,12,19,20]. It can be noticed that saturation of the adsorption sites and agglomeration could be the reason of the decrease in the adsorption capacity. However, the removal percentage of metal ions increases with increasing the adsorbent amount to an optimum value. In these experiments, the optimum amount of the adsorbent was taken 100 mg/l for each metal ion. In spite of the small amount of adsorbents, they have a lot of adsorption sites for metal ions $Pb^{2+} > Cu^{2+} > Cd^{2+}$.

As this study shows, the results have great importance for removing metal ions using a very small amount of adsorbent. As seen from the Table 1, both adsorbents have a high maximum adsorption capacity (199 mg/g) and percentage removal (99.38%) for Pb^{2+}

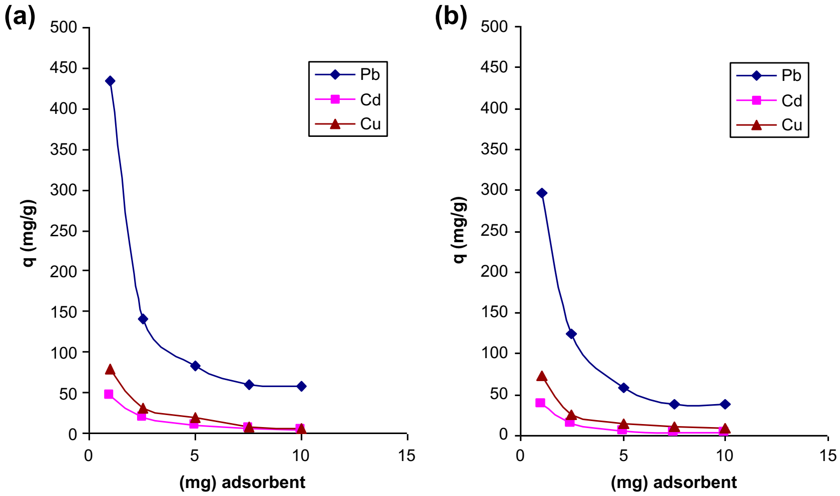

Fig. 7. Effect of the amounts of (a) poly-GPTS-Ti and (b) poly-GPTS on the adsorptions of metal ions.

Table 2
The isotherm models for adsorption of metal ions

Metal	Sorbent	Langmuir constant			Freundlich constant		
		R^2	Q_o (mg/g)	b_L (l/mg)	R^2	K_F (mg/g)	n_F
Pb^{2+}	Poly-GPTS	0.9926	172.4	10.54	0.6226	66.37	2.41
	Poly-GPTS-Ti	0.9997	181.2	7.86	0.2663	146.8	13.25
Cu^{2+}	Poly-GPTS	0.9809	39.06	2.37	0.5512	20.69	1.68
	Poly-GPTS-Ti	0.9818	44.64	2.36	0.6041	23.81	2.70
Cd^{2+}	Poly-GPTS	0.9782	35.71	3.64	0.5663	26.48	0.84
	Poly-GPTS-Ti	0.9732	35.84	5.58	0.4157	31.64	23.31

ion than the other two metal ions. As a result of the large number of highly electronegative oxygen atoms, the maximum capacity and percentage removal of adsorbed metal ions were higher in poly-GPTS-Ti than poly-GPTS. In other words, the Si–Ti adsorbent contains many oxygen atoms which can provide adsorption sites to bind metal ions. Therefore, the Si–Ti adsorbent was better than Si adsorbent to remove metal (2+) ions from individual metal solutions. These adsorption capacity values were also better than the literature values. The adsorption capacity of natural calcite and limestone for Pb^{2+} ion was only 19.92 and 0.0167 mg/g, respectively [21].

3.5. *Adsorption isotherms*

An adsorption isotherm can be used to characterize the interaction of metal ions ($Pb^{2+,}$ Cu^{2+}, and Cd^{2+}) with adsorbents. The isotherm provides a relationship between the concentration of metal ions in solution and the amount of metal ions adsorbed on the solid phase when both phases are in equilibrium. The adsorption isotherms were analyzed by the two most commonly used Langmuir and Freundlich equations. The adsorption isotherm models of Langmuir and Freundlich can be expressed as linear form of Eqs. (2) and (3), respectively [22].

$$\frac{Ce}{qe} = \frac{Ce}{Qo} + \frac{1}{Qob_L} \tag{2}$$

$$\ln\ qe = \ln K_F + \frac{1}{n_F}\ \ln\ Ce \tag{3}$$

where C_e (mg l^{-1}) and q_e (mg g^{-1}) are the concentration and adsorption capacity at the equilibrium, respectively. Q_o (mg g^{-1}) and b_L (l mg^{-1}) are adsorption capacity and binding enrgy of adsorption of Langmuir, respectively. K_F and n_F are Freundlich constants measuring the adsorption capacity and the adsorption intensity, respectively. The parameters calculated from the two models are presented in Table 2. The correlation coefficients (R^2) of Langmuir isotherm model were close to 1.0, which indicated that the adsorption process of the metal ions was described by the Langmuir isotherm model fit to adsorption. As seen from Tables 1 and 2, the maximum sorption capacity values obtained from isotherm models were consistent with the values calculated from Eq. (1).

4. Conclusions

In this study, novel inorganic–organic hybrid polymers for the adsorption of metal ions were synthesized by sol–gel process. These new adsorbents were used to remove metal (2+) ions from single metal solutions. It was concluded that these inorganic–organic hybrid polymers were promising as adsorbents and applied to remove and recover Pb^{2+}, Cu^{2+}, and Cd^{2+} ions from aqueous solution.

The maximum adsorption capacity of Si–Ti adsorbent was better than Si adsorbent for Pb^{2+}, Cu^{2+}, and Cd^{2+} ions. The maximum adsorption of Pb^{2+}, Cu^{2+}, and Cd^{2+} onto Si–Ti adsorbent was 199.0 mg/g (% removal 99.38), 42.79 mg/g (% removal 85.58), 39.41 mg/g(% removal 98.53), respectively.

The results given in Table 2 show that the adsorption of metal (2+) ions follows Langmuir isotherm model.

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References

[1] Q. Dong, J. Liu, L. Song, G. Shao, Novel zwitterionic inorganic-organic hybrids: Synthesis of hybrid adsorbents and their applications for Cu^{2+} removal, J. Hazard. Mater. 186 (2011) 1335–1342.

[2] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters, J. Environ. Manage. 92 (2011) 407–418.

[3] A.V. Borhade, A.G. Dholi, S.G. Wakchaure, D.R. Tope, Chemical modification of coal fly ash into iodate sodalite and its use for the removal of Cd^{2+}, Pb^{2+}, and Zn^{2+} from their aqueous solutions, Desalin. Water Treat. 50 (2012) 157–169.

[4] V. Singh, S. Pandey, S.K. Singh, R. Sanghi, Removal of cadmium from aqueous solutions by adsorption using poly (acrylamide) modified guar gum-silica nanocomposites, Sep. Purif. Technol. 67 (2009) 251–261.

[5] M.B. Ibrahim, W.L.O. Jimoh, Adsorption studies for the removal of Cr(VI) ion from aqueous solution, Bayero J. Pure Appl. Sci. 1 (2008) 99–103.

[6] X. Jin, C. Yu, Y. Li, Y. Qi, L. Yang, G. Zhao, H. Hu, Preparation of novel nano-adsorbent based on organic-inorganic hybrid and their adsorption for heavy metals and organic pollutants presented in water environment, J. Hazard. Mater. 186 (2011) 1672–1680.

[7] M. Arshadi, M. Ghiaci, A. Gil, Schiff base ligands immobilized on a nanosized SiO_2–Al_2O_3 mixed oxide as adsorbents for heavy metals, Ind. Eng. Chem. Res. 50 (2011) 13628–13635.

[8] Y. Pang, G. Zeng, L. Tang, Y. Zhang, Y. Liu, X. Lei, Z. Li, J. Zhang, G. Xie, PEI-grafted magnetic porous powder for highly effective adsorption of heavy metal ions, Desalination 281 (2011) 278–284.

[9] Y. Jiang, Q. Gao, H. Yu, Y. Chen, F. Deng, Intensively competitive adsorption for heavy metal ions by PAMAM-SBA-15 and EDTA-PAMAM-SBA-15 inorganic–organic hybrid materials, Micropor. Mesopor. Mater. 103 (2007) 316–324.

[10] R. Souag, D. Touaibia, B. Benayada, A. Boucenna, Adsorption of heavy metals (Cd, Zn and Pb) from water using keratin powder prepared from Algerian sheep hoofs, Eur. J. Sci. Res. 35 (2009) 416–425.

[11] L.-H. Wang, C.-I. Lin, Adsorption of chromium (III) ion from aqueous solution using rice hull ash, J. Chin. Inst. Chem. Eng. 39 (2008) 367–373.

[12] A. Shukla, Y.-H. Zhang, P. Dubey, J.L. Margrave, S.S. Shukla, The role of sawdust in the removal of unwanted materials from water, J. Hazard. Mater. B95 (2002) 137–152.

[13] H.T. Fan, J. Li, M.M. Guo, X.L. Fan, D.S. Zhang, Z.J. Su, J. Wang, Removal of arsenic from ammoniacal etching waste liquor by 3-(2-aminoethylamino)propyltrimethoxysilane functionalized silica gel sorbent, Desalin. Water Treat. 50 (2012) 51–58.

[14] R.K. Dey, T. Patnaik, V.K. Singh, S.K. Swain, M.A. de Melo, Jr, C. Airoldi, Al-centered functionalized inorganic–organic hybrid sorbent containing N and S donor atoms for effective removal of cadmium, Solid State Sci. 12 (2010) 440–447.

[15] G. Yalcin, A. Kayan, Synthesis and characterization of Zr, Ti, Al-phthalate and pyridine-2-carboxylate compounds and their use in ring opening polymerization, Appl. Catal.: A Gen. 434 (2012) 223–228.

[16] G. Bulut, E. Mercanci, A. Kayan, Complexation of zirconium alkoxides with 3-pentenoic acid and hydrolytic stability of their products, J. Inorg. Organomet. Polym. 14 (2004) 191–200.

[17] A. Kayan, Polymerization of 3-glycidyloxypropyltrimethoxysilane with different catalysts, J. Appl. Polym. Sci. 123 (2012) 3527–3534.

[18] G. Yalcin, U. Yildiz, A. Kayan, Preparation of Al, Ti, Zr-perfluoroheptanoate compounds and their use in ring opening polymerization, Appl. Catal.: A Gen. 424 (2012) 205–210.

[19] B. Pan, B. Pan, W. Zhang, L. Lv, Q. Zhang, S. Zheng, Development of polymeric and polymer-based hybrid adsorbents for pollutants removal from waters, Chem. Eng. J. 151 (2009) 19–29.

[20] A. Kayan, Preparation, characterization and application of inorganic–organic hybrid polymers, poly-GPTS/$M(CL)_xO$ (OH), Ind. Eng. Chem. Res. 51 (2012) 13339–13345.

[21] X. Ma, L. Li, L. Yang, C. Su, K. Wang, S. Yuan, J. Zhou, Adsorption of heavy metal ions using hierarchical $CaCO_3$–maltose meso/macroporous hybrid materials: Adsorption isotherms and kinetic studies, J. Hazard. Mater. 210 (2012) 467–477.

[22] Y. Zhou, Q. Jin, X. Hu, Q. Zhang, T. Mea, Heavy metal ions and organic dyes removal from water by cellulose modified with maleic anhydride, J. Mater. Sci. 47 (2012) 5019–5029.