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Simultaneous removal of Ag(I), Cd(II), Cr(III), Ni(II), Pb(II), and Zn(II) from wastewater using humic acid-coated aminopropyl silica gel

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ABSTRACT

Humic acid immobilized onto silica gel (Si-HA) was prepared and used for the removal of heavy metal ions; Ag(I), Cd(II), Cr(III), Ni(II), Pb(II), and Zn(II) from wastewater. The optimum pH from a batch system was as follows: 3–7 for Ag(I), 4–7 for Cr(III), Pb(II), and Zn (II), and 6–7 for Cd(II) and Ni(II). The equilibrium was reached within 30 min when a mixture of 100 mg of Si-HA, and 5 mL of 10 mg L^{-1} of each metal ion was used. The adsorption isotherm obeyed the Langmuir model for all metal ions. The calculated maximum sorption capacity order was Cr(III) > Pb(II) > Zn(II) ≈ Cd(II) > Ag(I) > Ni(II). Almost 100% of metal ions were adsorbed on the Si-HA column when the loading flow rate was in the range of 0.5–5.0 mL min^{-1}. The removal efficiency was improved when the amount of Si-HA increased. The elution of heavy metal ions was achieved using 10% (v/v) HNO_3. The presence of sodium, potassium, calcium, chloride, nitrate, and sulfate at the concentration of 5 g L^{-1} did not affect the removal efficiency.

Keywords: Humic acid; Heavy metals; Removal; Silica gel; Wastewater

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1. Introduction

Contamination of heavy metal ions in wastewater resulting from growing industries is currently an environmental problem. The removal of heavy metals from wastewater can be achieved by different techniques, such as precipitation, membrane filtration, and electrochemical techniques. However, these techniques are quite sophisticated and can be costly on a large scale. Adsorption is an optional method for the treatment of heavy metal-contaminated wastewater because of the commercial availability of adsorbents and the ability to be regenerated and reused. Many researchers have focused on finding low-cost adsorbents [1–4] and nanomaterial adsorbents [5] for this purpose. Humic matters are defined as a series of naturally occurring high molecular weight, amorphous, polydispersed substances with a yellow to brown-black color. They

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are hydrophilic and acidic molecules, which are the main components of organic matter in soil and natural water [6]. Humic acid (HA) can be utilized in wastewater treatment because its active carboxylic and hydroxyl functional groups can react with various heavy metal ions to form different complexes [7,8]. Four methods for the application of HA in heavy metal adsorption can be summarized as follows.

The first method involves blending HA with other substances to increase the removal efficiency. For example, HA was added to calcium alginate beads and used for the removal of heavy metals, such as Cd, Cu, Cr, Ni, Mn, Fe, and Zn from the leachates of hazardous solid wastes [9]. A mixture of an unrefined leonardite HA material and beach sand was used for the removal of Pb, Zn, Ni, Cu, Sr, Cd, As, Ag, and Mg ions from water [10]. This kind of material was only suitable for use under acidic conditions because soluble HA can be released at high pH.

The second method involves immobilizing or coating HA onto solid supports, such as styrene-divinylbenzene copolymers, cellulose, and siliceous materials [11–17], Fe–Mn nodule materials [18], aluminum hydroxide and clays [19,20], and titanium dioxide [21]. HA was immobilized onto magnesium oxychloride cement and used for the Cr(VI) removal from wastewater [22]. Recently, HA-coated chitosan and HA-coated magnetite were applied for Pb(II) and Cr(VI) adsorption, respectively [23,24]. This immobilization technique is widely used because the leaching of HA rarely occurs during adsorption. In addition, the sorbents can be regenerated and reused.

The third method involves the preparation of insolubilized humic acid (IHA) by heating original HA at high temperatures (330˚C). The IHA was used to extract heavy metal ions from an aqueous solution [25–27]. The main disadvantages of insolubilization are: difficulties encountered when attempting to separate IHA particles from suspensions and controlling the particle size and shape.

The last technique consists of the addition of soluble HA into water sample in order to form metallic complexes, which can be subsequently removed by adsorption onto a sorbent [28] or ultrafiltration [29,30].

The effective immobilization of HA on solid supports has been reported and the physicochemical properties of these materials have been deeply studied [11–13]. However, there are few studies concerning the application of HA sorbent for the simultaneous removal of heavy metal ions from wastewater. Therefore, this research aimed to prepare HA-coated silica gel, and was used for the removal of metal ions from wastewater using batch and column experiments.

2. Experimental

2.1. Apparatus

The pH measurements were made on a digital pH meter (Hanna pH211). A Fourier transform infrared spectrometer (FTIR, Nicolet Impact 410) was used for the characterization of the sorbent. A UV–vis spectrophotometer (Hewlett Packard model 8453) was used for the determination of HA concentration in the solution at 254 nm. A scanning electron microscope model JSM 5410LV (JEOL) was used for adsorbent imaging. A flame atomic absorption spectrometer (FAAS, AAnalyst 100, Perkin–Elmer) was used for the determination of metal concentrations using an air-acetylene flame. The instrumental parameters are as follows; the wavelengths used were 328.1, 228.8, 357.9, 323.2, 283.3, and 213.9 nm with the hollow-cathode lamp current of 15, 4, 25, 25, 10, and 15 mA for Ag, Cd, Cr, Ni, Pb, and Zn, respectively, the slit width was 0.7 nm for all analytes and 0.2 nm for Ni. The limit of detection of FAAS calculated by three standard deviations of the blank measurement ($n = 5$) were 8.4, 3.2, 24.5, 3.2 138, and 16.1 $\mu g\ L^{-1}$ for Ag, Cd, Cr, Ni, Pb, and Zn, respectively.

2.2. Materials and reagents

Humic acid (HA, total acidity 5.57 meq/g) was purchased from Sigma–Aldrich. Silica gel (70–230 mesh) was purchased from Merck. Working standard solutions of Ag(I), Cd(II), Cr(III), Ni(II), Pb(II), and Zn (II) were prepared by stepwise dilution of 1,000 mg L^{-1} stock standard solutions (BDH Laboratory Supplies and Fisher Scientific). All reagents and solvents were of standard analytical grade and used without further purification.

2.3. Preparation of sorbent

The coating procedure of HA onto aminopropyl silica (SiAP) was adapted from the direct adsorption method proposed by Koopal et al. [11]. A mixture of silica gel (50 g) with dried toluene (200 mL) was refluxed under nitrogen atmosphere for 2 h and then aminopropyltriethoxysilane (20 mL) was added dropwise. The mixture was refluxed again for 24 h. The SiAP solid was filtered, washed with ethanol, and dried. The elemental analysis of SiAP was as follows; C = 5.57%, H = 1.66%, and N = 2.19%. An aliquot of 30 mL of 10 g L^{-1} HA solution in 0.1 M NaOH was added to a vessel containing 1 g of SiAP and the volume of the mixture was adjusted to 50 mL with deionized water. The pH was adjusted to 7.5–8.0. The mixture was stirred for 20 h at room temperature. The solid was separated by centrifugation. Before drying, the sample was rinsed several times with water. The product was cured at 120˚C for 5 h. After curing, the product was rinsed several times with a solution of pH 10 to remove the loosely bound HA. The product Si-HA was characterized by FTIR. The solutions of HA before and after immersing SiAP were analyzed by UV–vis spectrophotometry at 254 nm.

2.4. Removal procedure

2.4.1. Batch method

The effect of pH and contact time on the removal efficiency was investigated. The pH of single metal ion solution (10.0 mg L^{-1}) was adjusted in the range of 1.0–7.0 using KOH and HNO_3 solutions. Then, 10.0 mL of the solution was added into a test-tube containing 100 mg of Si-HA and the mixture was stirred for 60 min at room temperature. For the study of the effect of contact time, the same Si-HA/metal solution mixture at optimum pH was stirred at different contact times ranging from 10 to 60 min at room temperature. To investigate the adsorption isotherm, a suspension of 50 mg of Si-HA in each single metal ion solution (1.0–50.0 mg L^{-1}) was stirred for 45 min at 298 ± 1 K. All experiments were performed in triplicate. Fresh HA-coated silica was used in each experiment. The solid sorbent was separated by centrifugation at 3,500 rpm for 5 min. The residual metal concentration in the supernatant was determined by FAAS.

2.4.2. Column method

The effects of flow rate, amount of sorbent, and interfering ions were studied by column method. Polyethylene columns (6 mL) were packed with 0.1, 0.3, 0.6, and 1.0 g Si-HA. An aliquot of 20.0 mL of mixed metal ion solution (10.0 mg L^{-1} of each metal) at pH 4–5 was passed through the column at different flow rates ranging from 0.5 to 5.0 mL min^{-1} by means of a vacuum manifold (Visiprep, Supelco). Fresh HA-coated silica was used in each experiment. Different amounts of nitrate salts of sodium, potassium, calcium and magnesium, and sodium salts of chloride and sulfate were individually added to the mixed metal ion solution for the study of interfering ions. Nitric acid (10% (v/v), 20 mL) was passed through the column. All solutions were collected and analyzed using FAAS.

2.5. Application to real samples

A wastewater sample was collected from the Eastern Seaboard Industrial Estate, Thailand. The sample was filtered and its pH was adjusted to 4–5. The amounts of metal ions in the sample were determined by FAAS. A spike method was used to evaluate the efficiency of the proposed removal procedure. The filtered wastewater (20.0 mL) of each metal ion (5 mg L^{-1}) was passed through a 0.6 g Si-HA column with a flow rate of 2.0 mL min^{-1}. The amount of each metal ion in the solution was determined by FAAS. This experiment was performed in triplicate. Fresh HA-coated silica was used in each experiment.

3. Results and discussion

3.1. Characterization of the sorbent

The HA and silica products were characterized by FTIR with the KBr pellet method (Fig. 1). The IR bands of carboxyl and phenolic hydroxyl O–H stretching (3,200–3,800 cm^{-1}), aliphatic C–H stretching (2,917, 2,817 cm^{-1}), and aromatic C=C and C=O stretching (1,582 cm^{-1}) were observed in the HA spectrum. The absorption bands of N–H stretching of amino groups (3,300–3,600 cm^{-1}), Si–O vibrations (1,091 cm^{-1}) were observed in the SiAP spectrum. The combination of absorption bands of HA and SiAP was observed in the Si-HA spectrum. This result revealed that the SiAP was successfully coated by HA. The color change from white SiAP to brown Si-HA was visually observed. The amount of coated HA calculated from UV–vis measurement was 147 mg HA/g SiAP. SEM image of Si-HA is shown in Fig. 1 (inset).

3.2. Batch removal

The removal efficiency is reported in terms of removal percentage, as defined in Eq. (1):

$$\text{Removal}\ \ (\%) = [(n_\mathrm{i} - n_\mathrm{f})/n_\mathrm{i}] \times 100 \tag{1}$$

where n_i is the initial amount of the metal (mg), and n_f is the amount of metal in the supernatant (mg).

3.2.1. Effect of pH on metal removal

The influence of pH on the removal efficiency is shown in Fig. 2. The contact time was fixed at 60 min in order to ensure the adsorption equilibrium. When the pH values of solutions increased, the adsorption

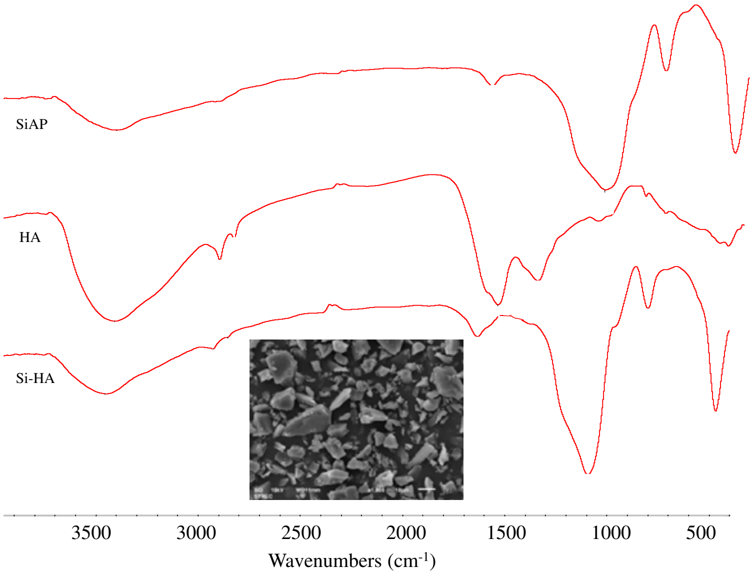

Fig. 1. Infrared spectra of aminopropyl silica (SiAP), HA, and HA-coated on aminopropyl silica (Si-HA), inset: SEM image of Si-HA.

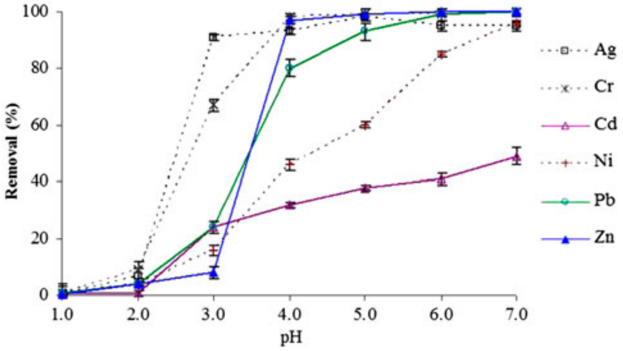

Fig. 2. Effect of pH of metal solutions on metal ion removal by Si-HA (contact time 60 min, *n* = 3).

efficiency of Ag(I), Cd(II), Cr(III), Ni(II), Pb(II), and Zn (II) increased. The maximum sorption capacity of these metal ions onto Si-HA was observed at the pH range of 4–7.

At the pH lower than 3, the carboxylic groups (–COOH) on HA molecules could hardly dissociate [6], and at low pH, hydrogen ions would be in competition with metal ions for the binding sites; as a result, the metal adsorption efficiency was low. When the pH values of solution increased, carboxylic moieties dissociated to carboxylates ($-COO^-$), which are a good electron donor for metal ions, resulting in higher adsorption efficiency. At pH 3, Cr(III) could be extracted better than other divalent cations due to the fact that Cr(III) is a hard Lewis acid that prefers to form complex with the $-COO^-$ moieties. An increase in pH value resulted in an increased removal efficiency. It is possible that the adsorption mechanism of these cations with Si-HA was complexation combined with ion exchange [20].

3.2.2. *Effect of contact time*

The removal efficiencies as a function of contact time are shown in Fig. 3. The contact time required for reaching an adsorption equilibrium was 30 min for all metal ions except for Ni(II). The adsorption equilibrium of Ni(II) was not attained within 60 min. It appears that the removal of Ni(II) by batch methods is not recommended because of the long time required to reach equilibrium.

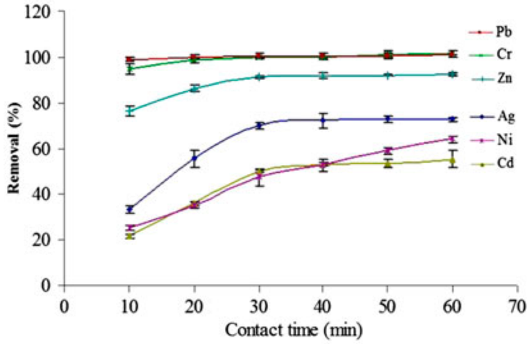

Fig. 3. Effect of contact time on heavy metal ion removal by Si-HA (*n* = 3).

Pseudo-first-order and pseudo-second-order kinetic models were applied to model the kinetics of Ni(II) adsorption, given by Eqs. (2) and (3), respectively:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where q_e is the amount of metal ions adsorbed per gram of sorbent at equilibrium (mmol/g), q_t is the amount of metal ions adsorbed per gram sorbent at any time (mmol/g), k_1 is the pseudo-first-order rate constant (min^{-1}), k_2 is the pseudo-second-order rate constant (g mmol^{-1} min^{-1}), and t is the sorption time (min).

The experimental data of Ni(III) adsorption were fitted with the two kinetic models (Fig. 4). The correlation coefficient (R^2) for the pseudo-second-order model was higher than the value obtained for the pseudo-first-order model. The adsorption mechanism was presupposed to be chemisorption. Similar results were achieved for the adsorption of Cu(II), Cd(II), and Cr(III) using HA-modified Ca-montmorillonite [20].

3.2.3. Adsorption isotherm

The adsorption isotherm was investigated by Langmuir and Freundlich models. The Langmuir model is based on the assumption that a maximum adsorption corresponds to the saturated monolayer of adsorbed species on the sorbent surface [31]. The experimental data reveals that the adsorption behavior follows the Langmuir model, according to Eq. (4):

$$\frac{C}{N_f} = \frac{C}{N_f^s} + \frac{1}{bN_f^s} \tag{4}$$

where C is the concentration of metal ions at equilibrium (mol L^{-1}), N_f is the amount of metal ion per gram of the sorbent (mol g^{-1}), b is the Langmuir constant related to an energy of adsorption (L mol^{-1}), and N_f^s is the maximum amount of metal ions adsorbed per gram of sorbent (mol g^{-1}).

The Freundlich isotherm represents multilayer sorption and can be expressed by Eq. (5) [32]:

$$\log N_f = \log K_F + \frac{1}{n} \log C \tag{5}$$

where n and K_F are Freundlich constants. The values of correlation coefficient (R^2) of the plot of $\log N_f$ vs. $\log C$ i.e. 0.9201, 0.3831, 0.9016, 0.0417, 0.7439, 0.0046 for Ag(I), Cd(II), Cr(III), Ni(II), Pb(II), and Zn(II), respectively, reveal that the adsorption did not fit the Freundlich model.

The results in Fig. 5 show the linearity of the adsorption isotherm derived from the plot of C/N_f as a function of C, indicating that the adsorption isotherm of all metal ions onto Si-HA obeyed the Langmuir model. The calculated parameters, including the maximum sorption capacities (N_f^s), b values, and R^2 from the Langmuir plots are reported in Table 1. The results show that the adsorption of all metal ions on Si-HA fitted the Langmuir model with acceptable R^2 values (>0.93), suggesting that the adsorption of these metal ions onto the surface was in the form of a monolayer [33]. The order of b values is Cd(II) > Zn (II) ≈ Ni(II) > Pb(II) ≈ Cr(III) > Ag(I). The observed b values correspond to a strong binding affinity of metal ions onto Si-HA. The calculated Langmuir maximum sorption capacities order is Cr(III) > Pb(II) > Zn (II) ≈ Cd(II) > Ag(I) ≈ Ni(II). This observation is different from the literature reported for unmodified silica [32] and iron oxide-coated silica [34]. There is also complexation apart from ion exchange.

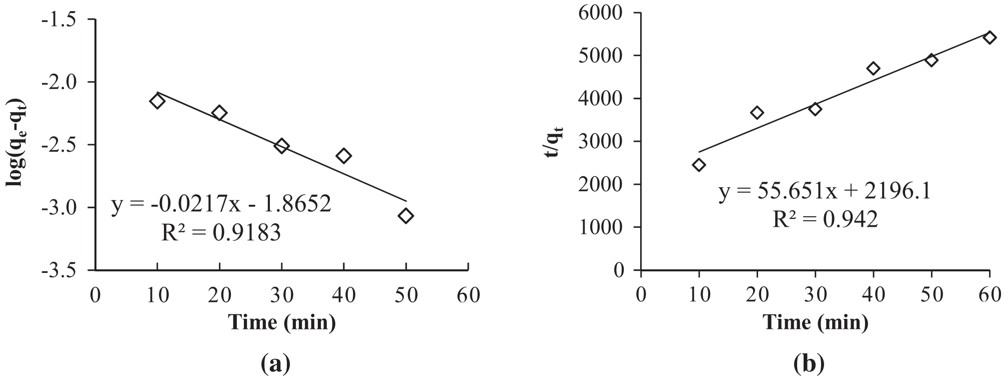

Fig. 4. (a) Pseudo-first-order and (b) pseudo-second-order kinetic plots for Ni(II) adsorption.

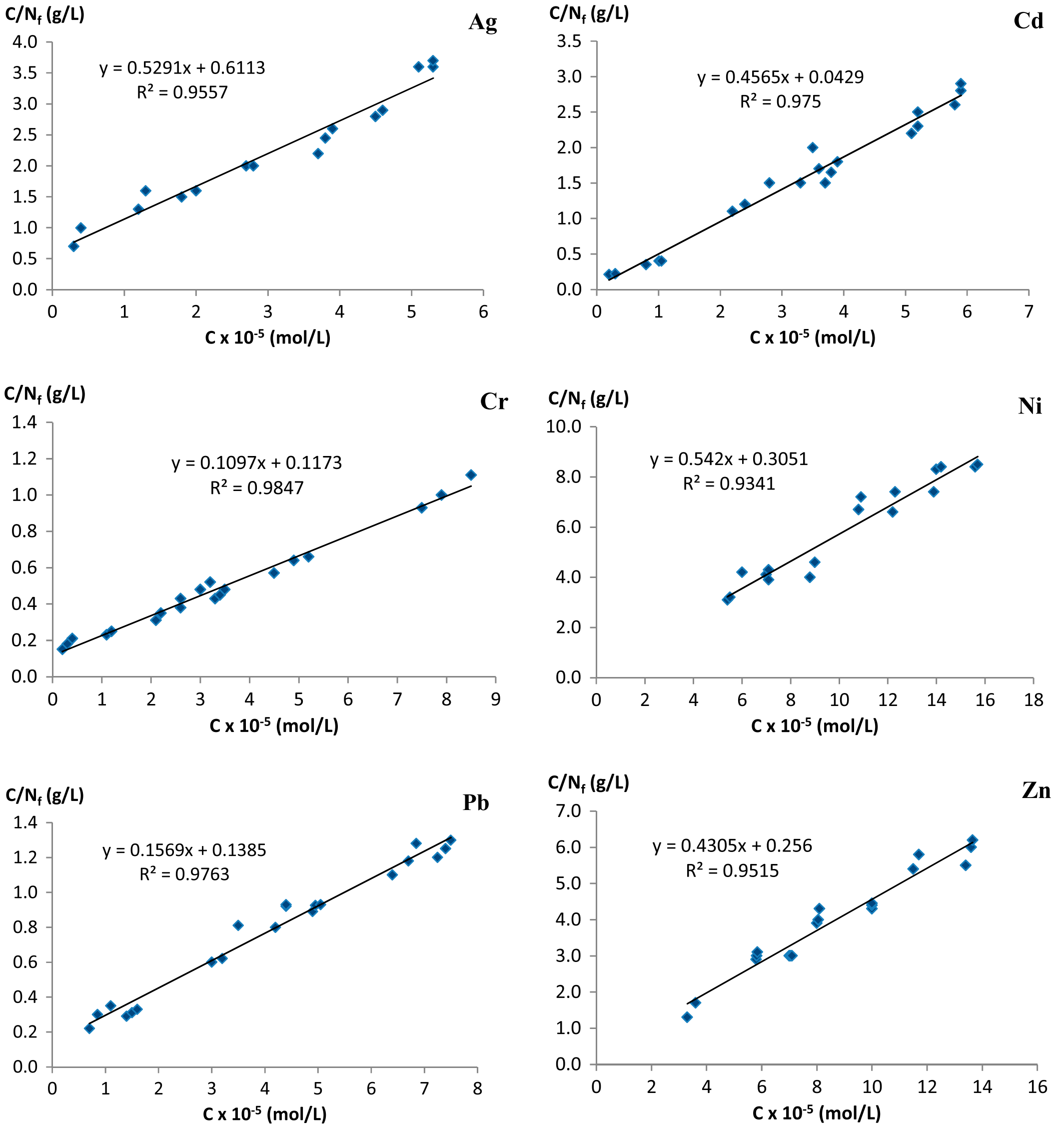

Fig. 5. Langmuir plots of metal ions adsorbed onto Si-HA at 298 K.

Table 1
Fitted parameters of Langmuir isotherm for metal ion adsorption onto Si-HA at 298 K

Metal	N_f^s (mol g^{-1}) ×10^{-5}	b (L mol^{-1}) ×10^4	R^2
Ag(I)	1.89	8.55	0.9557
Cd(II)	2.19	102	0.9750
Cr(III)	9.12	9.35	0.9847
Ni(II)	1.85	17.8	0.9341
Pb(II)	6.37	11.3	0.9763
Zn(II)	2.32	16.8	0.9515

3.3. Column method

3.3.1. Effect of loading flow rate

The loading flow rate of sample should be optimized to ensure quantitative retention along with minimization of the time required for sample processing. The adsorption of metal ions onto Si-HA columns was studied at five flow rates, i.e. 0.5, 1.3, 2.6, 3.5, and 5.0 mL min^{-1}. Fig. 6 shows that the loading flow rate did not affect the removal efficiency. The overall removal percentages were over 98%. The flow rate within the range of 0.5–5.0 mL min^{-1} was

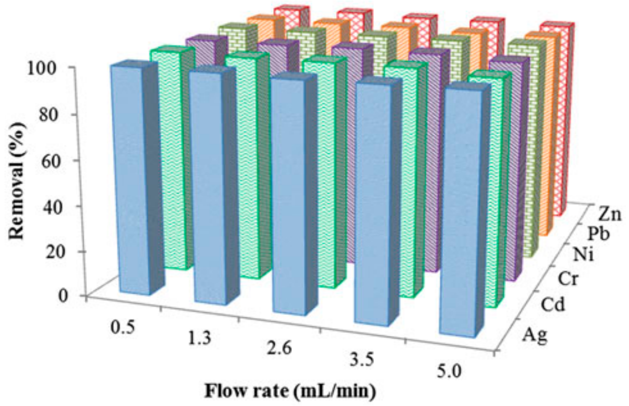

Fig. 6. Effect of sample loading flow rate on removal of 10.0 mg L^{-1} of metal ions onto Si-HA column (1.0 g), pH 5 (*n* = 3).

recommended for maximizing the removal efficiency. However, an optimum flow rate depends on both the initial concentration of metal ions and the amount of sorbent used.

3.3.2. *Effect of sorbent amount*

The amount of Si-HA used was 0.1, 0.3, and 0.6 g. The flow rate was fixed at 3.5 mL min^{-1}. As mentioned earlier, the optimum flow rate depends on the initial concentration of metal ions and the amount of the sorbent used. This flow rate allowed rapid operation with an acceptable efficiency. The results are summarized in Fig. 7.

The sorbent amount of 0.1 g strongly affected the removal efficiency. This could be attributed to the fact that the active sites on Si-HA for metal ions were less than the number of metal ions in the solution. On the other hand, an increase in sorbent amount up to 0.3 and 0.6 g resulted in an increase in removal efficiency due to a larger number of available active sites. Moreover, it was observed that, when there is a limited number of active sites (in case of 0.1 g Si-HA), Cr(III), Pb(II), and Zn(II) could be adsorbed onto Si-HA better than Cd(II) and Ag(I). This trend is in agreement with the maximum sorption capacity order mentioned above.

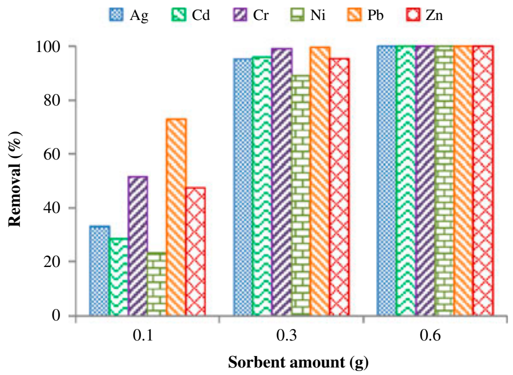

Fig. 7. Effect of sorbent amount on metal ion removal (*n* = 3): initial concentration = 10 mg L^{-1} (20 mL).

3.3.3. *Effect of interfering ions*

The presence of interfering ions in water samples may cause problems when employing the adsorbent. In particular, due to their usually high levels, they may compete with target metal ions. Cations and anions used in this study were chosen from their major abundance in wastewater, such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^- and SO_4^{2-}. The experiments were performed with three concentrations (10, 100, and 1,000 mg L^{-1}).

Most of the interfering ions hardly affected the efficiency of adsorption of the metal ions. For Ag(I), chloride ions strongly affected its adsorption efficiency, probably due to the formation of AgCl. For other metal ions, the results indicated that all interfering ions did not affect their adsorption. It could be explained that the target metal ions can coordinate with the carboxyl and/or phenolic functional groups of HA, while alkali and alkali-earth interfering ions cannot form complexes with HA. Moreover, it seems that the adsorption of heavy metal ions via complexation is likely to occur rather than ion exchange [7,8,28–30].

3.3.4. *Elution study*

The elution of adsorbed metal ions was studied at five flow rates i.e. 0.5, 1.3, 2.6, 3.5, and 5.0 mL min^{-1}. The loading flow rate of all the metal solutions was 2.0 mL min^{-1}. The demonstration of elution was done using 10% (v/v) HNO_3 based on the fact that protons from the acid could displace the adsorbed metal ions and interrupted the chelation of metal ions with HA. The result shows that the elution flow rate did not affect the elution efficiency. The elution percentages of all divalent ions were close to 100%, while those of Ag (I) and Cr(III) were 80 and 90% at every flow rate, respectively.

Unfortunately, a strong acidic solution is harmful for silica and silica-based materials. This elution condition is only recommended for disposal purpose of the used sorbent. For this reason, fresh HA-coated silica should be used in the adsorption process.

Table 2
Comparison of adsorption efficiency with various types of previous published adsorbents

Adsorbent	Metal ions	Sorption capacity (μmol/g)	Applications B = batch method C = column method	Refs.
Activated alumina powder	Cr, Ni, Cu	6.01, 2.66, 1.97	B/bench scale	[35]
Aminopropyl-silica	Ni	1	B/bench scale	[36]
Activated sludge biomass	Cu, Cd, Pb	478, 358, 280	B/bench scale	[37]
Cationic exchange resin (ceralite IR 120)	Cu, Ni, Zn	2,581, 1,857, 1,606	B & C/bench scale	[38]
Harboxymethylcellulose-based hydrogel	Cu, Pb	960, 270	B/bench scale	[39]
Castor hull	Cd	62	B/bench scale	[40]
Modified cashew nut shell	Cu, Cd, Zn, Ni	6,399, 3,879 6,970, 7,775	B/bench scale	[41]
Modified rice husk	Cr^{VI}, As^{V}	Not available	B/bench scale	[42]
Silica modified by humin extracted from Sphagnum peat moss	Cd, Cu, Ni Pb, Cr	5.3, 63, 100 4.5, 131.1	C/bench scale	[43]
Magnetite nanoparticles	Pb, Cr	16.6, 61.4	B/bench scale	[44]
Si-HA	Ag, Cd, Cr, Ni, Pb, Zn	18.9, 21.9, 91.2, 18.5, 63.7, 23.2	B & C/bench scale	This work

3.4. Application to real sample

The proposed method was applied for the removal of heavy metal ions using Si-HA columns. Based on the previous study, the selected flow rate of 3.5 mL min^{-1} could not be operated for the real wastewater, probably due to the clogging of the column caused by the dissolved matters in the sample. Therefore, the flow rate of 2.0 mL min^{-1} was applied. The removal percentages of all metal ions in wastewater were close to 100%. These results showed a great potential application of the Si-HA sorbent for the metal ion removal from real wastewaters. Furthermore, the elution of metals from the column was performed, and it was observed that the elution efficiency using 10% (v/v) HNO_3 was higher than 93%.

3.5. Comparison with existing adsorbents

The performance of the prepared Si-HA sorbent was compared with other sorbents in terms of adsorption efficiency and applications, as shown in Table 2. It seems that biosorbents show higher maximum sorption capacity towards metal ions, but they have less ability for the simultaneous sorption of several ions in solution, unlike some inorganic-based sorbents. In comparison with activated alumina powder [35], aminopropyl-silica [36], and silica modified by humin extracted from Sphagnum peat moss [43], our Si-HA shows higher adsorption capacity, especially for Ag(I), Cd(II), Pb(II), and Zn(II). Thus, the prepared Si-HA presented in this work is a promising sorbent for the simultaneous removal of metal ions.

4. Conclusions

HA-coated aminopropyl silica gel (Si-HA) with the loading of 147 mg g^{-1} was successfully prepared and used for the removal of Ag(I), Cd(II), Cr(III), Ni(II), Pb (II), and Zn(II) from wastewater. The optimal pH, contact time, and adsorption capacities of 18.9, 21.9, 91.2, 18.5, 63.7, 23.2 μmol g^{-1} for Ag(I), Cd(II), Cr(III), Ni(II), Pb(II), and Zn(II), respectively, were achieved. Suitable conditions for the adsorption of metal ions were obtained by using a column system. Removal percentages of almost 100% and elution percentages ranging from 80 to 100% using 10% (v/v) HNO_3 were achieved. In addition, sodium, potassium, calcium, chloride, nitrate, and sulfate ions with high concentrations up to 5 g L^{-1} did not affect the adsorption efficiencies. The proposed method is uncomplicated, easy to operate, and suitable for heavy metal removal from wastewater, especially wastewater with a high salt content.

Acknowledgments

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