

Reuse of waste silica as adsorbent for metal removal by iron oxide modification

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Abstract

Silica gel is widely used in research laboratories, especially for the purification of organic compounds. Consequently, waste silica gel is generated in increasing amounts. In this work, waste silica was modified by coating its surface with iron oxide aiming to obtain an effective adsorbent for metal removal from wastewater. In the preparation of the adsorbent, the optimal pretreatment temperature and iron concentration were investigated. The coated waste silica was characterized for BET surface area, pore size, specific pore volume and iron content. Iron oxide-coated waste silica was tested for the adsorption of Pb(II), Cu(II), Cd(II) and Ni(II) from solutions in a batch system. The effect of contact time, pH and salt concentration on metal adsorption was investigated. It was found that the adsorption of metals occurred rapidly and reached equilibrium within 30 min. The pH suitable for metal adsorption was between 6 and 7 and leaching of iron from the coating was observed only at pH 3 or lower. The presence of salt reduced the adsorption efficiency of the adsorbent. The adsorption behavior followed both Langmuir and Freundlich isotherms (25 °C). Finally, the efficacy of the adsorbents was investigated using aqueous lab waste where removal efficiencies ranging from 62 to 89% were achieved when the initial metal concentrations ranged from 13 to 42 mg L⁻¹.

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1. Introduction

Following the growing activities of research and education, the amount of waste generated from laboratories has been increasing, especially chemical wastes, e.g. organic solvents, toxic metal waste and solid waste. These waste products are often hazardous and need to be treated before disposal. To reduce waste treatment expenses, certain waste products can be recycled or reused. In this study, waste silica gel from chemical laboratories was reused to produce a low-cost adsorbent for metal adsorption. In general, many adsorbents can be used for metal removal from water. In particular, low-cost adsorbents have drawn much attention and a significant amount of research has been carried out using such

materials [1]. In this study, we are interested in modifying waste silica gel with iron oxide for use in metal adsorption.

Iron oxide precipitates have relatively high surface area and surface charge. They have been used in water treatment as flocculants for organic compounds and in metal removal, often in the form of hydroxide compounds [2]. The use of iron oxide powder for metal removal has also been investigated [3–5]. However, the use of iron oxide powder is limited by difficulties in solid/liquid separation. The oxides alone are not suitable for use as a filter medium due to their low hydraulic conductivity. To overcome these problems, different media have been used as supports for iron oxide coating such as sand [6–12], polymeric materials [13] and cement [14]. These research investigations demonstrated that iron oxide coated media were able to remove metals from water. Recently, high surface area materials (e.g. clay, zeolites and activated carbon) were also used for iron oxide coating [15–17].

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Silica gel is an adsorbent widely used in the purification and separation of organic mixtures due to its adsorption properties, high surface area and porosity. Relatively little research has been carried out using silica gel as a support for iron oxide. Recently, Zeng [18] proposed a method for preparing a silica-containing iron(III) oxide adsorbent. Their synthesis was based on the *in situ* generation of a hydrous ferric oxide sol and silica sol, and the resulting adsorbent was used to remove arsenic from water. Xu and Axe [19] have also studied conditions for preparing iron oxide-coated silica. In this case, the silica supported adsorbent showed a greater affinity for Ni(II) compared to uncoated silica. To our knowledge, waste silica gel has never been used as a support for iron oxide for metal removal from wastewater.

In this work, waste silica coated with iron oxide was prepared and characterized. The prepared adsorbents were tested in adsorption studies of Cu(II), Pb(II), Cd(II) and Ni(II). The effect of contact time, pH and the presence of salt on metal adsorption was investigated. Finally, the adsorbents were studied for their ability to remove metals from aqueous lab waste.

2. Materials and methods

Waste silica gel (0.063–0.2 mm in diameter) was collected from synthetic organic laboratories. The silica gel 60 (Merck) having pore volume of 0.74–0.84 mL g⁻¹ and a specific surface area of 480–540 m² g⁻¹ was used for column chromatography to purify and separate organic substances. The waste silica from column chromatography was dried at room temperature to remove residual organic solvents before sampling. Fe(NO₃)₃·9H₂O was purchased from Carlo Erba Reagenti (Rodano). Cu(NO₃)₂, Pb(NO₃)₂, 3CdSO₄·8H₂O and Ni(NO₃)₂·6H₂O were obtained from Merck (Germany). The metal solutions used for adsorption experiments were prepared by dissolving the appropriate metal salt in de-ionized water without adjusting pH. The analytical standard solutions for metal determination by atomic absorption spectrometry were prepared by stepwise dilution of 1000 mg L⁻¹ stock standard solutions from BDH Laboratory Supplies (England). The pH of the solutions was adjusted to the desired value using either NaOH or HCl solutions. All reagents were analytical grade and used without further purification. The iron oxide-coated silica was characterized for specific surface area by using a surface area analyzer (Thermo Finnigan, Sorptomatic 1990). An X-ray fluorescence spectrometer (Philips, PW 2400) was used to demonstrate the presence of iron on the surface of the silica. The iron content on the adsorbent was also determined by acid digestion followed by determination the concentration of iron using flame atomic absorption spectrometry (FAAS) (Perkin-Elmer, Analyst 100). Silica (0.04 g) was added to 10 mL concentrated HCl before adding 10 mL concentrated HF. The mixture was heated to dryness. Then, HF was added (ca. 30 mL) to ensure complete dissolution of silica and the mixture was heated to dryness. Ten milliliters of a HCl/HNO₃ solution (6:1 v/v) was added to the residue and the mixture was heated to dryness. Finally, the residue was dissolved in 5 mL HCl (6 M) and the volume was adjusted to 50 mL with de-ionized water. The final solution was

analyzed for iron concentration by FAAS at an analytical wavelength of 248.3 nm.

2.1. Preparation of iron oxide-coated waste silica

The adsorbent preparation method used in this study was based on the coating method proposed by Meng and Letterman [20]. Waste silica was collected from synthetic organic laboratories and treated at the specified pretreatment temperature before coating. The coating was performed by adding 5 g of waste silica to 25 mL of solution containing 0.5 g Fe(NO₃)₃·9H₂O (0.28%, w/v Fe). The pH of the mixture was increased to 7.0 ± 0.5 with NaOH. The mixture was stirred for 1 h and the solid was separated and washed with de-ionized water until the pH of the runoff was constant (pH 6–7). The resulting solid was dried at 80 °C for 10 h prior to treatment at a coating temperature of 550 °C for 6 h. The solid was finally stored in a closed plastic bottle for further use.

2.2. Adsorption experiments

The adsorption experiments were carried out using a batch method. A 0.25 g of coated silica gel was added to 25 mL of solution containing metal ions (Cu(II), Cd(II), Ni(II)). In the case of Pb(II) adsorption, an adsorbent dose of 0.10 g was used. The initial concentration of metals was 40 mg L⁻¹ except for Pb (50 mg L⁻¹). In the adsorption isotherm study, a concentration range of 20–80 mg L⁻¹ and temperature of 25 °C were used. The mixtures were shaken at 160 rpm for 30 min at room temperature and the solid was then separated by centrifugation. The solutions were analyzed using a flame atomic absorption spectrometer to determine the residual metal concentration. The analytical wavelengths of Cd, Cu, Pb and Ni were 228.8, 324.8, 283.3 and 232.0 nm, respectively. The pH of the solutions was monitored before and after adsorption. The initial pH of the metal solutions ranged from 5.5 to 5.7, except for the study of the effect of pH. It was observed that the pH of the solutions after addition of the adsorbent was between 5.5 and 6.0 for Pb and Cu solutions and between 6.0 and 7.0 for Cd and Ni solutions. In this pH range, precipitation of metal hydroxides is unlikely. Detachment of the iron oxide coating was not observed during adsorption experiments. All adsorption experiments were carried out in triplicate.

3. Results and discussion

3.1. Preparation of iron oxide-coated waste silica

In the preparation of adsorbents, the effect of waste pretreatment and initial iron concentration was investigated. Waste silica from a synthetic organic laboratory was pretreated in an oven under different conditions: 100 °C for 24 h or 500 °C for 3 h. A black carbonaceous residue was found in the waste after a pretreatment at 500 °C and was removed by sieving prior to coating and adsorption experiments. Furthermore, different initial concentrations of Fe were used in the coating process. The initial concentration was varied within the range of 0.06–1.11% (w/v). The effect of coating parameters was evaluated by comparing

Table 1
Effect of silica waste pretreatment and initial concentration of Fe on adsorption capacity for Cu(II)

Parameters	Adsorption capacity for Cu(II) (mg g ⁻¹) ^c	
	Uncoated waste silica	Coated waste silica
Waste pretreatment ^d		
No pretreatment	0.36 ± 0.10	0.89 ± 0.10
Pretreatment at 100 °C (24 h)	0.42 ± 0.08	1.11 ± 0.06
Pretreatment at 500 °C (3 h)	0.51 ± 0.06	2.27 ± 0.21
Initial Fe concentration (% w/v) ^b		
0.00		0.84 ± 0.20
0.06		1.62 ± 0.03
0.14		2.36 ± 0.15
0.28		2.38 ± 0.32
0.55		2.73 ± 0.25
1.11		2.50 ± 0.29

^a A 0.28% (w/v) Fe was used in the coating.

^b Waste silica was pretreated at 500 °C for 3 h before coating.

^c Mean ± S.D. (n = 3).

adsorption capacities for Cu(II) and the results are shown in Table 1.

It was found that the iron oxide-coated waste silica can adsorb Cu(II) to a larger extent than the uncoated silica. Regarding the pretreatment, a slight increase in metal adsorption of the uncoated waste was observed in the silica pretreated at both 100 and 500 °C compared to silica without high temperature pretreatment. Moreover, when the waste silica was coated with iron oxide, its adsorption efficiency for Cu(II) increased significantly with increasing treatment temperature. The adsorbent obtained from coating the waste silica pretreated at 500 °C had higher adsorption efficiency than either the waste silica pretreated at 100 °C or the untreated waste silica. It is believed that the thermal pretreatment removes volatile substances and organic residue on the waste silica gel thus increasing the available active sites for coating. To obtain higher adsorption efficiencies, the thermal pretreatment of waste silica was desirable and pretreatment at 500 °C for 3 h was chosen for the remaining studies.

An increasing concentration of Fe within the range of 0.06–0.28% (w/v) leads to an increase in adsorption efficiency and the efficiency remains constant at higher initial Fe concentrations. The adsorbents prepared by using different concentrations of ferric nitrate were analyzed by X-ray fluorescence spectroscopy (XRF) for iron oxide content. It was found that the %Fe₂O₃ on the adsorbent increased from 0.63 to 2.02% (w/w) with increasing Fe concentrations from 0.06 to 0.28% (w/v) and no significant change in %Fe₂O₃ was observed at higher Fe concentrations. The adsorption capacity is also relatively constant when these concentrations of ferric nitrate were used. Therefore, it was concluded that the adsorption efficiency of Cu(II) is likely related to the iron oxide content on the adsorbents.

3.2. Properties of iron oxide-coated waste silica

The chosen conditions for the coating were 0.28% (w/v) Fe (pH 7.0 ± 0.5) and the waste silica was pretreated at 500 °C

Table 2
Properties of uncoated and coated waste silica

	Uncoated waste silica	Coated waste silica
Fe (mg Fe g ⁻¹)	0.2 ^a	8.91 ^b
Specific surface area (m ² g ⁻¹) ^c	353	236
Pore specific volume (cm ³ g ⁻¹)	0.56	0.62
Pore range (Å)	36–48	64–84

^a Measured by X-ray fluorescence spectroscopy (XRF).

^b Obtained by acid digestion followed by determination of the concentration of Fe by FAAS.

^c Measured by multipoint BET.

before use. The properties of the resulting coated silica are summarized in Table 2.

The properties of the coated waste silica are clearly different from the uncoated waste silica. The coating leads to a change in specific surface area and pore size while no significant difference in pore specific volume was observed. The coated silica had an average pore size larger than that of the uncoated silica and thus, its specific surface area was smaller. A change in the average pore size range is likely due to the iron oxide coating. The iron oxide possibly blocks certain pores of the silica support, in particular small diameter pores, and thus the surface of the silica was modified. Consequently, the size of the pores in the coated silica is expected to be larger, on average, than that of the uncoated silica. The elimination of the smaller pores upon coating results in a decrease in overall surface area. Scheidegger et al. [7] demonstrated that the experimental surface area of the goethite coated silica sand can be estimated by the theoretical sum of the surface areas of the pure silica sand and the corresponding weight fraction of goethite. Regarding the iron oxide coating in this study, iron oxide (hematite) was reported to exhibit a surface area in a range of 42.5–67.5 m² g⁻¹ [21,22]. When compared to waste silica, its surface area is much lower than that of the uncoated waste silica (353 m² g⁻¹). This demonstrates that when the iron oxide was coated on the silica support, the surface area of the resulting adsorbent decreases. On the other hand, Xu and Axe [19] reported that the coating of iron oxide on the surface of pure silica gel of larger particle size (0.9 mm) leads to an increase in specific surface area. This suggests that change in surface area as a result of the coating is likely related to the initial particle size of the silica. This is in agreement with what was reported by Kitis et al. [23] who found that the change in surface area of iron coated pumices depended on the particle size of the adsorbent media. A reduction in surface area was observed when small particle size pumices were used while an increase in surface area was achieved when using large particle size pumices.

Despite the reduction in surface area, the adsorption efficiency of the coated waste silica for metals was higher than that of the uncoated waste silica. The increase in adsorption efficiency is believed to be due to the presence of iron oxide on the adsorbent surface. The interactions between iron oxide and the silica surface potentially involve electrostatic, van der Waals and/or chemical bonds [7,19]. Regarding the pH used in the coating process (pH 7.0), it is likely that the attachment of goethite

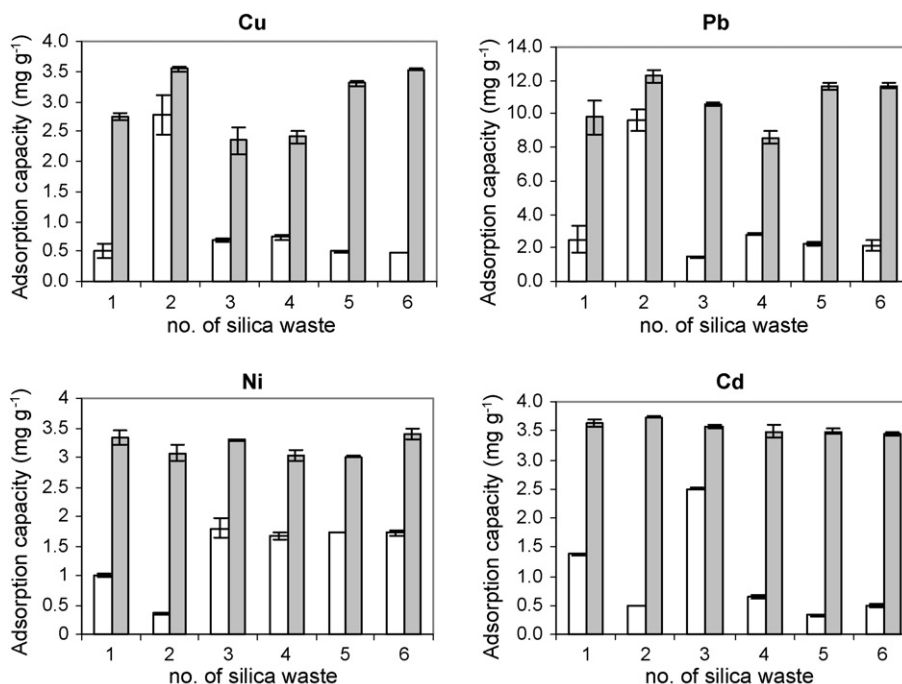


Fig. 1. Adsorption capacity of uncoated (white bar) and coated (grey bar) silica waste from different laboratories.

on the silica surface is due to electrostatic interactions ($\text{pH}_{\text{PZC}} \text{ silica} = 2.85$, $\text{pH}_{\text{PZC}} \text{ goethite} = 8.78$ [19]). When the obtained adsorbent was exposed to a coating temperature of 550°C , the form of iron oxide was possibly transformed to hematite. In an attempt to identify the form of iron oxide, the adsorbents were analyzed by X-ray diffraction spectrometry (XRD). Only silica was observed in the XRD patterns as a broad peak at $20\text{--}30^\circ 2\theta$. Furthermore, iron oxide was prepared in the same way as the adsorbent without adding waste silica gel. The oxides alone were analyzed by XRD and confirmed to be hematite (Fe_2O_3) as observed in the XRD pattern at 24.1° , 33.1° , 35.6° , 40.8° , 49.4° and $54.0^\circ 2\theta$.

3.3. Coating of waste silica gel from different sources

In order to investigate the consistency of the coating method, waste silica from different organic chemistry laboratories was collected and used to prepare adsorbents. In all cases, the silica gel was first used for column chromatography. The extent of organic residues left on silica gel was probably different depending on the laboratory. The particle size of the silica gel was in the range of $0.063\text{--}0.2$ mm in diameter. The waste silica was pretreated at 500°C before coating process. The metal adsorption capacity of coated waste silica from different sources is presented in Fig. 1.

The results show that the coating helps increase the adsorption efficiency of silica gel for Cu(II), Pb(II), Cd(II) and Ni(II). Moreover, the degree of increasing adsorption capacity seems to be dependent on the source of waste silica and type of metal ion. The coated waste silica from six sources had adsorption capacities for Cu(II), Pb(II), Cd(II) and Ni(II) in the range of $2.37\text{--}3.54$, $8.57\text{--}12.24$, $3.45\text{--}3.73$ and $3.01\text{--}3.39$ mg g^{-1} , respectively. On

the other hand, Tran et al. [24] demonstrated using Langmuir isotherms that unmodified non-waste silica gel ($0.2\text{--}0.5$ mm in diameter) had adsorption capacities of 0.52 , 1.86 , 0.66 and 0.45 mg g^{-1} for Cu(II), Pb(II), Cd(II) and Ni(II), respectively. The results obtained in this study indicate that the iron oxide-coated waste silica has higher metal adsorption capacity than those of non-waste and waste silica gel. By using the proposed coating method, the results suggest that waste silica can potentially be used in metal removal from waste water. The parameters of metal adsorption were investigated further and are described below.

3.4. Effect of contact time on metal adsorption

The adsorption experiments were carried out using contact times ranging from 5 to 60 min and the results are shown in Fig. 2. It was observed that metal adsorption occurred rapidly. The adsorption efficiency of Pb(II) increased gradually with increasing contact times up to 30 min and reached a plateau afterwards. On the other hand, there was no change in adsorption efficiency for Cu(II), Cd(II) and Ni(II) between 15 and 60 min of contact time. Thus, for the adsorption study of these metal ions, a contact time of 30 min was used as the equilibration time.

3.5. Effect of pH on metal adsorption and iron leaching

To study the effect of pH on metal adsorption, the initial pH of metal solutions was varied between 1 and 7 for Cd(II) and Ni(II) solutions and between 3 and 6 for Cu(II) and Pb(II) solutions. At these pH values, the precipitation of metal hydroxide was unlikely. The measurement of pH at equilibrium was carried out after 30 min of contact time. It was observed that the pH

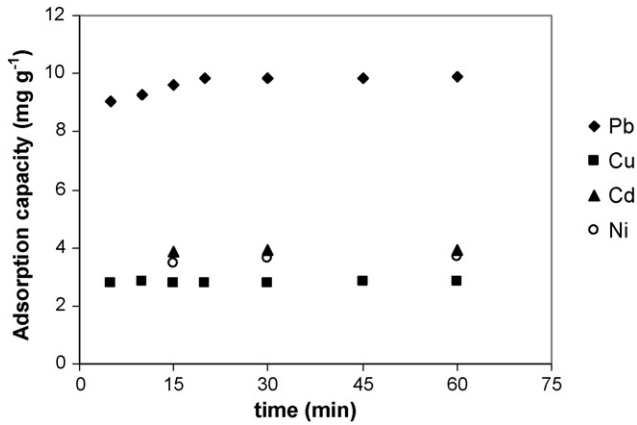


Fig. 2. Effect of contact time on metal adsorption.

at equilibrium changed only slightly when the initial pH was 1 and 2 but increased to between 4.6 and 5.0 when the initial pH of the solution was 3. At initial pH values higher than 4, the pH at equilibrium increased to between 6.0 and 6.5 for Pb(II) and Cu(II) and between 7.0 and 7.5 for Cd(II) and Ni(II). It is possible that the increase in pH is due to the dissolution of base, which was left on the adsorbent after the preparation. A plot of adsorption capacities as a function of pH at equilibrium is presented in Fig. 3. The leaching of iron from the coating into the solution was also investigated by measuring dissolved iron concentration in the metal solution after contact with the adsorbent.

The adsorption of metals was not observed at very low pH (between 1 and 2). On the other hand, the adsorption efficiency increased rapidly upon increasing the pH at equilibrium from 4 to 5 and increased gradually afterwards. When the pH attained a value of 7, there was no difference in adsorption efficiencies for Cd(II) and Ni(II). The increase in adsorption efficiencies observed as the pH increased can be attributed to the favorable change in surface charge and to the extent of hydrolysis of metal ions [5]. Upon increasing the pH of the solution, the surface charge becomes more negative and attracts metal cations resulting in higher adsorption efficiencies. At very low pH, the surface charge of the iron oxide and silica gel would probably be pos-

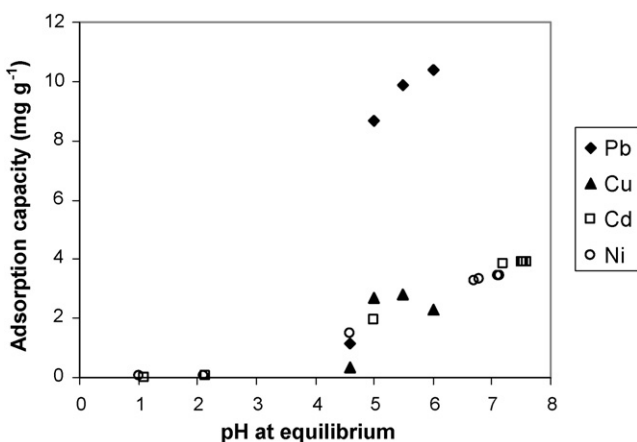


Fig. 3. Effect of pH on metal adsorption capacity.

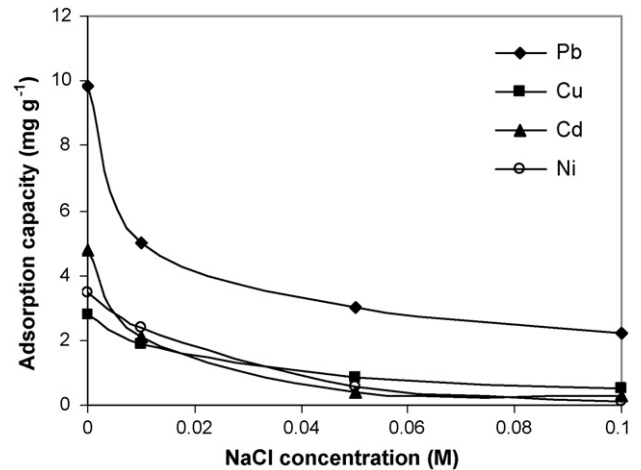


Fig. 4. Effect of salt concentration on metal adsorption of iron oxide-coated waste silica.

itive ($\text{pH}_{\text{PZC}} \text{ silica} = 2.85$ [19], $\text{pH}_{\text{PZC}} \text{ hematite} = 7.0\text{--}9.4$ [21]). Therefore, metal ions are less likely to interact with the surface *via* electrostatic interactions. The optimal pH suitable for metal adsorption was determined to be between 6 and 7.

The leaching of iron from the coating was observed when the initial pH was 3 and lower. An iron concentration of 0.20 mg L^{-1} was observed in Cu(II) and Pb(II) solutions with an initial pH of 3. When the initial pH of the metal solution was 1 and 2, the concentration of iron found in solution was 24 and 12 mg L^{-1} , respectively. A major leaching of iron at pH 1 and 2 also explains the low adsorption of metal ions at these pH values.

3.6. Effect of salt concentration on adsorption capacity

In water, salt is present in a wide range of concentrations depending on the source and the quality of the water. The presence of salt or co-ions in solution can affect the adsorption of metal ions onto a charged surface. In this study, the effect of salt concentration on adsorption capacity was also investigated. NaCl was chosen and added to the metal solutions at concentrations of 0.01, 0.05 and 0.10 M. The results are shown in Fig. 4.

Metal adsorption capacity decreased markedly in the presence of 0.01 M NaCl. Higher salt concentrations resulted in a decrease in adsorption capacity of the adsorbent. This is in agreement with results reported by Cristenti and Sverjensky [25] in their investigation of the role of electrolyte anions (ClO_4^- , NO_3^- , Cl^-) in divalent metal adsorption on oxide and hydroxide surface in salt solutions. It was observed in most cases that in NaCl solutions, metal adsorption decreased with increasing ionic strength. In this study, it is possible that Na ions present at a high concentration compared to metal ions probably compete with metal cations for adsorption sites on the surface. This results in a decrease in metal removal from solution. The results reveal that this adsorbent is suitable for metal removal from water containing low salt concentrations such as those found in natural water.

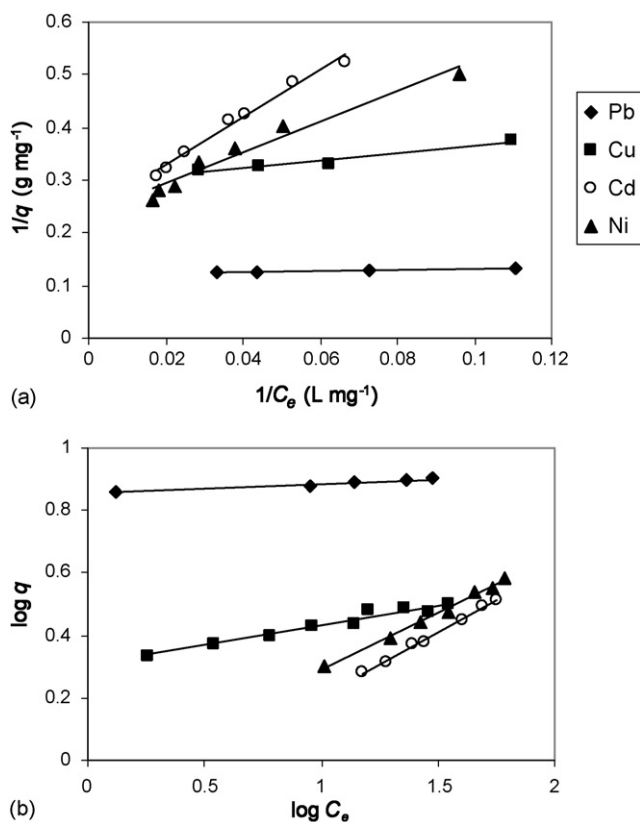


Fig. 5. Langmuir (a) and Freundlich (b), adsorption isotherms for adsorption of metals by iron oxide-coated waste silica (25 °C).

3.7. Adsorption isotherms

The distribution of metal ions between the liquid and solid phase at equilibrium can be expressed by adsorption isotherms. In this study, Langmuir and Freundlich isotherms were implemented. The Langmuir and Freundlich plots are displayed in Fig. 5. The Langmuir relation assumes monolayer sorption onto the homogeneous surface with a specific number of equivalent sites and can be expressed as:

$$\frac{1}{q} = \frac{1}{q_m} + \left(\frac{1}{bq_m} \right) \left(\frac{1}{C_e} \right) \quad (1)$$

where C_e is the solute concentration at equilibrium (mg L⁻¹), q the adsorption capacity at equilibrium (mg g⁻¹), q_m the maximum adsorption capacity (mg g⁻¹) and b is the Langmuir constant related to binding energy of the sorption system. The values of q_m and b can be calculated from the intercept and the slope of the linear plot of $1/q$ versus $1/C_e$, respectively. The Langmuir constants are presented in Table 3.

The Freundlich isotherm represents multilayer sorption and can be expressed as:

$$\log q = \log K_f + \left(\frac{1}{n} \right) \log C_e \quad (2)$$

where n and K_f are Freundlich constants. The values of $1/n$ and K_f (Table 3) were obtained from the slope and the intercept of the linear plot of $\log q$ versus $\log C_e$, respectively.

Table 3

Langmuir and Freundlich constants for adsorption of metals by iron oxide coated waste silica (25 °C)

Metal	Langmuir constants			Freundlich constants		
	q_m (mg g ⁻¹)	b (L mg ⁻¹)	R^2	K_f	n	R^2
Pb	8.18	1.33	0.9929	7.12	30.95	0.9682
Cu	3.39	0.37	0.9670	2.01	7.94	0.9564
Cd	4.23	0.05	0.9851	0.62	2.43	0.9980
Ni	4.25	0.08	0.9557	0.84	2.75	0.9936

The results show that the adsorption of metals can be described by both Langmuir and Freundlich isotherms ($R^2 > 0.95$). It is possible that the concentration range used in this study (20–80 mg L⁻¹) is in the monolayer regime. A higher concentration range could be used to differentiate both adsorption models. However, both Langmuir and Freundlich constants indicate that the adsorption of Pb(II) onto the adsorbent is more favorable than Cu(II), Ni(II) and Cd(II). Lai and Chen [11] also found that, by using Langmuir isotherm, the equilibrium constant of Pb(II) adsorption onto iron oxide-coated sand was higher than that of Cu(II). The metal affinity order (Pb(II) > Cu(II) > Ni(II) > Cd(II)) observed in this study was not in agreement with the electronegativity order or hydrated radii (R_H) order of these metal ions (electronegativity Pb(II) = 1.80, Cu(II) = 1.90, Ni(II) = 1.91, Cd(II) = 1.69 [26] and R_H in Å (number of waters of hydration) Ni(II) = 2.06 (6.0), Cu(II) = 1.96 (equatorial) and 2.30 (axial) (6.0), Cd(II) = 2.30 (6.0) [27]). Nevertheless, Tran et al. [24] studied the metal adsorption of unmodified silica gel and observed the same metal affinity trend (Pb(II) > Cu(II) > Ni(II) > Zn(II) > Cd(II)) which was explained by the free energy change of metal ion–silica gel reactions (Cu(II) > Zn(II) \approx Ni(II) \approx Cd(II)). On the other hand, Schwertmann and Taylor [28] showed that metal affinity order for goethite followed Cu(II) > Pb(II) > Zn(II) > Cd(II) > Co(II) > Ni(II) > Mn(II) which is consistent with the electronegativity trend, while Christophi and Axe [29] observed a metal affinity order Pb(II) > Cu(II) > Cd(II) which is in agreement with the hydrated radii trend (R_H Pb(II) < Cu(II) < Cd(II)). The results observed in this study showed that the metal affinity order for iron oxide-coated media is different from that observed on goethite. It is believed that the difference can be attributed to a difference in surface characteristics of the adsorbent. The adsorbents prepared in this study were composed of both silica and iron oxide, which may exhibit different surface characteristics from pure silica and pure iron oxide.

The adsorption capacities (mmol g⁻¹) observed in this study were 0.039, 0.053, 0.038 and 0.072 mmol g⁻¹ for Pb(II), Cu(II), Cd(II) and Ni(II), respectively. The adsorption capacity order followed Ni(II) > Cu(II) > Pb(II) \approx Cd(II) which is in agreement with the hydrated radius (R_H) order of these cations (R_H Ni(II) < Cu(II) < Cd(II)). On the other hand, Christophi and Axe [29] reported that metal capacity on the goethite surface was found to increase with metal electronegativity. This difference is possibly attributable to the difference in adsorbent properties (e.g. surface characteristics) and experimental conditions.

Table 4
Removal of metal ions from water

Metal	Initial concentration (mg L ⁻¹)	Final concentration (mg L ⁻¹)	Removal (%)
Pb	22.7	2.4	89.4
Cu	13.1	2.2	83.2
Cd	35.2	5.5	84.4
Ni	42.5	16.3	61.6

Conditions: adsorbent dose 0.25 g for Cu(II), Cd(II), Ni(II) removal and 0.10 g for Pb(II) removal (25 mL of solution), contact time 30 min at room temperature.

3.8. Application to water treatment

The prepared adsorbents were tested for the treatment of aqueous waste containing each metal ion from a laboratory. The pH of the aqueous waste was between 2.2 and 2.5 and was raised to approximately 5.5–7 prior to the adsorption experiments. The initial metal concentrations and the residual metal concentrations were determined by using FAAS. The percent metal removal is summarized in Table 4.

The results show that 62–89% of metals were removed from the aqueous lab waste. The adsorption capacity was found to be 4.41, 1.05, 2.98 and 2.61 mg g⁻¹ for Pb(II), Cu(II), Cd(II) and Ni(II), respectively. These are significantly lower than the q_m values reported in Table 3. This is probably because of the presence of co-ions (e.g. Na⁺) which are present in the wastewater and from the pH adjustment step. To obtain better removal efficiencies, higher adsorbent doses are recommended.

4. Conclusion

This research demonstrates a preparation method for coating waste silica gel with iron oxide for use in metal removal. The preparation parameters studied included the silica waste pre-treatment temperature and the initial concentration of iron. The results show that the coated waste silica had higher adsorption efficiencies for metal ions (Pb(II), Cu(II), Cd(II) and Ni(II)) than the uncoated waste silica. Moreover, the parameters of metal adsorption were investigated. It was found that the optimal pH suitable for metal removal is between 6 and 7 and the presence of salt decreases the removal efficiency. The adsorption isotherm studies indicate that the adsorption of metals follows both Langmuir and Freundlich isotherms. Preliminary tests of the adsorbent towards real wastewater treatment were carried out. This work shows a potential to use modified waste silica gel for metal removal from water, especially water with low salt content such as natural water. We are currently optimizing adsorption conditions for further improvement and investigating the morphology of the coated silica to gain better insight on the mechanism of metal adsorption.

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