

Heavy metals' removal from aqueous environments using silica sulfuric acid

Nasrin Hosseinahli, Maherram Hasanov and Maryam Abbasi

ABSTRACT

There is a growing environmental and health concern associated with contamination by heavy metals. It has also been intensified due to an increase of the exposure to such pollutants as a result of industrial and technological growth. Therefore, it is necessary to remove heavy metals in contaminated water to eliminate the associated risks. This study focused on the removal of heavy metal ions using silica sulfuric acid (SSA). A comprehensive study was conducted to assess the effect of different factors on the adsorption by SSA as well as selectivity properties of the adsorbent, kinetic and thermodynamic studies of the adsorption process. A batch test was used to remove heavy metals from a multi-element solution containing Ni(II), Pb(II), Mn(II), Cu(II), and Cd(II). The results showed that removal rate reached its peak at pH, string time, and adsorbent amount equal to 8, 60 min, and 0.04 g/mL of solution, respectively. The removal efficiency of Ni²⁺, Cd²⁺, Mn²⁺ dropped by increasing the volume of solution and smoothed at 150 mL while the removal of Pb²⁺ and Cu²⁺ did not vary with the volume. The removal efficiency by SSA was decreased as Pb > > Mn > > Ni ≥ Cu > Cd. In general, SSA successfully removed heavy metals from contaminated water.

Key words | adsorption, heavy metal, silica sulfuric acid, wastewater, water

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HIGHLIGHTS

- The first study of heavy metal removal using SSA as an adsorbent.
- A comprehensive study of adsorption by SSA including mechanism, thermodynamics, and kinetics.
- The effect of different factors on the adsorption has been investigated.
- Adsorption of heavy metals has been achieved for both synthetic and real samples.

INTRODUCTION

Discharge of industrial wastewater to rivers and lakes leads to the deposition of pollutants in the sediments. Pollutants containing heavy metals entering the food chain have put public health at risk (Riley *et al.* 2011; Duprey *et al.* 2014). Heavy metals cannot be destroyed through the biodegradation process, so they are carried by many organic

pollutants (Ainscough *et al.* 2017; Al-Qodah & Al-Shannag 2017). Outbreaks of disease caused by the accumulation of heavy metals in fish, shellfish, bivalve shells, sediments, and other components of aquatic ecosystems for years have been reported from around the world (Eisler 2006; Gunnison 2012). As a result, the removal of heavy metals from wastewater and aquatic ecosystems is necessary to prevent the spread of environmental pollution.

Currently, different methods are used to remove heavy metals from wastewater or contaminated water, including

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chemical precipitation (Perret *et al.* 2000; Ku & Jung 2001), ion exchange (Mier *et al.* 2001; Inglezakis *et al.* 2002), reverse osmosis (Ozaki *et al.* 2002; Patnukao *et al.* 2008), nanofiltration (Al-Rashdi *et al.* 2013; Zhu *et al.* 2015), electrodialysis (Pedersen *et al.* 2003), electrochemical reduction (Hunsom *et al.* 2005; Bazrafshan *et al.* 2015), insoluble starch xanthate process (Tare & Chaudhari 1987; Pedersen *et al.* 2003), electrodeposition (McIntyre & Peck 1976; Tonini & Ruotolo 2017), biosorption (Fan *et al.* 2014; Suzaki *et al.* 2017), and solvent extraction (Lin & Juang 2001). These methods have been extensively employed in practice; although, some drawbacks have been reported in the literature. The ion exchange resins showed poor thermostability performance, and their regeneration is not simple (Hosseini *et al.* 2020). Membrane filtration successfully removes heavy metal ions, but high maintenance cost is needed in operation (Foong *et al.* 2020). Chemical precipitation would result in massive sludge and, consequently, secondary pollution (Wu *et al.* 2019). Electrodeposition requires energy with insufficient performance on low concentration wastewater (Allioux *et al.* 2018). In comparison with metal removal methods, adsorption has a high removal efficiency, quick adsorption kinetics, and possible metal ion selectivity depending on the synthesis methods; therefore, it is an ideal candidate for the treatment of complex metal-containing wastewaters or industrial effluents (Gao *et al.* 2020). Adsorption is the result of the chemical bond between the adsorbent and adsorbed molecules. Therefore, this type of specific adsorption is a chemical type. At irreversible adsorption atomic properties, the sorbent change consequently (Ding *et al.* 2014). So far, numerous studies have been done to remove heavy metals using a variety of adsorbents. Patoczka *et al.* (1998) used ferric chloride to remove trace amounts of Pb, Cd, Ni, Cr, and Cu of three different waste streams and proved ferric salts were one of the selective sorbents which were able to decrease heavy metals' concentration levels below 1 mg/L in complex industrial wastewater (Patoczka *et al.* 1998). The results of this study showed that different elimination processes could lead to the removal of heavy metals up to ppb levels in the case of soluble, complex, colloidal, emulsion compounds. On the other hand, conventional methods failed to control pH and, consequently, were unsuccessful in the removal of heavy metals below 1 mg/L. However, in all cases,

adsorption/co-precipitation with ferric chloride was effective to remove heavy metals. The range of concentrations for Ni and Cr was obtained as 0.01 mg/L and it was 0.04, 0.1, and 0.75 mg/L for Cd, Pb, and Cu, respectively. Adsorption properties of natural zeolite for metal finishing removal from wastewater were studied by Erdem *et al.* (2004). A batch method was used in the range of metal concentration of 100–400 mg/L. The ratio of metal cations extracted to clinoptilolite was fitted by Langmuir adsorption isotherm, Freundlich, and Dubinin–Kaganer–Radushkevich models. Sequence selectivity of metal cation extraction was obtained as $\text{Co}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$.

Mohammadi *et al.* (2004) estimated and compared the efficiency of sand, soil (lime and limestone), and organic matter (rice husk and leaf compost) for the removal of heavy metals Cu(II), Zn(II), Ni(II), and chromium from industrial wastewater. A pilot study was carried out with four treatments and four repetitions. This study indicated that low soil cation exchange capacity of the organic matter did not necessarily reduce its adsorption power. Rice husk was a suitable adsorbent of Cr(II), and leaf compost was appropriate for Zn(II) and Ni(II) removal. Moreover, sand was effectively able to adsorb heavy metals in the wastewater of an electroplating factory.

Afkhami *et al.* (2010) used alumina modified with 2,4-dinitrophenylhydrazine for simultaneous removal of heavy metal ions including Pb(II), Mn(II), Ni(II), Co(II), Cr(III), and Cd(II) from wastewater. The effect of pH, stirring time, and adsorbent dosage on removal efficiency was examined, and Freundlich isotherm models and Langmuir model were applied to model the adsorption process. This study showed that the highest adsorption capacity pertained to Pb(II), Cd(II), and Cr(III).

One of the adsorbents used for heavy metal removal is silica, which is a solid mineral. This adsorbent is cheap, non-toxic, and recyclable. The adsorbent is reusable up to five times and has high thermal stability (up to 200 °C). Using silica sulfuric acid (SSA) benefits from specific reactor volume compared to other adsorbents, dry synthesis, absence of solvents and byproducts, and ease of handling (Hajipour *et al.* 2004; Shylesh & Singh 2004; Shaterian *et al.* 2008).

Heidari *et al.* (2009) studied the use of mesoporous silica, MCM-41, nano-MCM-41, MCM-41-NH₂, and

MCM-41-NH₂ nanoparticles for removal of Ni(II), Cd(II), and Pb(II) from aqueous solutions. The effect of various parameters was investigated, and MCM-41-NH₂ had the highest efficiency and effectiveness of ions' removal raised by the increase in pH. Comparison of Langmuir and Freundlich models showed that the Langmuir equation had the highest correlation. Barkatt *et al.* (2007) utilized silica and silica gel for treating heavy metals from water. Their study showed that Cu²⁺ and Pb²⁺ ions were adsorbed on silica gel for less than 2 h to reach the equilibrium. Pb²⁺-containing samples were adsorbed in the presence of Cu²⁺. The use of silica gels with a large specific surface area and smaller pore leads to a slight increase in Cu²⁺ and Pb²⁺ adsorption. Also, the dissolution of the silica from the adsorbent surface was kinetically controlled, unlike Cu and Pb adsorption. Therefore, they argued that the measured silica dissolution changed with time, temperature, and specific surface area of silica. Green chemistry focuses on using a process with minimum hazardous substances generation.

Moreover, there is a growing interest in heterogeneous systems due to the critical role in industrial activities, especially in developing technologies (Shaterian *et al.* 2008). Adsorption is a green and environmentally friendly method to remove heavy metals from water and wastewater due to its simplicity and low cost (Gao *et al.* 2020). The adsorbents can be easily prepared, functionalized, separated, and regenerated; however, low adsorption capacities and adsorption rates are their disadvantages. Therefore, it is essential to conduct studies on the adsorbents and find the sorbents with high adsorption capacity. SSA is safe, easy to handle, environmentally benign with fewer disposal problems and has been used as an efficient adsorbent and catalyst in chemical processes. To the best of the authors' knowledge, there is no study on heavy metal removal by SSA.

The main objective of this study is to assess the removal efficiency of heavy metals using SSA. We examined the effect of initial pH, stirring time, solution volume, initial concentration of metal ions, simultaneous effect of initial pH and their concentration as well as study of selectivity properties of the adsorbent, kinetic and thermodynamic studies of the adsorption process. Moreover, SSA was used for heavy metal removals from samples in two case studies.

MATERIALS AND METHODS

Synthesis of silica sulfuric acid

A 500 mL round-bottom flask containing 60 g silica gel was used to produce SSA. The flask was equipped with a constant pressure dropper containing 13.3 mL chlorosulfonic acid. This flask was connected to a gas outlet tube to allow transfer of produced HCL gas into water. Chlorosulfonic acid was dropped on silica gel for 30 min at room temperature. HCL gas was released rapidly from the reaction vessel. During and after completion of the reaction, the reaction mixture was stirred for 30 min. Finally, a 76 g white solid, called silica sulfuric acid, was obtained. It should be noted that the preparation of SSA could generate acidic wastewater and the hazards associated with waste generated from SSA production need to be considered in practical purposes.

Batch tests

Batch tests were conducted for removing heavy metals by mixing 1 g adsorbent in 25 mL of a multi-element solution containing 5 mg/L of Ni(II), Pb(II), Mn(II), Cu(II), and Cd(II). A series of batch tests was carried out to find the effect of pH, equilibrium time, kinetics of adsorption, the effect of temperature, thermodynamic characteristics, and effect of interfering ions. All tests were repeated three times to avoid data inconsistencies, and to obtain reasonable data deviation, heavy metals were not buffered to simulate industrial operation (Afkhami *et al.* 2010). The percentage of metal ions' removal was calculated by Equation (1):

$$R = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where R is the removal efficiency of metal ions, C_0 is initial concentration of metal ions, and C_t is the concentration at time t .

Effect of initial pH of solution, stirring time, and solution volume

To evaluate the effect of pH on cation adsorption, the experiment was done at pH 1.7, 3, 5, 7, 8, 8.5, and 9. At each pH,

the experiment was repeated with different stirring times ranging from 10 to 75 min, and the volume of metal-containing solution changed from 25 to 1,000 mL. Therefore, the optimum condition of adsorption was obtained at this stage.

Effect of the initial concentration of metal ions

Under optimum condition, the batch test was done by adding 5–25 mL of the multi-metal solution. Regarding mass balance law, the amount of adsorbed metal on adsorbent was calculated using Equation (2):

$$q_t = \frac{(C_0 - C_t) \cdot V}{W} \quad (2)$$

where C_0 is initial concentration of metal ions, q_t is mass of metal adsorbed per unit mass of adsorbent at time t , C_t is concentration of metal ions at time t , W is adsorbent weight, and V is volume of the multi-metal solution.

Simultaneous effect of initial pH and concentration and study of selectivity properties of the adsorbent

To investigate the simultaneous effect of initial pH and concentration, solutions with 50 mg/L, 10 mg/L, and 30 mg/L of Ca, Ni, Pb, Mn, and Cu at pH of 3, 5, and 7 were tested by the batch method.

In this study, Kurbatov curve was used to assess the selectivity properties of the adsorbent.

Kinetic studies of the adsorption process

The batch tests were implemented at 20, 30, 40, and 50 °C and thermodynamic parameters such as changes in Gibbs free energy, enthalpy, and entropy were estimated as a function of temperature.

Since industrial wastewater contains a variety of ions which makes adsorption difficult, samples with different cations and anions including sulfate, nitrate, and chloride cations and sodium anions were prepared for study.

Removal of heavy metals from case study samples

The samples used in this study were collected from Tabriz wastewater treatment plant, which is located in

Table 1 | Monthly wastewater quality in Tabriz wastewater treatment plant

Wastewater	Parameter	Unit	Minimum	Mean	Maximum
Raw	BOD	mg/L	283.3	345.4	447.1
	COD	mg/L	421.3	520.3	658.5
	TSS	mg/L	134.1	273.3	337.95
Treated	BOD	mg/L	12.4	25.73	42.7
	COD	mg/L	26.93	41.06	68.3
	TSS	mg/L	6.02	17.09	29.6

northwestern Iran. Tabriz wastewater quality is monitored constantly. The heavy metal concentration varies during a year. Samples were taken having low concentrations of heavy metal at sampling time; therefore, heavy metals were added to simulate the average level of heavy metal concentration. Table 1 summarizes the monthly average properties of raw and treated wastewater. Heavy metal concentrations in the initial sample before adding standard solution were not measurable by atomic adsorption method. Spiked samples with 5 mg/L concentration of each cation and a mixture of metals were investigated at the optimum condition to measure remaining concentrations by flame atomic adsorption spectrometry (Savant AA Σ , GBC Australia). pH measurements were performed by SUNTEX TS-1 digital calibration pH meter. For measuring temperature and thermodynamic, PECO shaking incubator (model AT BIN MEGA) was used, and for separating solid phase from aqueous solution, an RR-12 centrifuge was used. A GF-300 digital scale with an accuracy of ± 0.001 g was used to weigh materials.

Standard solutions of heavy metals were prepared using nitrate salts of copper, lead, nickel, and cadmium and manganese chloride and hydrochloric acid 37% (HCL) and 65% nitric acid (HNO₃). All chemicals were manufactured by Merck Germany Company with high purity.

RESULTS AND DISCUSSION

Effect of initial pH of the solution

Figure 1 shows the effect of pH on heavy metal removal by SSA. As seen in the figure, adsorption of nickel, cadmium, manganese, and copper was low in an acidic environment.

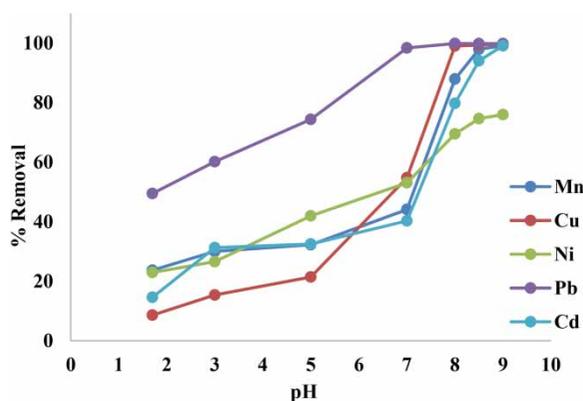


Figure 1 | Effect of pH on adsorbent efficiency for metal ions' removal.

The minimum adsorption was observed for Cu ions. However, the removal of lead ions was high even in the acidic condition and reached its peak at pH equal to 7.

The low Cu removal rate may be related to stable copper complexes with water molecules based on Irving–Williams series. Hydroxide ions in an alkaline environment can form a complex with the majority of heavy metals and precipitate. Results also verified this as removal of copper suddenly rose at pH above 5.5 (Figure 1). The sudden increase could be due to the formation of hydroxyl complexes and precipitation of copper hydroxide as a solid. Metal hydroxide formation depends on pH and concentration so that an increase in pH and concentration intensifies this process. In the studied concentration range, 5–100 mg/L, at 5.5–6 pH, solid copper hydroxide began to form and for heavy metals ions, this occurred at pH greater than 8. Despite the fact that hydroxide compounds can be in aquatic form, deposition of metallic hydroxides in pores and on the surface of the adsorbent is hardly possible because adsorption is quicker from precipitation kinetically. Therefore, it can be concluded that even though there was a possibility of precipitation, the dominant process for the removal of heavy metals was adsorption.

Even though the optimum pH was obtained at 8.5–9, pH equal to 8 was selected as the optimum pH to avoid precipitation of metal hydroxide except for copper and possible silica destruction at pH higher than 8. At optimum pH, removal efficiencies of Cd, Ni, Mn, Pb, and Cu were 79.75, 69.44, 87.87, 99.83, and 98.99, respectively. The standard deviation of results was below 0.006 at this stage. In general, the acidic condition was not suitable for adsorption by SSA

due to competition between protons and metal species. Increased removal efficiency by increasing pH may be related to reduction of H^+ on the adsorbent surface and, consequently, increase in negative charge on the surface which strengthens adsorption power of metal ions by adsorbent; and deprotonation of oxygen atoms in an alkaline environment which is suitable for coordination with metal ions.

In fact, metals' removal was not affected totally by the adsorption on SSA. The metals were precipitated at high pH. Some metals such as Pb, Cr, and Cu were precipitated at slightly alkaline media. Therefore, the removal cannot refer to SSA only. Metals' precipitation is controlled mainly by the 'solubility product' law. Changing the pH values affects the initial concentration of metals according to the degree of pH level. Each metal has different stability at higher pH values (Abdel-Shafy 2015).

Effect of adsorbent amount

The adsorbent amount is a crucial parameter which determines the adsorption capacity. The removal of metal ions increases with an increase in the adsorbent dosage. As shown in Figure 2, removal of Ni and Cd increased with an increase in the amount of adsorbent. Increasing the amount of adsorbent results in a rise in adsorption surface and, consequently, raising the chance of removal. The trend of increase in removal capacity can be associated with the availability of more adsorption sites for the metal ions. Removal of Mn^{2+} , Pb^{2+} , and Cu^{2+} ions was high and did not change by adding more adsorbent. This can be explained based on further results obtained during the tests on adsorbent's

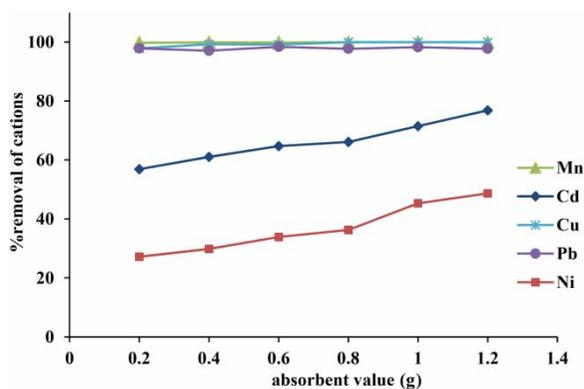


Figure 2 | Effect of adsorbent amount on heavy metal removal.

selectivity which showed the better adsorbance of these ions than other metal ions. One gram of adsorbent was selected as the optimal value for metal removal in the study.

Effect of stirring time

Contact between the adsorbent and adsorbate increases the probability of the adsorption and it increases with longer contact time. In this study, stirring time varied from 10 to 75 min. The results are illustrated in Figure 3. As shown in the graph, Cu^{2+} , Pb^{2+} , and Mn^{2+} were removed at 10 min. Nickel and cadmium determined the reaction and equilibrium time. Ni^{2+} and Cd^{2+} removal rates peaked after 60 min and thus the optimal time to complete the reaction was 60 min. As the contact time increased, the adsorption capacity of adsorbent also increased. The increase in the adsorption capacity in the first 60 min was rapid. This might be due to the sorption of ions into the surface pores of SSA. After 60 min, the increase was gradual probably due to the migration of ions from the upper adsorbent surface to inner pores. After 74 min, there is no significant change with the increase in time because all the active sites have been occupied while reaching this time. Therefore, 60 min is considered as the optimum contact time for the adsorption. The standard deviation was less than 0.004.

Effect of the volume of the solution

Effect of the solution volume on adsorption capacity of SSA and removal efficiency of heavy metals was investigated. Different volumes of the solution containing heavy metals were tested in the range of 25–1,000 mL. Results are

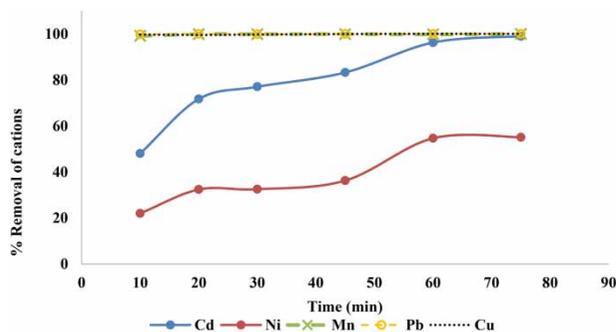


Figure 3 | Effect of stirring time on heavy metal removal.

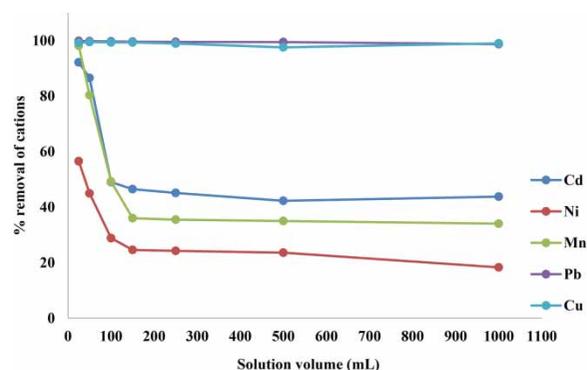


Figure 4 | Effect of the volume of the solution on heavy metal removal.

illustrated in Figure 4. As shown in the graph, removal efficiency for Ni^{2+} , Cd^{2+} , and Mn^{2+} dropped by increasing the volume from 25 to 150 mL and then smoothed at volumes more than 150 mL. On the other hand, the removal efficiency of Pb^{2+} and Cu^{2+} did not vary with the volume. The standard deviation was less than 0.005.

Effect of the initial concentration of metal ions

Solutions with different concentration were tested by the batch method, as illustrated in Figure 5. When the initial concentration rose from 5 to 20 mg/L, the heavy metal removal efficiency of Cd^{2+} and Ni^{2+} dropped about 40%. However, adsorption capacity increased from 70 to 269 $\mu\text{g/g}$ for Cd^{2+} and 64 to 216 for Ni^{2+} . At concentrations between 20 and 100 mg/L, removal of Cd^{2+} and Ni^{2+} increased by 30% approximately. This could be the consequence of an increased formation of nickel hydroxide and cadmium at higher concentrations samples. For Mn^{2+} , removal efficiency decreased at concentrations of

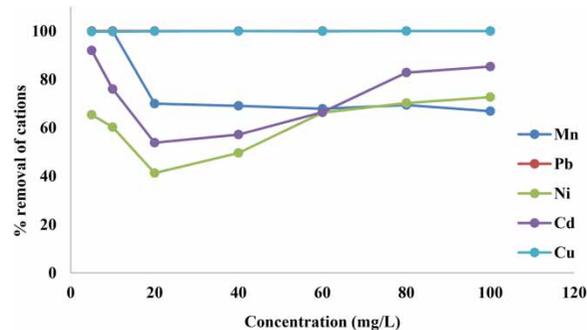


Figure 5 | Effect of the initial concentration of the solution on heavy metal removal.

5–100 mg/L, but adsorption capacity increased from 125 to 1,890 $\mu\text{g/g}$. Pb^{2+} and Cu^{2+} were almost removed at all concentrations. As mentioned above, this was due to Cu^{2+} and Pb^{2+} removal in the form of hydroxide precipitate. In samples containing Pb^{2+} up to 1,000 mg/L concentration,

the adsorption process was maintained until complete removal of lead ions. Ultimately, both the removal mechanism of adsorption and deposition took place in this case. Consequently, none of the Langmuir and Freundlich models could explain the adsorption process. Therefore,

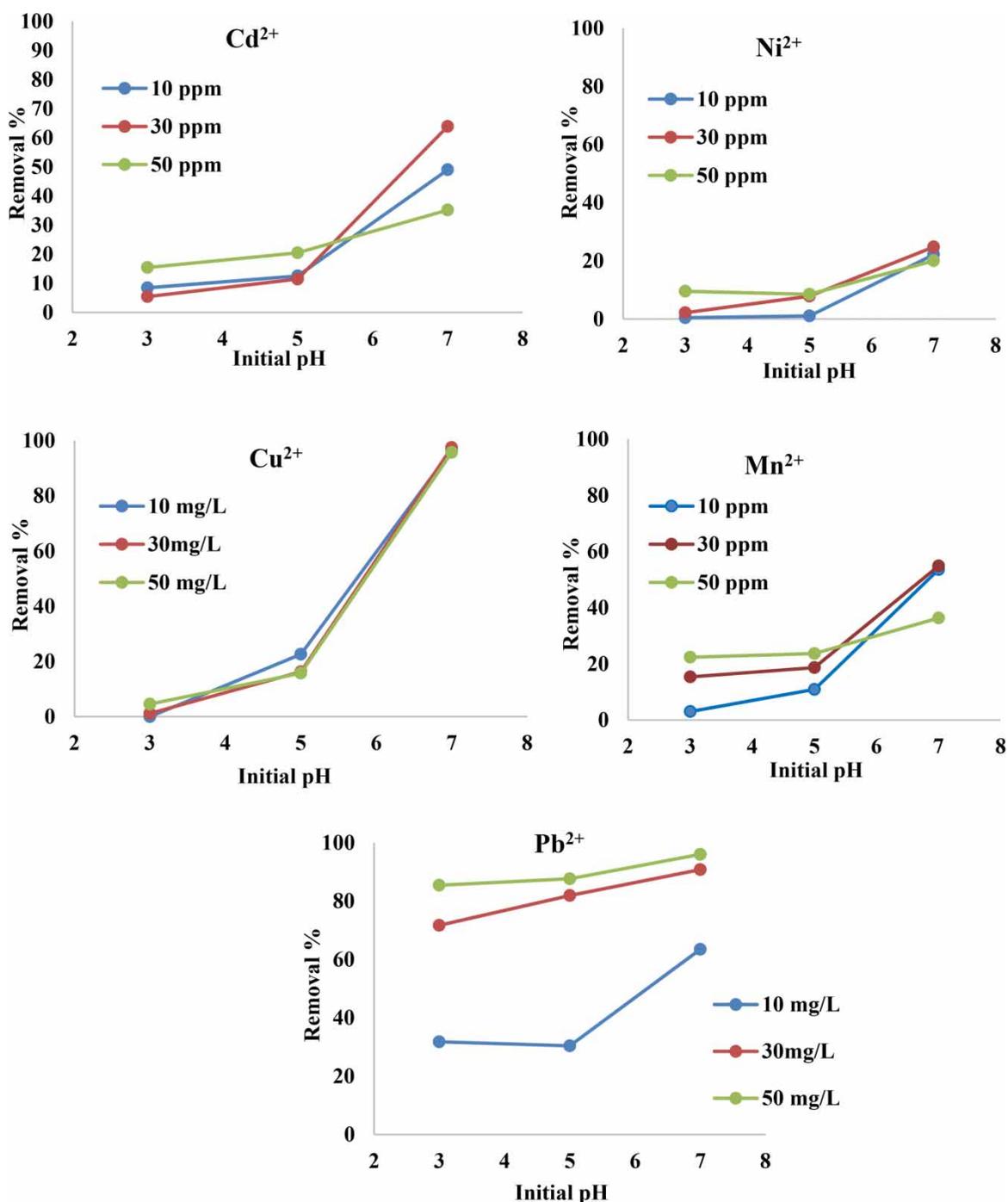


Figure 6 | Effect of pH and concentration of the solution on heavy metal removal.

it can be concluded that adsorption of multiple metal solutions changed the adsorption process compared to that of single metal solutions, and the maximum adsorption capacity cannot be estimated. In these experiments, the standard deviation of the results was less than 0.004.

Effect of both pH and concentration

During this stage of the study, the selectivity of adsorbent was determined, and it was adjusted such that adsorbent tended to adsorb lead. Lead removal was greater than other metals, even at high concentrations and acidic condition. At the concentration of 50 mg/L and pH 3, lead

removal adsorption efficiency was 85.4% (Figure 6). The sharp increase of Cu^{2+} reduction at an elevation of pH from 5 to 7 testified to the participation of copper in the form of copper hydroxide. The removal efficiency of cadmium, nickel, and manganese at 1 g of adsorbent increased even in an acidic environment which indicated an increase in the number of the ions and adsorbent collisions followed by an increase in the possibility of adsorption. As shown in Figure 7, the adsorption decreased in the order of $\text{Pb} \gg \text{Mn} \gg \text{Ni} \geq \text{Cu} > \text{Cd}$. Moreover, the results showed by increasing pH, divalent metal retention on the surfaces via adsorption, inner sphere surface complexation and/or precipitation increases. In other words, increasing pH resulted in increasing the sorption sites.

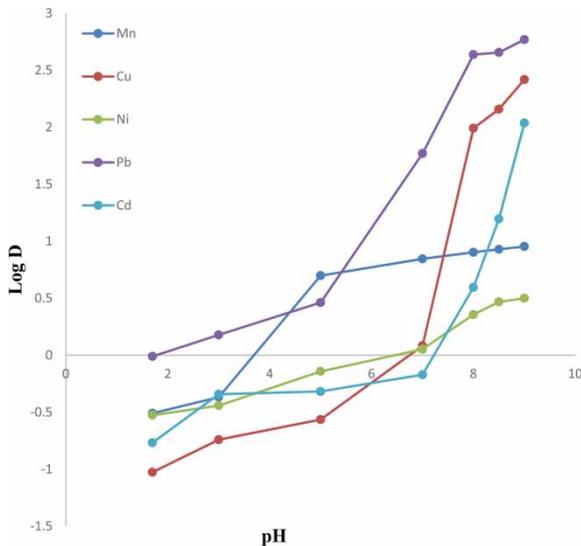


Figure 7 | Kurbatov curve for study of selectivity of silica sulfuric acid.

Kinetics studies of adsorption process

Adsorption of cadmium and nickel ions on the surface of SSA from the solution was as a function of mixing time. As shown in Figure 8(a) and 8(b), adsorption of these ions occurred quickly so that more than 95% of nickel and 54% of cadmium were removed after 60 min. However, there was no significant change in the adsorption at times longer than 60 min. Morris kinetics equation was used to investigate the adsorption. K_i was determined as 0.055 and $0.109 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{min}^{-1/2}$ for cadmium and nickel, respectively.

Kinetics of nickel and cadmium adsorption were analyzed by first order Lagrangian equations (Aguado *et al.* 2009; Ahmed 2011). The correlation coefficient was low, and this model could not explain the adsorption of these ions.

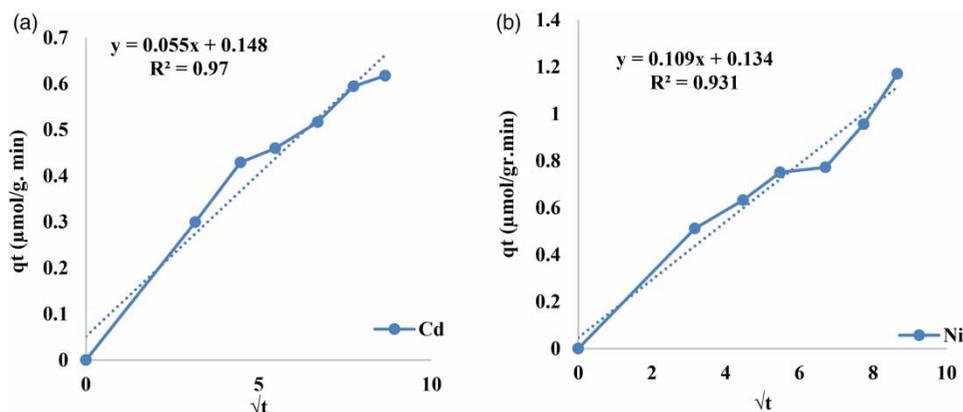


Figure 8 | Kinetics curve (a) for cadmium and (b) nickel.

Morris–Weber transition diagrams of the particle, shown in Figure 8, could prove the multistage adsorption of nickel and cadmium on SSA. As stated in the following, ΔH° values obtained for nickel, cadmium, and manganese cations showed both physical and chemical adsorption.

Effect of temperature and thermodynamic parameters

The experiment was implemented at 20, 30, 40, and 50 °C temperatures to study the effect of temperature on the

Table 2 | Thermodynamic parameters of adsorption of cadmium, nickel, and magnesium

	T (K)	K_d	ΔG° (J.mol)	ΔH° (J.mol)	ΔS° (J.mol K)
Cadmium	293	45.101	-37.11253	11,662	40.78
	303	19.128	-61.12226		
	313	67.135	-76.12777		
	323	25.163	-03.13683		
Nickel	293	95.8	-84.5339	28,231	70.114
	303	1.09	-30.6479		
	313	76.2	-10.7893		
	323	45.25	-38.8692		
Magnesium	293	62.8	-70.5248	24,273	80.1
	303	25.13	-40.6509		
	313	31.14	-23.6924		
	323	45.23	-11.8472		

adsorption of cadmium, nickel, manganese, lead, and copper cations by SSA. As seen in Table 1, removal of Cd, Ni, and Mn increased as temperature rose. The increase in the adsorption of cadmium, nickel, and manganese cations with increasing temperature showed that the highest removal of these cations on the SSA surface could be achieved at high temperature. This was due to the increase in the mobility of cations and diffusion of ions to adsorbent at high temperature. Besides, growth in temperature may result in swelling of adsorbent and create more space for large metal cations like cadmium. On the other hand, complete removal was obtained for copper and lead at all temperatures.

Since the Gibbs free energy graph was linear for all metals, enthalpy and entropy were determined by the slope and intercept of the line summarized in Table 2. Negative values of Gibbs free energy changes at different temperatures reflected that the nature of the adsorption process was spontaneous. Positive entropy values indicated an increase in entropy for all metals. Positive enthalpy means that the adsorption process was endothermic. It also showed that adsorption enthalpy of nickel and manganese on SSA was chemical while adsorption of cadmium ions was physical.

Table 3 | Effect of addition of ions on heavy metal removal by SSA

Removal ^a (%) Ion	Concentration (mg-L)	Salt	Cd ²⁺	Ni ²⁺	Mn ²⁺	Pb ²⁺	Cu ²⁺
Al ³⁺	50	Al ₂ (SO ₄) ₃	4 ± 35	6 ± 18	3 ± 18	97.2 ± 0.1	98.8 ± 0.2
	500		2 ± 31	3 ± 61	6 ± 55	1 ± 98.7	99.2 ± 0.5
F ⁻	50	NaF	1 ± 31	1 ± 6	6 ± 29	99.9 ± 0.1	98.5 ± 0.3
	500		6 ± 31	4 ± 18	4 ± 35	99.9 ± 0.1	98.9 ± 0.2
Mg ²⁺	50	Mg(NO ₃) ₂	6 ± 36	1 ± 19	2 ± 45	99.7 ± 0.3	99.2 ± 0.2
	500		6 ± 54	6 ± 42	1 ± 91	99.4 ± 0.1	99.6 ± 0.1
Na ⁺ , Cl ⁻	50	NaCl	5 ± 45	5 ± 23	5 ± 75	99.9 ± 0.1	99.1 ± 0.2
	500		6 ± 48	1 ± 21	4 ± 96	99.4 ± 0.2	99.5 ± 0.1
PO ₄ ³⁻	50	Na ₃ PO ₄	2 ± 65	1 ± 28	5 ± 60	99.1 ± 0.9	99.3 ± 0.2
	500		3 ± 94	0.3 ± 59	5 ± 95	99.7 ± 0.4	99.7 ± 0.1
K ⁺ , NO ₃ ⁻	50	KNO ₃	5 ± 54	2 ± 28	3 ± 28	99.8 ± 0.2	99.5 ± 0.2
	500		1 ± 52	5 ± 25	2 ± 25	99.7 ± 0.1	99.3 ± 0.1
Ca ²⁺	50	CaCl ₂	1 ± 61	1 ± 35	5 ± 45	99.8 ± 0.3	0.1 ± 99.4
	500		3 ± 56	2 ± 39	5 ± 70	99.9 ± 0.1	99.1 ± 0.2
Fe ³⁺	50	FeCl ₃	5 ± 45	3 ± 38	4 ± 41	99.4 ± 0.2	98.4 ± 0.1
	500		4 ± 67	4 ± 60	2 ± 77	98.4 ± 0.1	0.1 ± 99.0

^aAverage ± standard deviation.

Table 4 | Heavy metal removal by SSA from Tabriz wastewater treatment plant

Samples from Tabriz wastewater treatment plant	Added ($\mu\text{g.mL}$)	Measured ($\mu\text{g.mL}$)	Removal ^a (%)
Cd ²⁺	5	0.773	84.5 \pm 0.8
Ni ²⁺	5	2.822	43.6 \pm 0.4
Mn ²⁺	5	1.100	78.0 \pm 1.3
Pb ²⁺	5	0.232	95.3 \pm 1.5
Cu ²⁺	5	0.138	97.2 \pm 3.2

^aAverage \pm standard deviation.

Effect of addition of ions

Sulfate, nitrate, phosphate, nitrate, and chloride salts, as well as sodium, calcium, ferric, potassium salts, were added to the solution containing heavy metals with a ratio of 1–10 and 1–100 towards heavy metal content. Results are illustrated in Table 3. As seen, added ions did not perturb adsorption of Pb²⁺ and Cu²⁺. During the test, phosphate was deposited due to the dominance of deposition to adsorption. Therefore, metal removal increased at higher phosphate concentrations.

Heavy metal removal from case study wastewater

A similar method was used to remove heavy metal from Tabriz wastewater treatment plant. Results are presented in Table 4. As seen, SSA successfully removed heavy metals. Removal efficiency compared to laboratory samples did not show a significant difference and was in good agreement with the results of this study.

CONCLUSION

In this study, silica sulfuric acid was used as an adsorbent to remove heavy metals including nickel, cadmium, magnesium, lead, and copper ions. The experiment was done on laboratory samples and case study samples by the batch method. SSA peaked in its efficiency for heavy metal at weak alkaline conditions and 0.04 g of adsorbent/g of solution. The highest tendency for adsorption was for lead, and the least was for chromium. SSA adsorption is an inexpensive method for purifying wastewater contaminated with low to moderate amounts of heavy metals.

The reaction kinetics of adsorption followed the first-order kinetic model. Thermodynamic studies showed that the removal of cations enhanced with increase in temperature. According to negative values, ΔG° obtained for cadmium, nickel, and manganese, surface adsorption process on SSA was a spontaneous reaction. Positive values of ΔS° represent an increase of irregularities during the process, and positive ΔH° means that the reaction on the surface of the adsorbent nature was endothermic. Also, the amount of change in obtained enthalpy (ΔH°) showed that Cd(II) ions on SSA were physical adsorption, but adsorption of Ni(II) and Mn(II) ions were chemical ones.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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