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Removal of Heavy Metal Ions from Aqueous Solutions using Silica Aerogel as Adsorbent

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Abstract

The removal of Zn(II), V(II), by silica aerogel has been found to be concentration, , contact time, adsorbent dose and temperature dependent. ion exchange are the major removal mechanisms involved. The adsorption isotherm studies clearly indicated that the adsorptive behaviour of metal ions on silica aerogel was satisfied. The applicability of the Lagergren kinetic model has also been investigated. Thermodynamic constant (Kad), standard free energy (ΔG^0),enthalpy (ΔH^0) and entropy (ΔS^0) were calculated for predicting the nature of adsorption.

Keywords: silica aerogel; metal ions; adsorption

1. INTRODUCTION

The pollution of water resources due to the indiscriminate disposal of heavy metals has been causing worldwide concern for the last few decades. It is well known that some metals can have toxic or harmful effects on many forms of life. Metals, which are significantly toxic to human beings and ecological environments, include chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), manganese (Mn), cadmium (Cd), nickel (Ni), zinc (Zn) and iron (Fe),Vanadium(V) etc. Wastewater from many industries such as metallurgical, tannery, chemical manufacturing, mining, battery manufacturing industries, etc. contains one or more ofthese toxic heavy metals [1]. Today silica gel, also knownas silica, silicic acid, Kiesel gel, is th emost widely used polar adsorbent, especially in its deactivated form in all branches of chromatography and solid phase applications. Its main advantages over other solid supports are relative activity, large adsorption capacity, easy preparation of its different types with different pore size and total surface area under standard conditions. In addition, the possibility of surface modication or coating with an impregnation medium or reagent is also reported as an advantage [2-5].

Silica aerogels are novel mesoporous materials with many intriguing properties such as low bulk density (~0.1 g/cm^3), continuous porosities, high speci.c surface area (500–1000 m^2/g) and extremely low thermal conductivity (~0.02 $W\ m^{-1}K^{-1}$) [6–10]. These properties are derived from the nanoporous network of interconnected primary particles. Because of their unique texture, silica aerogels are promising materials as super-thermal insulators, catalytic supports, adsorbents, host materials for drug delivery systems [11–15].

2. EXPERIMENTAL

At first we take spectra of silica aerogel Figure 1 shows the FT-IR spectra of the silica aerogel powder by using BRUKER/TENSER 27.

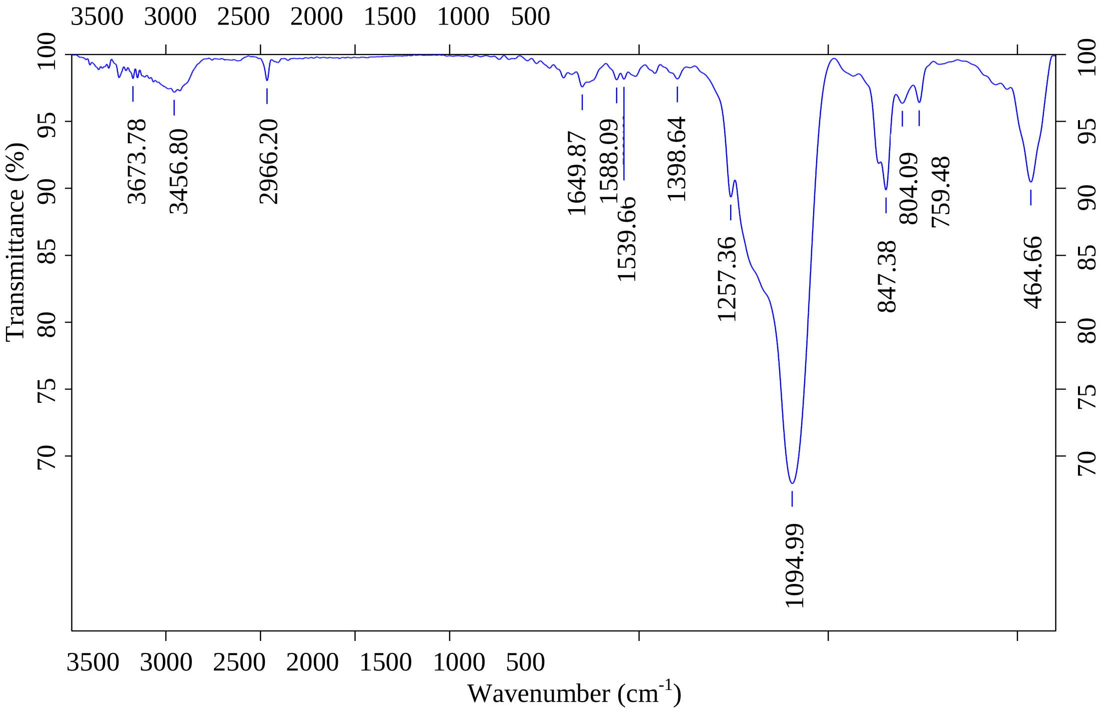

Figure 1: FT-IR spectra of silica aerogel powder

And then PG 990 AA atomic adsorption spectrometer (AAS) operating with an air acetylene flame was used to analyze the concentration of heavy metals.Synthetic stock solution of heavy metals was prepared by dissolving required quantity of Analar grade salts in the distilled demineralised water. The salts used are cadmium chloride, zinc chloride, manganese chloride, mercury chloride, nickel nitrate, copper nitrate, lead nitrate for Zn(II), V(II), respectively, for the preparation of stock solution. The stock solution was further diluted with distilled demineralised water to desired concentration for obtaining the test solutions.

Silica aerogels are new and emerging adsorbent materials composed of covalently bonded nanometer sized determined by running the blank experiments was found negligible.

The results of these studies were used to obtain the optimum conditions for maximum heavy metals removal from aqueous solution. The percent heavy metal removal was calculated using Eq.(1);

$$\text{metal ion removal (\%)} = (C0 - Ce) \times 100 / C0 \qquad (1)$$

where C0: initial metal ion concentration of test solution, mg/L; Ce: final equilibrium concentration of test solution, mg/L.

3. RESULTS AND DISCUSSION

3.1 Effect of Initial Concentration of Heavy Metal

The effect of initial concentration on the percentage removal of heavy metals by silica aerogel is shown in Figure 2. It can be seen from the figure that the percentage removal decreases with the increase in initial heavy metal concentration.the initial metal ions concentration range 1-5 mg/L for 5 g/L adsorbent dose, at higher concentrations of heavy metal ions are relatively higher compared to availability of adsorption sites. Hence, the percent removal of heavy metals depends on the initial metal ions concentration and decreases with increase in initial metal ions concentration.

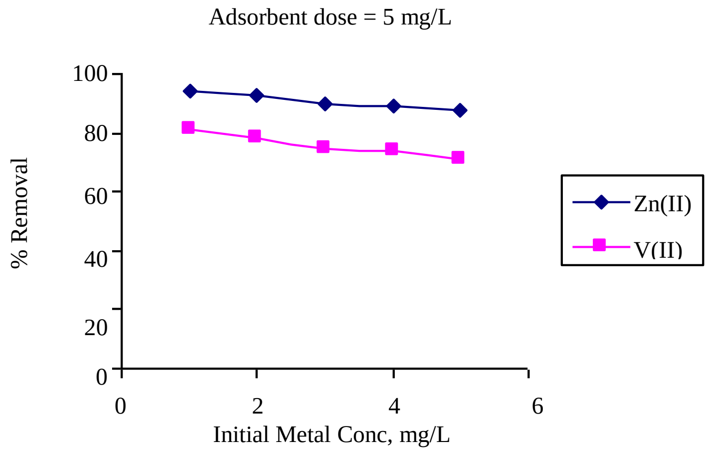

Figure 2: Effect of initial metal concentration on percent removal of heavy metals by silica aerogel.

3.2. Effect of Contact Time

Figure 3 shows the variation in the percentage removal of heavy metals with contact time using 5 g/L of silics aerogel, we study the time affect in the optimum concentration in fact in optimum concentration we have maximum removal percent and that was 1mg/L . It is observed that in all cases the percentage removal is comparatively lower for 24 h contact time, with increasing removal efficiencies at higher contact time.

For the same concentration, the percentage removal of heavy metal increases with increase of contact time till equilibrium is attained. The optimal contact time to attain equilibrium with silica aerogel was experimentally found to be about 24 h.

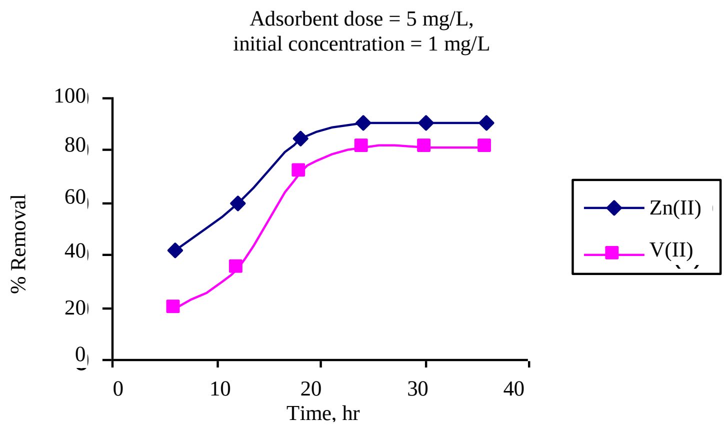

Figure 3: Effect of contact time on percent removal of heavy metals by silica aerogel.

3.3. Effect of Temperature

In the optimum concentration (1mg/L) we study the metal ions adsorption in difference temperate 20 -60C^0 and we find out with increase the temperate the metal ions adsorption were decrease(Figure 4)

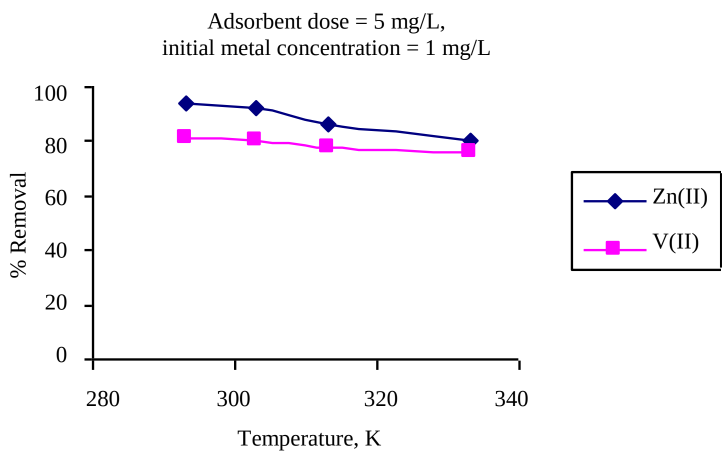

Figure 4: Effect of temperate on percent removal of heavy metals by silica aerogel

The thermodynamic parameters, such as free energy(ΔG), enthalpy change (ΔH), and entropy change (ΔS) were determined using the following equations and presented in Table 1;

$$Kc = CAc/Ce \quad (2)$$

where, Kc is the equilibrium constant, CAc and Ce are the equilibrium concentration (mg/L) of the metal ion on adsorbent and in the solution, respectively. The free energy change (ΔG) was calculated from the relation:

$$\Delta G = RT \ln Kc \qquad (3)$$

where, T is temperature in Kelvin (273 K) and R is gas constant (8.314×103 kJ/mol K). Enthalpy change (ΔH) was calculated from the following equation

$$\Delta G = \Delta H\text{-}T\Delta S \qquad (4)$$

$$\log Kc = \Delta S/2.303R - \Delta H/2.303RT \qquad (5)$$

ΔH and ΔS were obtained from the slope and intercept of Vant Hoff plots of log Kc versus 1/T (Figure 5). Positive values of ΔH thermodynamically substantiate the assumption that the adsorption of metal ions on the silica aerogel is endothermic. The negative values of ΔG indicate feasibility and spontaneous nature of adsorption of metal ions on the adsorbent. ΔS is estimated to be very small in the experimental conditions. Therefore, the entropic change occurring from adsorption is though to be negligible.

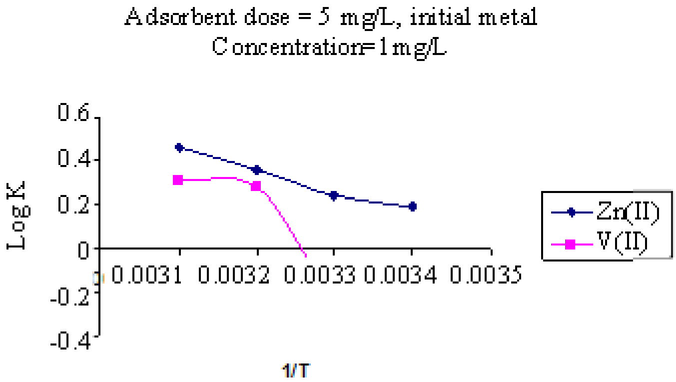

Figure 5: Plot of log *K*c and 1/*T* for heavy metals on silica aerogel.

Table 1: Equilibrium constants and thermodynamic parameters for the adsorption of heavy metal ions on silica aerogel

Metal	Temperature,Ɵ	Kc	ΔG(KJ/mol)	ΔS(KJ/molK)	ΔH (KJ/mol)
Zn(II)	20	2.8840	-2.5802	0.0088	-0.0018
Zn(II)	30	2.2908	-2.0881	0.0068	-0.0277
Zn(II)	40	1.7378	-1.4380	0.0045	-0.0295
Zn(II)	60	1.5488	-1.2111	0.0036	0.0123
V(II)	20	2.0147	-1.7387	0.0059	-0.0010
V(II)	30	1.9054	-1.6240	0.0053	-0.0181
V(II)	40	0.6606	1.0789	-0.0034	0.0147
V(II)	60	0.6309	1.2752	-0.0028	0.3512

3.4. Adsorption Kinetics

The adsorption kinetics of heavy metal ion adsorption on silica aerogel follows first order rate expression given by Lagergren and Svenka [16].

$$\log (qe-q) = \log qe - Kad \cdot t/2.303 \quad (6)$$

where, Kad (1/h) is the rate constant of adsorbent, q and qe are the amount of heavy metal ions adsorbed (mg/L) at time t (h) and equilibrium time. Linear plots of log10 (qe q) versus t (Figure 6) show the applicability of above equation for silica aerogel. The Kad values at a metal ion concentrations were calculated from the slop of linear plots and presented in Table 2 the Kad values were comparable with recently reported values for heavy metal ions removal by silica aerogel.

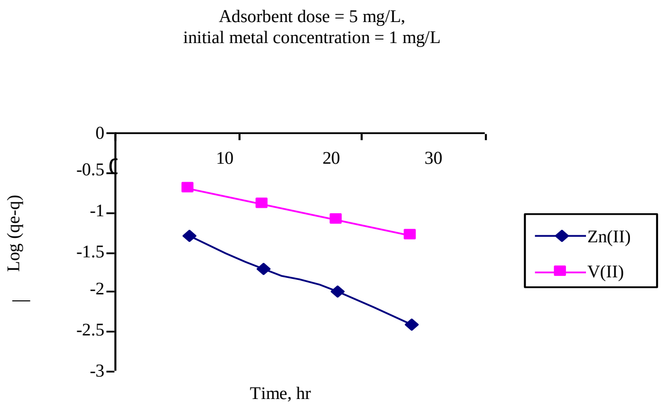

Figure 6: Plot for Lagergren rate constant for adsorption of heavy metal ions by silica aerogel.

Table 2: Kinetics constant for heavy metal ions adsorption

Metal ions	Adsorption rate constant (Kad)(1/h)
Zn(II)	0.1218
V(II)	0.0766

4. CONCLUSIONS

- Silica aerogel showed nearly 100% adsorptive removal of heavy metal ions under optimized conditions of dosage 5 g/L for aqueous solutions containing 1 mg/L metal ions in 24 h.
- The adsorption follows first order kinetics.
- The applicability of Lagergren kinetic model had been investigated. Adsorption rate constant (Kad) was determined.
- Thermodynamic parameters such as standard free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were calculated for predicting the nature of adsorption.
- These experimental studies on adsorbents would be quite useful in developing an appropriate technology for the removal of heavy metal ions from contaminated industrial effluents.

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