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Synthesis of Vulcanized Silica and Its application in Removing Hg(II) and Pb(II) From Water Samples

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The ability of the newly synthesized vulcanized silica for removing Hg^{2+} and Pb^{2+} at different optimized conditions of concentrations, amounts of absorbent and pH has been studied. Maximum adsorption for both the cations has been obtained at nearly neutral pH. Flame atomic absorption spectrometry was used for measuring lead and mercury concentration in stripped solutions. The isotherm curves for adsorption of two cations were obtained.

Key Words: Synthesized vulcanized silica, Hg(II), Pb(II), Adsorption, Water samples.

INTRODUCTION

Industrial processes that feature physical and chemical changes have traditionally been designed without much thought to process wastes and adverse environmental impacts of emissions and discharges[1]. Therefore, in recent years there has been increasing pressure on the chemical industry from governmental authorities to develop more environmentally friendly processes[2]. One area of research that has seen increasing interest in this context is in the use of supported reagents as alternatives to more traditional reagents and catalysts. Several outstanding reviews on the subject have also been published[2–7]. It has been shown that the type of support material used is a critical factor in the performance of the resulting supported reagent or catalyst. Two main factors should be considered when employing a material as a support. Firstly, the material needs to be stable both thermally and chemically during the reaction process. Secondly, the structure of the support needs to be such that the active sites are well dispersed on its surface and that these sites are easily accessible.

One of the most effective materials is silica gel as this offers high thermal and chemical stability (except for a few small neuclophiles, notably OH^- and F^-). Silica gel is an amorphous inorganic polymer composed of internal siloxane group

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(Si—O—Si) with silanol groups (Si—OH) distributed on the surface[8,9]. The active hydrogen atom of the silanol groups of silica gel has the ability to react with agents containing organosilyl functions, to give some organic nature to the precursor inorganic support. These covalently bonded groups are resistant to removal from the surface by organic solvents or water[9,10]. In addition, silica can possess high surface areas[2] and with low cost. Thus, the chemical modification of silica gel for producing a valuable solid support could be recommended.

The principal success of such inorganic solid surfaces modified with organo-functional groups is the immobilization of the desired reactive atomic group, which causes a great versatility on this surface in developing various functions[11,12]. Thus, chemically modified silica gel can be used in various areas of chemistry such as heterogeneous catalysis[13], ion-exchange chromatography[14–16] as a stationary phase in adsorption chromatography[17,18] and for metal ion preconcentration[19].

On the other hand, disulfur dichloride (S_2Cl_2) is an important industrial compound. The main use for S_2Cl_2 is in the vapour-phase vulcanization of certain rubbers, but other uses include its chlorinating action in the preparation of mono and dichlorohydrins, and the opening of some materials in extractive metallurgy.

Recently, many researchers reported silica gels modified with both inorganic and organic functionalities which have been used for different purposes[20], notably in clean technology and particularly in green industry[7,21,22]. Modified silica gels have been also used in the separation of trace metals from aqueous systems[2]. Therefore, we decided to treat silica gel with S_2Cl_2 for producing vulcanized silica (**Scheme-1**), and using it for removing of Hg^{2+} and Pb^{2+} from several water samples with excellent efficiency.

EXPERIMENTAL

Silica gel (Merck, 70–230 mesh) was used as a supporting material. Stock solutions (1000 mg L^{-1}) of Hg^{2+} and Pb^{2+} were prepared from titrisol concentrates (Merck) and further diluted with triply distilled water to prepared standard solutions. A Shimadzu atomic absorption spectrometer model 670 was used for determination of the concentration of mercury and lead ions. The following conditions were used:

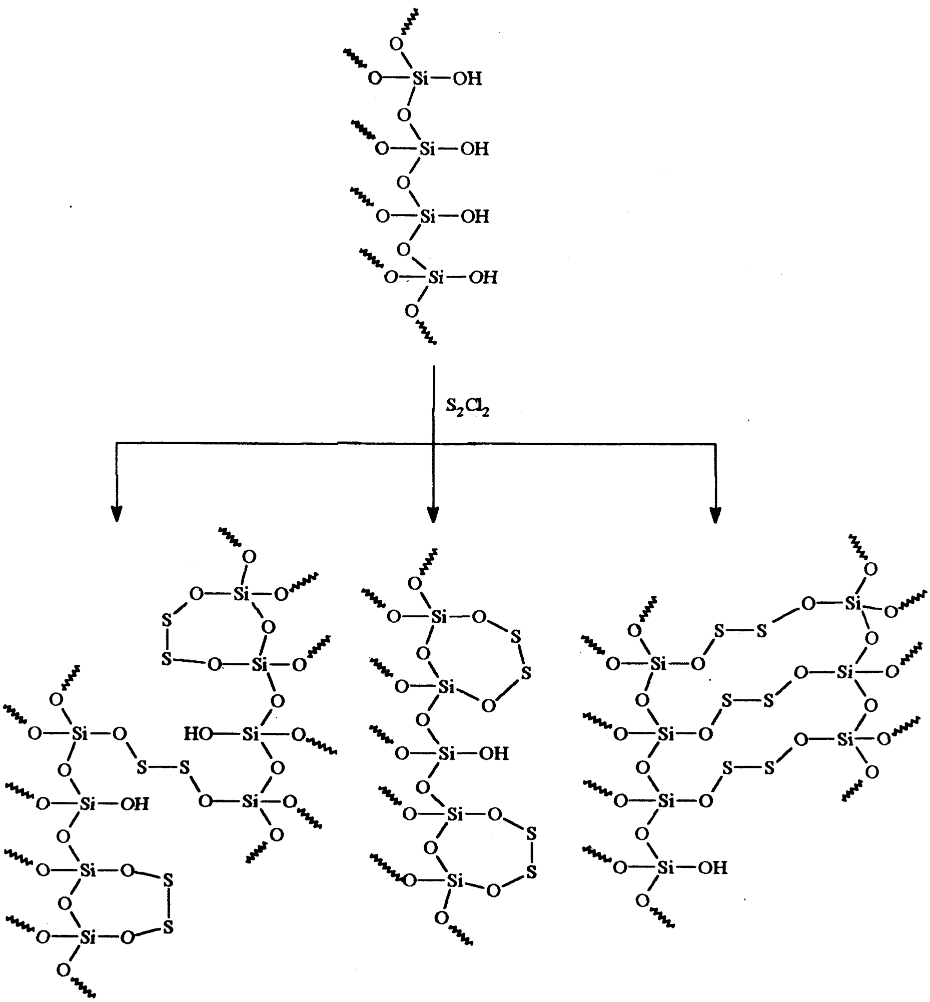
Hg^{2+}: Absorption line: 253.7 nm; slit width: 0.7 nm; lamp current: 2 mA

Pb^{2+}: Absorption line: 283.3 nm; slit width: 1.0 nm; lamp current: 5 mA

The flow rates of air and acetylene were set as recommended by manufacturer.

Preparation of vulcanized silica: Silica gel was treated with S_2Cl_2 for producing vulcanized silica (proposed structures such as **1, 2** and **3** in **Scheme-1**)[2,6], and applying it for removing Hg^{2+} and Pb^{2+} from water samples.

To an oven-dried (120°C, vacuum) silica gel (60.1 g, 1 mol) in a beaker (250 mL) under effective hood, was added disulfur dichloride (80.5 mL, 1 mol) and shaken for 2 h. CS_2 (200 mL) was added to the resulting mixture and stirred for 15 min. The resulting mixture was filtered. Then the residue was washed with CH_2Cl_2 (3 × 50 mL). Vulcanized silica as a pale yellow solid was obtained.



1 2 3

Scheme-1

Preparation of column: An accurately weighed amount (0.20 g) of sample was transferred into a column of 20 cm length and 0.5 cm diameter. The column had been washed with triply distilled water. Then 50.0 mL of a water sample that contained variable concentrations of Hg^{2+} and Pb^{2+} was passed through the column at a flow rate of approximately 2 mL min^{-1}, which was found to be optimum. The concentrations of Hg^{2+} and Pb^{2+} in the stripped solutions were then measured by AAS at 253.7 and 283.3 nm respectively. The column was then eluted by 10 mL of 0.10 mol L^{-1} HCl at an elution rate of 2 mL min^{-1}.

RESULTS AND DISCUSSION

Fig. 1 represents the effect of pH on the adsorption of 20 mg/L of Hg^{2+} and Pb^{2+} by synthetic reagent. As Fig. 1 shows, the adsorption of Hg^{2+} and Pb^{2+} on the column increased by increasing pH and up to about 6.0 and decreased at higher pH values. Therefore, a pH of 6.0 was selected as the optimum pH.

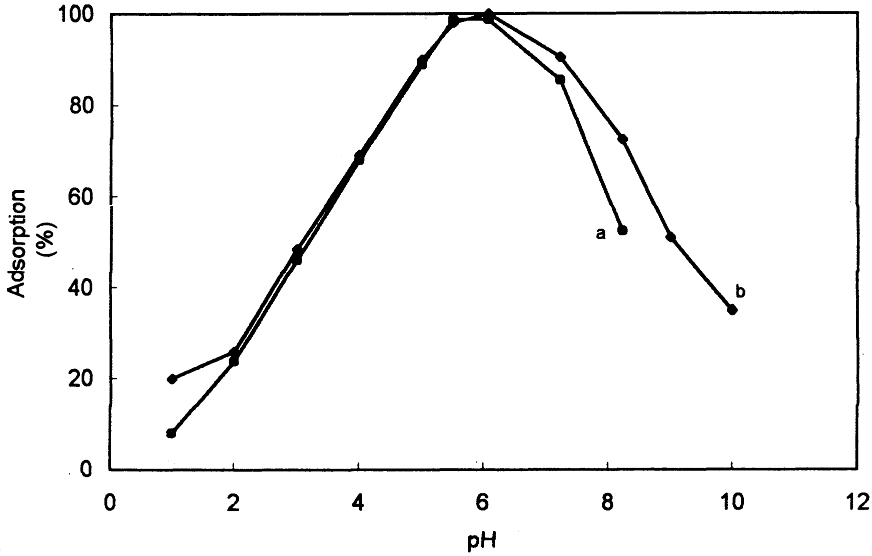


Fig. 1. Effect of pH on the adsorption for 20 mg/L of a: Hg^{2+} and b: Pb^{2+} on vulcanized silica

Adsorption isotherm: The adsorption isotherm for 20 mg/L of Hg^{2+} and Pb^{2+} adsorption from water at vulcanized silica is shown in Figs. 2 and 3

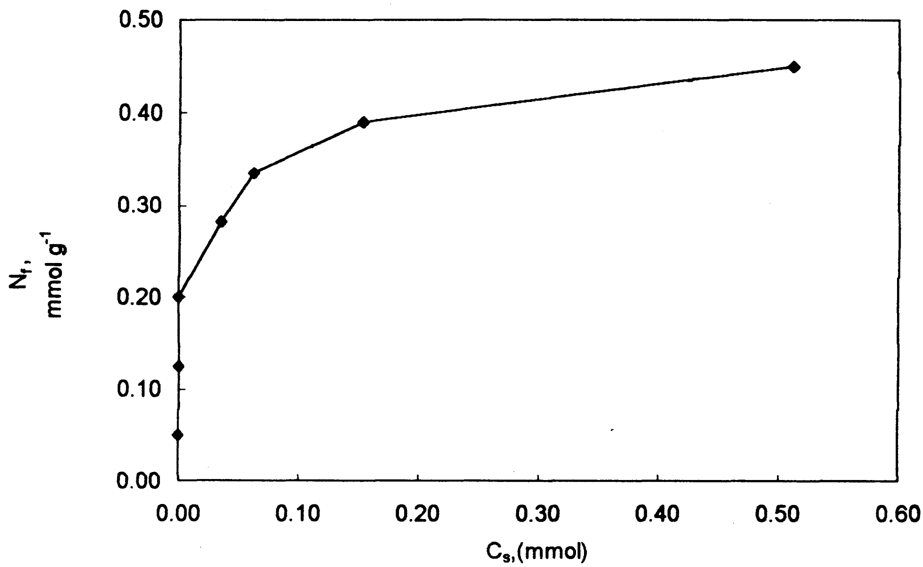


Fig. 2. Adsorption isotherm for 20 mg/L of Hg^{2+} on vulcanized silica

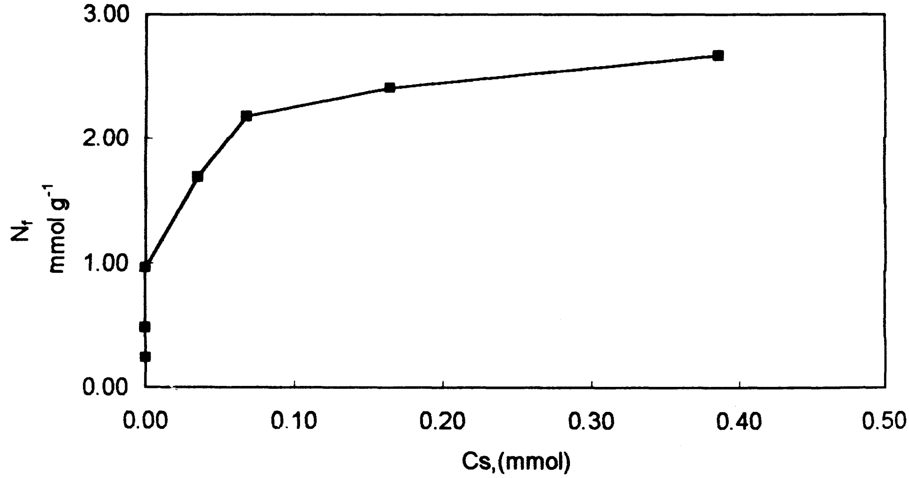


Fig. 3. Adsorption isotherm for 20 mg/L of Pb^{2+} on vulcanized silica

respectively. The number of moles adsorbed per g of adsorbent (N_f) *vs.* the equilibrium concentration of cation is illustrated. For the isotherm, the data reveal that the adsorption processes conform to the Langmuir model. Such isotherms are generally associated with mono-layer adsorption.

The Langmuir isotherm shows that the amount of cation adsorbed increases as the concentration increases, up to a saturation point. As long as there are available sites, adsorption will increase with increasing concentrations, but as soon as all of the sites are occupied, a further increase in concentrations of cations will not increase the amount of cations on adsorbents.

The Langmuir equation was used to calculate the maximum retention capacity (N_s) and standard Gibbs free energy of adsorption (ΔG_{ads})[23-25]. The general form of Langmuir isotherm is:

$$Y = KC_s/(1 + KC_s) \qquad (1)$$

where Y is the fraction of adsorbent surface covered by adsorbed species, K is a constant and C_s is the equilibrium concentration of the cation solution. $Y = N_f / N_s$, where N_s is the maximum amount of solute adsorbed per gram of surface (mmol/g) which depends on the number of adsorption sites. After linearization of the Langmuir isotherm (eqn. (1)), we obtain:

$$C_s/N_f = (C_s/N_s) + (1/KN_s) \qquad (2)$$

This adsorption study was based on the linearization form of the Langmuir isotherm derived from C_s/N_f as a function of C_s. The plots for Hg^{2+} and Pb^{2+} are shown in Fig. 4. The plot of C_s/N_f vs. C_s gives a straight line with the slope equal to $1 / N_s$, and the intercept of $1/KN_s$. Therefore, maximum retention capacity for Hg^{2+} ($N_s = 0.320$ mmol/g) and Pb^{2+} (2.40 mmol/g) was determined for cation-surface interaction from the slope, and value of K was determined from the intercept of the curve (892 L mol^{-1} for Hg^{2+} and 347 L mol^{-1} for Pb^{2+}).

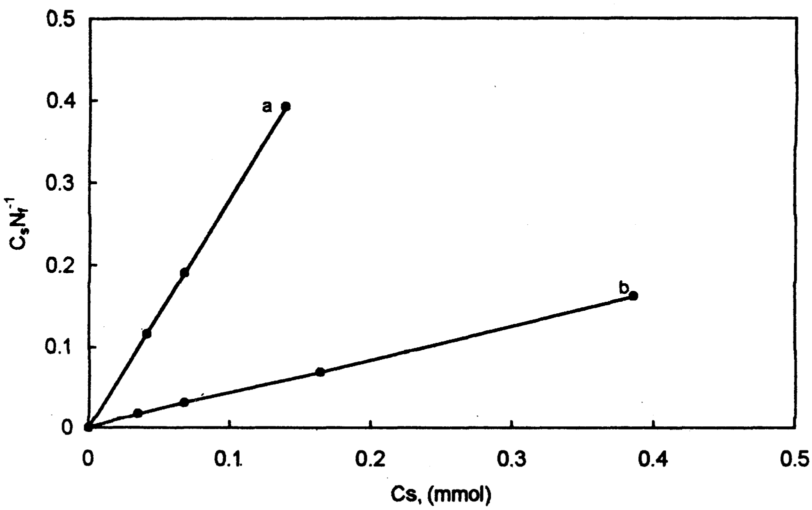


Fig. 4. Linearization of the adsorption isotherm of a: Hg^{2+} and b: Pb^{2+} on vulcanized silica

Effect of amount of vulcanized silica: The effect of the amount of adsorbent on the adsorption of Hg^{2+} and Pb^{2+} was studied. A solution containing 50 mg/L of Hg^{2+} was passed through the column containing a known weight of vulcanized silica. After passing, the Hg^{2+} concentration in stripped solution was determined by measuring the adsorbance of the solution at 253.7 nm by AAS. The same procedured was repeated for Pb^{2+}. The results are shown in Fig. 5. As in Fig. 5, the adsorption increased by increasing vulcanized silica, up to 20 mg and remained nearly constant at higher values. Therefore, 20 mg, of vulcanized silica was used for routing works.

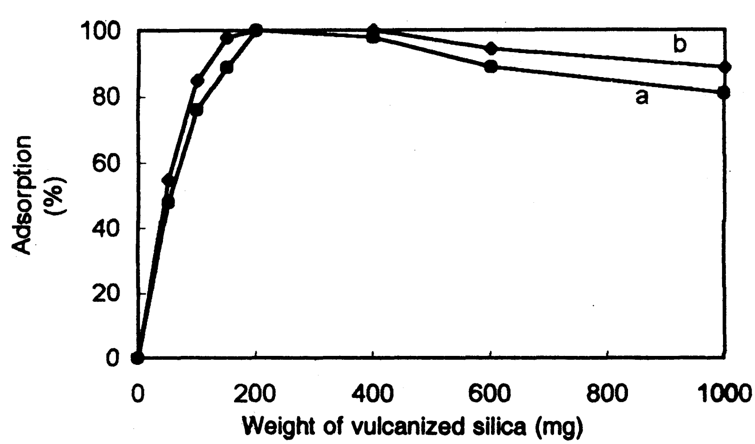


Fig. 5. Effect of the amount of vulcanized silica on the adsorption of 20 mg/L of a: Hg^{2+} and

Effect of flow rate: It was found that increasing the rate of the solution up to 2 mL min^{-1} has no effect on the adsorption of two cations, but the quantity adsorbed decreased at higher flow rates. Therefore, a flow rate of 2 mL min^{-1} was employed in order to obtain both maximum adsorption and high speed.

Recycling the vulcanized silica: The column was recycled by removing the retained Hg^{2+} and Pb^{2+}. The cations retained on the column were eluted by elution of the column with 10 mL of a 0.1 M HCl solution. The column was then washed with triply distilled water until the pH of elute reached to about 5.5. In order to investigate the efficiency of the recycled reagent, it ws used for the removal of Hg^{2+} and Pb^{2+} from standard Hg^{2+} and Pb^{2+} solutions as described above. The results showed that the efficiency of the recycled reagent for removing two ions was nearly the same as that of the fresh ones even after 5 times recycling.

Removal of Hg^{2+} and Pb^{2+} from water samples: In order to evaluate the analytical applicability of the synthesized reagents for removal of Hg^{2+} and Pb^{2+} from real samples, several water samples were tested. As the tested water sample was found to be free from mercury content, therefore, synthetic samples were prepared by adding known amounts of Hg^{2+} and Pb^{2+} to them. The concentrations of Hg^{2+} and Pb^{2+} in the stripped solution were then measured by atomic absorption spectrophotometer at 253.7 and 283.3 nm respectively, after passing 50 mL of water samples through the column. The results are given in Table-1. As Table-1 shows, the recoveries were satisfactory. In the other work, a mixture of Hg^{2+} and Pb^{2+} that contained 30 mg/L of Hg^{2+} and 40 mg/L of Pb^{2+} was passed through the column. Absorbance of the stripped solution was measured. The results did not show the presence of each of the two cations in the stripped solutions.

TABLE-1

THE CONCENTRATION OF Hg^{2+} AND Pb^{2+} IN FEED AND STRIPPED WATER SAMPLES FOR COLUMN PACKED WITH VULCANIZED SILICA

Sample	Amount of added Hg^{2+} and Pb^{2+} to feed solution		Amount of Hg^{2+} and Pb^{2+} in stripped solution	
	Hg^{2+} (mg L^{-1})	Pb^{2+} (mg L^{-1})	Hg^{2+} (mg L^{-1})	Pb^{2+} (mg L^{-1})
Tap water 1	10	10	0.0	0.0
Spring water 1	20	25	0.0	0.0
Tap water 2	45	60	0.0	0.0
Spring water 2	80	90	12.5	5.6

Conclusion

In conclusion, vulcanized silica is an attractive and inexpensive medium for the sorption of mercury and lead from natural water samples. This synthetic reagent possesses a great sorption capacity and fast response to the sorption of mercury and lead at neutral pH. In contrast to the modified silica with organofunctional groups, the stripped water by using vulcanized silica does not have any carbon content. Moreover, the new element here is that the process is heterogeneous; this could be worthwhile in an industrial setting.

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