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Synthesis of Silica Based Sorbents and their Uses in Removal of Hg^{2+} Ions from Water

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The mercury sorption properties of commercial silica (CS), activated carbon (AC) and a cation exchange resin (CER) were investigated by the batch process. Thiolfunctionalized silica (TFS), functionalized hexagonal mesoporous silica (FHMC), silylated malonamide silica (SMS), dithiocarbamate anchored silica gel (DASG) were synthesized. The mercury removal from water was estimated over a wide range of initial Hg^{2+} concentration 1-20 mg/L, contact time 1-12 h, sorbent dose 1-10 g/L, pH 2-7 at temperature 25 ºC and rpm 190. The sorption increased with increasing contact time but the equilibrium was attained in 6 h. The order of metal removing capacities for these chemical sorbents was SMS > CER > DASG > TFS > FHMS > AC > CS. The sorption followed Freundlich as well as Langmuir isotherms. The present paper shows the possibility of using functionalized silica in designing treatment plants for industrial effluents having low levels of heavy metals.

Key Words: Silica, Sorbents, Hg^{2+}, Removal.

INTRODUCTION

Mercury is widely used in many industries, mainly in sodium hydroxide and chlorine gas production. Mercury toxicity is a world wide problem as mercury and its salts are industrial health hazards. Excess of Hg (more than 100 mg) cause headache, abdominal pain, diarrhea and minamata diseases. Mercury also affects the central nervous system. The human body contains about 13 mg Hg, about 70 % of which present in fat and muscle tissue.

Studies on the treatment of effluents bearing heavy metals reveal mercury selective ion exchange resin and sorption to be the most promising technique because it is highly effective, cheap, easy and ecofriendly method among all the physico-chemical processes. Sorption of Hg(II) by various materials has been studies[1-6]. The present study is carried out to synthesize silica based composite materials to be used as sorbents for mercury in water.

EXPERIMENTAL

The mercury sorption properties, of commercial silica (CS), activated carbon (AC) and a cation exchange resin (CER) were investigated by the batch process and the results were compared with those obtained with the synthesized silica based sorbents (SBSS). Batch tests were conducted under different steady state and transient rate, conditions such as initial toxic concentration, contact time, pH sorbent dose, *etc*. The Initial mercury concentrations of the solutions were determined using a Perkin-Elmer Analyst 100 AAS as per standard methods[7]. Experiments were repeated thrice and results averaged. All experiments were conducted at room temperature. The mercury removal from water was estimated over a wide range of initial Hg^{2+} concentration 1-20 mg/L, contact time 1-10 h, sorbent dose 10 g/L, pH 2-8 at temperature 25 ºC and rpm 190.

Silylated malonamide silica (SMS) was synthesized from malonamide precursors. For this N,N,N,N-tetraethyl malonamide was alkylated with allyl bromide at central carbon, followed by hydrosylilation with triethoxysilane in the presence of a platinum catalyst. Thiol functionalized silica (TFS) was prepared using a one step functionalization method adapted to the microspherical MSU-X synthesis, produce described by Bibby and Mercier[8]. Functionalized hexagonal mesoporous silica (FHMC) was obtained by functionalization of HMC (hexagonal mesoporous silica) with terminated silane 1-(2-aminoethyl)-3-(aminopropyl-trimethoxysilane).

RESULTS AND DISCUSSION

The sorption increased with increasing contact time but the equilibrium was attained in 5 h for most of the SBSS. The order of metal removing capacities for these chemical sorbents was SMS > CER > DASG > TFS > FHMS > AC > CS. The present studies shows the possibility of using functionalized silica in designing treatment plants for industrial effluents having law levels of heavy metals and such silicas hold a promise for commercial exploitation. Absorption decreases with rise in mercury concentration (Table-1) but increases with increase in contact time (Table-2) adsorbent dose (Fig. 1). The maximum sorption was at pH 5.5 (Fig. 2) for most of the sorbents. In most cases, equilibrium was attained in 5 h and the maximum removal was at pH 5.5. Thus acidic medium favoured the removal.

TABLE-1
REMOVAL % OF Hg AT DIFFERENT CONCENTRATIONS AND AT SORBENT DOSE 5g/L, pH 6.5, CONTACT TIME 6 h, TEMPERATURE 25 ºC AND rpm 190

Concentration (mg/L)	SMS	CER	DASG	TFS	FHMS	AC
1	91.9	91.6	90.4	88.9	86.5	85.4
5	89.8	86.5	84.2	82.5	80.4	78.5
10	82.9	82.4	80.9	80.4	70.5	75.6
20	81.7	80.5	80.4	78.8	76.6	72.5

The experimental data were analyzed using four sorption kinetic models. The pseudo first order, the Ritchi second order, the modified second order and the Elowich equation The value of rate constant k were calculated for all the sorbents and were found constant. Calculation was done using the first order equation. The data were also analyzed using Langmuir and Freundlich equations (Table-3).

TABLE-2
REMOVAL % OF Hg AT DIFFERENT AGITATION TIMES AND AT INITIAL CONCENTRATION 10 mg/L, SORBENT DOSE 6 g/L, pH 6.5, TEMPERATURE 25 ºC AND rpm 190

Contact time (h)	SMS	CER	DASG	TFS	FHMS	AC
1	74.5	72.2	71.3	68.9	65.8	64.5
3	76.8	73.4	72.8	70.8	70.2	78.1
6	86.7	85.5	84.6	81.7	79.9	77.6
12	89.4	89.1	85.8	82.5	80.1	79.9

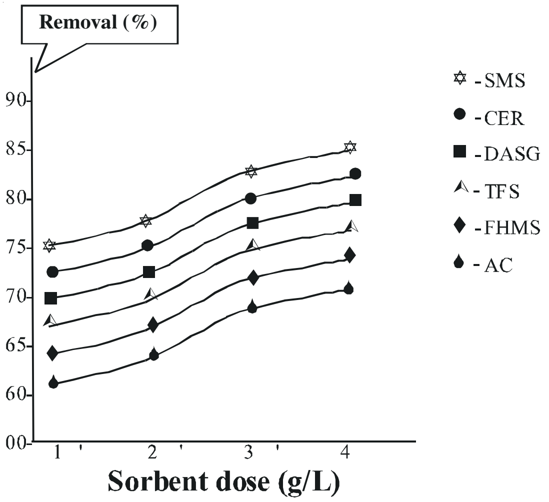

Fig. 1. Removal % of Hg at different sorbent doses and at initial concentration 10 mg/L, pH 6.5, contact time 6 h temperature 25 ºC and rpm 190

TABLE-3
ANALYSIS OF DATA USING KINETIC AND ISOTHERM MODELS

Sorbent	First order rate constant	Langmuir constants and R^2			Freundlich constants and R^2		
	K (1/min)	Q (mg/g)	b (L/mg)	R^2	K (mg/g)	1/n	R^2
SMS	0.0098	9.8632	0.0823	0.9823	6.2226	0.0212	0.6512
CER	0.0097	9.2631	0.0923	0.9698	6.0144	0.0572	0.8023
DASG	0.0094	8.5632	0.0625	0.9522	5.9133	0.0472	0.7945
TFS	0.0093	8.0425	0.0742	0.9756	5.0224	0.0544	0.7872
FHMC	0.0071	7.7124	0.0462	0.9564	4.6124	0.0334	0.7234
AC	0.0073	8.8112	0.0502	0.9723	4.8042	0.0514	0.7412

$$\log a = \log K + 1/n \log c \qquad \text{Freundlich equation}$$

$$C/a = 1/Qb + c/b \qquad \text{Langmuir equation}$$

where a (mg/g) is the adsorbet sorbed by per unit mass of sorbent (a = x/m where x mg of adsorbet is sorbed on m grams of sorbent) K and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively and Q and b are Langmuir constants. The sorption data fitted well to the Langmuir isotherm as well as the Freundlich equation. The values of Q and K clearly indicate the sorption capacities of different sorbents are in the order SMS > CER > DASG > TFS > FHMS > AC > CS.

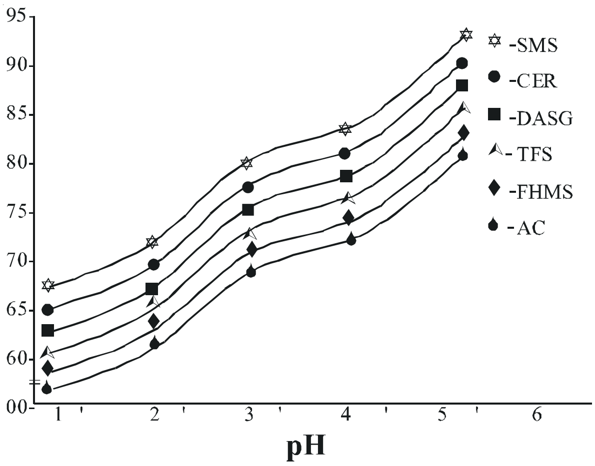

Fig. 2. Removal % of Hg at different pH values and at initial concentration 10 mg/L, sorbent dose 5 g/L, contact time 6 h; temperature 25 ºC and rpm 190

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