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Research Article

REMOVAL OF CADMIUM FROM AQUEOUS SOLUTION USING COBALTSILICATEPRECIPITATIONTUBE (CoSPT) ASADSORBENT

Kavita Parmar

Ranchi, India

ABSTRACT

Cobalt silicate precipitation tube (CoSPT), prepared through 'silica garden' route was found to be a potential adsorbent for removal of cadmium from aqueous medium. Detail adsorption study of Cd(II) on CoSPT was investigated. Batch adsorption studies were carried out as a function of contact time, adsorbent dose, adsorbate concentration (50-300 mg L^{-1}), temperature (298-323K). Cd(II) loading on CoSPT was dependent on initial Cd(II) concentration. Experimental adsorption data were modeled using Freundlich and Langmuir isotherm equations. pH variation study revealed that the adsorption increased with increase in pH of the solution. Cd(II) loading capacity of CoSPT was estimated at 319 mg g^{-1}, which ranks high amongst efficient Cd(II) adsorbents. Adsorption data were analyzed using two kinetic models, Lagergren first order and pseudo second order. It was observed that pseudo second order rate equation represented the best correlation.

Keywords: Cadmium, Cobalt silicate precipitation tube (CoSPT), adsorption, kinetics

INTRODUCTION

Cadmium is the one of the toxic metals and has received attention. It is accumulated in the human body, causing nausea, erythrocyte destruction, salivation, diarrhea and muscular cramps, renal degradation, skeleton deformity and pulmonary problems (Dinesh and Singh **2002**; Ozer and Piricci**2006**). Cadmium is an extremely toxic metal commonly found in industrial workplaces. The main source of cadmium in waste water is discharging of waste from metallurgical alloying, ceramics, metal plating, photograph, pigment works, textile printing industries, lead mining and sewage sludge (Eckenfelder, **1989**). The conventional method for cadmium removal from waste water is precipitation method.

Precipitation methods are costly and create problems with metal-bearing sludge. Adsorption is the other method that can be used for heavy metal removal from waste water.

Gravity defying self-organized tubular structures developed through precipitation reaction of metal salt crystals with aqueous sodium silicate is popularly known as "silica garden''. This phenomenon is known for more than at least three centuries though applicability of this interesting class of compounds has remained less explored (Collins et al. **1999**; Parmar et al. **2009**; Parmar et al. **2010**; Parmar et al. **2011**; Parmar et al. **2012**).

Cobalt silicate precipitation tube (CoSPT) prepared through 'silica garden' route exhibits adsorption potential for heavy metal ions through typical surface charge. CoSPT was studied in detail as Cu(II) adsorbent in aqueous medium (Parmar et al. **2011**).

This communication reports detailed investigation on Cd(II) adsorption on CoSPT in aqueous medium. The objective of this study was to establish adsorption as a new application area for this interesting class of compounds.

MATERIALS AND METHODS

Adsorbent [CoSPT]:

Cobalt silicate precipitation tube(CoSPT) synthesized through 'silica garden' route was used as an adsorbent for the removal of cadmium(II) from aqueous solution.

Adsorbate [Cd(II)]:

AR grade $CdCl_2$, was used for making Cd(II) solutions. Solutions were prepared from 1000 mg l^{-1} stock solution through serial dilution as appropriate. 18 MΩ ASTM Grade 1 water was used for making the solutions.

Instrumentation:

Atomic absorption spectrometer (GBC AVANTA), equipped with an air acetylene burner was used to determine the concentration of metal ions in aqueous solution.

Adsorption experiments:

All adsorption experiments were carried out in batches. 50 ml of cadmium solution of desired strength (initial concentration, C_0), pH and a known weight (m) of the powdered CoSPT were taken in a stoppered conical flask and shaken in a horizontal shaker for adsorb ate-adsorbent contact.

For kinetic study contact time was varied from 5 -180 min. while for other experiments it was 60 min.The adsorption processes was found to attain equilibrium within 60 min. After shaking, contents of the conical flask were allowed to settle for 30 min., filtered and the filtrate was analyzed for Pb(II) (final concentration, C_e). Cd(II) trapped on the CoSPT surface was calculated by subtraction (C_0-C_e). All experiments were carried out at room temperature (27°C).

Adsorption/desorption envelope of Cd(II) on CoSPT surface was developed in the pH range of 2-9. Dilute NaOH and HCl were used for making pH adjustments. For adsorption, process described above was followed in the pH range of 2-9. For desorption, Cd (II) was adsorbed over CoSPT without any pH adjustment for 60 min. This was followed by pH adjustment of the mixture in the range 2-9, another contact session of 60 min. in the horizontal shaker, settling for 30 min., filtration and analysis of the filtrate for final ion concentration (C_e). Amount of metal ion trapped on the CaSPT surface after desorption was calculated by subtraction (C_0-C_e).

RESULTS AND DISCUSSION

Characterization of CoSPT:

Details on synthesis, characterization and surface property of CoSPT may be found elsewhere (Parmar et al. **2009**; Parmar et al. **2011**). These tubes were finely crushed before using as adsorbent.

Optimization of contact time:

Preliminary kinetic experiments were carried out to assess the time needed for the adsorption process to attain equilibrium, the results of which have been shown in Fig.**1**. It may be seen that the equilibrium is attained within 60 min. In all subsequent adsorption experiments, otherwise mentioned, 60 min. contact time was maintained.

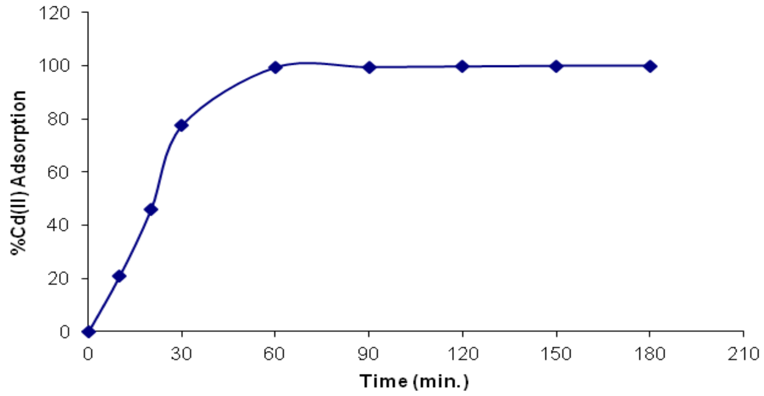

Figure 1: Effect of contact time on Cd(II) removal by CoSPT.

Effect of adsorbent dose:

The effect of adsorbent dose on Cd(II) uptake by CoSPT has been shown in Fig.**2**. Expectedly Cd(II) removal increases with increase in adsorbent dose. It was gratifying to note that almost 100% Cd(II) could be removed from 50 ml 50.2 mgl^{-1} Cd(II) solution using 0.07 gm of CoSPT.

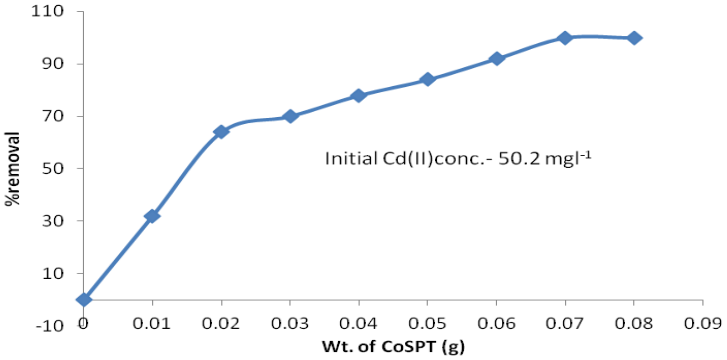

Figure 2: Effect of adsorbent dose on Cd(II) removal by CoSPT.

Effect of initial Cd(II) concentration:

The effect of initial concentration on Cd(II) uptake by 0.01 g of CoSPT has been shown in Fig.**3**. Interestingly Cd(II) uptake increases in a non-linear manner with increase in the initial Cd(II) concentration. It is apparent from Figs. **2** and **3** that Cd(II) uptake by CoSPT is a nonlinear function of adsorbent weight and initial adsorbate concentration.

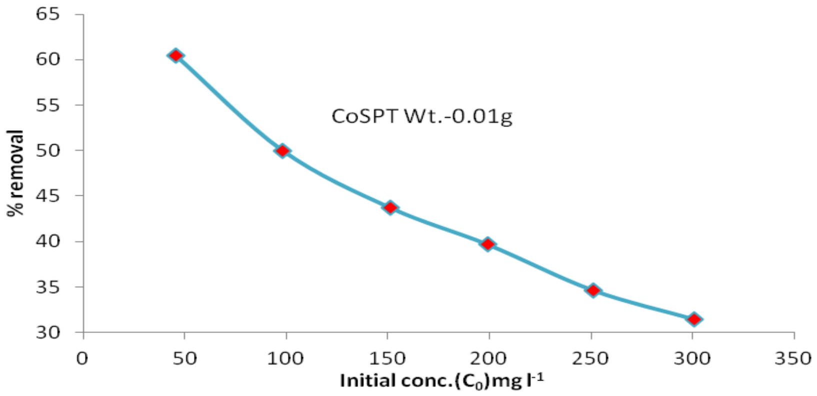

Figure 3: Effect of initial Cd(II) concentration on Cd(II) removal by CoSPT.

Effect of pH on adsorption/desorption:

Adsorption-desorption envelope of Cd(II) on CoSPT surface, experimental details for which have been described in section **2.4**, has been shown in Fig.**4** in the pH range of 2-9. One may observe in Fig.**4** that almost 100% adsorption could be achieved at pH 9; while at pH 2 there was no adsorption. It was also interesting to observe that desorption followed the adsorption path in the range 9-6 after which it deviated and again met adsorption curve at pH 2. This hysteresis clearly identifies the pH region in which Cd(II) desorption from CoSPT surface is likely to occur.

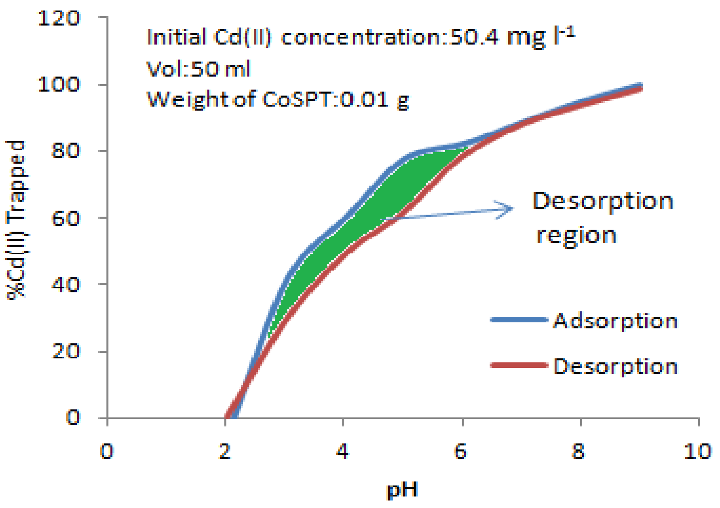

Figure 4: Adsorption-desorption hysteresis of Cd(II) on CoSPT.

Adsorption isotherm:

Experimental adsorption data were modeled with commonly used Langmuir and

Freundlichisotherms, expressions for which have been shown below.

Langmuir equation:

$$q_e = \frac{bVmC_e}{1+bC_e} \text{------------} (1)$$

Freundlich equation:

$$q_e = k_f \, .C_e{}^{1/n} \text{----------} (2)$$

Where C_e is the Cd(II) concentration at equilibrium (mg l^{-1}), q_e is the Cd(II) adsorbed per unit weight of CoSPT at equilibrium (mg g^{-1}), V_m is the Langmuir monolayer coverage (mg g^{-1}), b (L mg^{-1}) is Langmuir parameter representing adsorption bond energy, $K_f$and n are Freundlich parameters.

b, V_m, K_f and n were determined through linearization of equations 1 and 2 as well as through optimization using MS-Excel-SOLVER programme. Langmuir and Freundlich parameters determined through both the techniques have been listed in Table **1** along with goodness of fit (R^2) in each case. Goodness of fit (R^2) indicates agreement between $[q_e]_{exp}$ and $[q_e]_{cal}$ using the corresponding isotherm parameters. It appears from Table **1** that both Langmuir and Freundlich models are ideally suitable for explaining adsorption data. Langmuir is better than Freundlich model. Cd(II) loading capacity of CoSPT as returned by Langmuir model is 319 mg g^{-1} which is placed in the top category of high Cd(II) loading adsorbents.

CoSPT wt., g	Cd(II)	**Langmuir**			**Freundlich**		
		b ml mg^{-1}	V_m mg g^{-1}	R^2	K_f mg g^{-1}	n	R^2
0.01	Solver	0.0132	319.4	0.996	21.08	2.18	0.990
	Linear	0.0173	285.7	0.990	16.2	1.95	0.989

Table 1: Freundlich and Langmuir isotherm constants for Cd(II) adsorption on CoSPT

Table **2** lists loading capacities of a number of Cd(II) adsorbents for comparison (Gupta and Sharma **2002**; Mohapatra et al. **2007**; Mohapatra et al. **2009a**; Mohapatra et al. **2009b**; Rout et al. **2009a**; Rout et al. **2009b**; Samir, **2008**).

Adsorbent	**Adsorption Loading capacity mg g^{-1}**	**References**
Nickel laterite (low iron)	11.0	(Mohapatra et al., 2009a)
Nickel laterite (high iron)	13.2	(Mohapatra et al., 2009a)
Water washed clay	11.6	(Samir,2008)
Chemically treated clay	12.6	(Samir,2008)
Washed and treated clay	24.4	(Samir,2008)
Red mud	13.0	(Gupta and Sharma, 2002)
Chromite mine overburden	22.4	(Mohapatra et al., 2007)
Iron ore slime	34.7	(Mohapatra et al., 2009a)
Nalco Plant Sand	58.1	(Mohapatra et al., 2009b)
Red bauxite	38.7	(Rout et al., 2009a)
Low grade manganese ore	59.1	(Rout et al., 2009b)
CoSPT	**319.4**	**Present work**

Table2: Comparison of Cd(II) loading capacity of CoSPT with some high loading adsorbents

The Langmuir and Freundlich isotherm plots obtained through SOLVER programme have been shown in Figure5. It is apparent from Figure 5 that experimental adsorption data fit reasonably well in Langmuir and Freundlich isotherm equations using direct optimization (SOLVER) as well as linearization techniques.

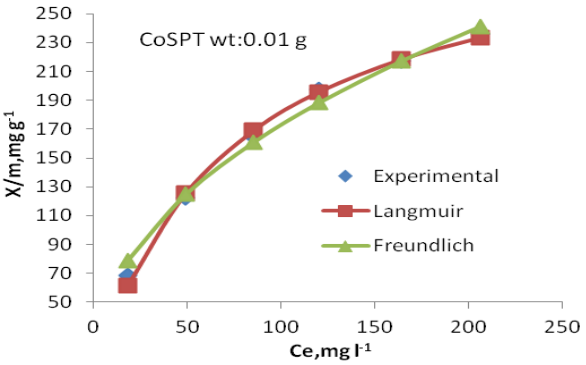

Figure 5: Langmuir and Freundlich isotherm plots of Cd(II) adsorption on CoSPT using MS-Excel-Solver.

Feasibility of an adsorption process may be ascertained through a dimensionless separation factor, R_L defined as,

$$R_L = \frac{1}{1 + bC_e} ------------(3)$$

b and C_e have been defined before. The adsorption process as a function of R_L may be described as,

$R_L > 1$; unfavorable, $R_L = 1$; Linear, $0 < R_L < 1$; favorable and $R_L = 0$; irreversible (Seed, 2003). The values of R_L calculated from different initial Cd(II) concentrations have been shown in Table **3.**

It is apparent from Table **3** that Cd(II) adsorption on CoSPT is a favourable process in the concentration range of 48.5 - 298 mg l^{-1} that moves towards irreversibility as the initial Cd(II) concentration is increased.

Initial Cd(II) conc., C_0 mg l^{-1}	**R_L**
48.5	0.808
98.2	0.607
150.8	0.471
196.8	0.387
251.5	0.316
298.2	0.269

Table 3:R_L values obtained for of Cd(II) adsorption on CoSPT using 'b' values estimated with SOLVER.

Adsorption kinetics:

Adsorption kinetics of Cd(II) on CoSPT surface was studied at temperature(298-323K), experimental details of which have been described in section **Adsorption experiments**. Lagergren first order (Lagergren, **1898**) and pseudo second order (Ho and McKay, **2000**) rate equations as shown below were employed for interpreting the kinetic data. All kinetic experiments were carried out using 50 ml of 50.2 mg l^{-1}Cd(II) solution and 0.01 g CoSPT .

Lagergren's first order rate equation:

$$\log\left(q_{\infty}-q_{t}\right)=\log q_{\infty}-\frac{k_{L}}{2.303}t-----------(4)$$

Pseudo second order rate equation:

$$\frac{t}{q_{t}}=\frac{1}{k_{p}\,q_{\infty}^{2}}+\frac{t}{q_{\infty}}------------------(5)$$

Where,

q_{∞} = Cd(II) adsorbed per unit weight of CoSPT at equilibrium (t=∞),

q_t = Cd(II) adsorbed per unit weight of CoSPT at time t,

k_L = First order specific rate constant,

k_P = Pseudo second order specific rate constant.

Specific rate constants $k_L$and k_p calculated from experimental data by linear regression have been listed in **Table 4** along with correlation coefficient.

Temp., K	**Lagergren first order**			**Pseudo second order**		
	k_L min^{-1}	**R^2**	**E_a KJ mol^{-1}**	**k_p×10^3 g mg ^{1}min^{-1}**	**R^2**	**E_a KJ mol^{-1}**
298	0.014	0.93	28.02	0.22	0.98	9.08
303	0.015	0.95		0.24	0.99	
313	0.020	0.99		0.25	0.99	
323	0.030	0.91		0.30	0.99	

Table 4: Kinetic parameters of Lagergren first order and pseudo second order rate equation for Cd(II) adsorption on CoSPT at 27˚C.

It is apparent from Fig.**6**, **7** and Table **4** that kinetic data fit is better with pseudo second order model.

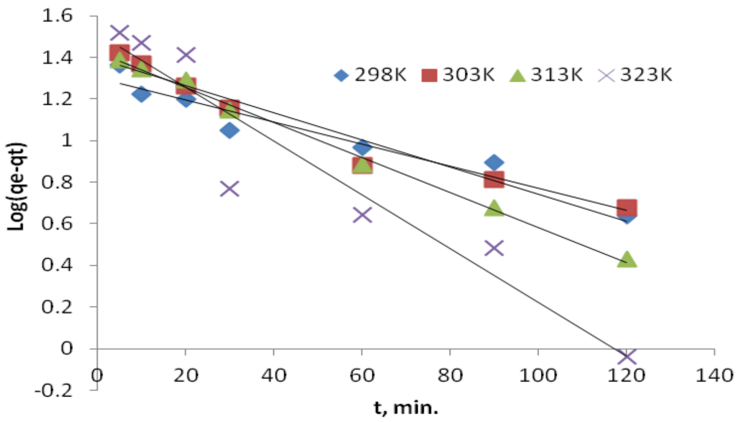

Figure 6: Lagergren First order plot of Cd(II) on CoSPT

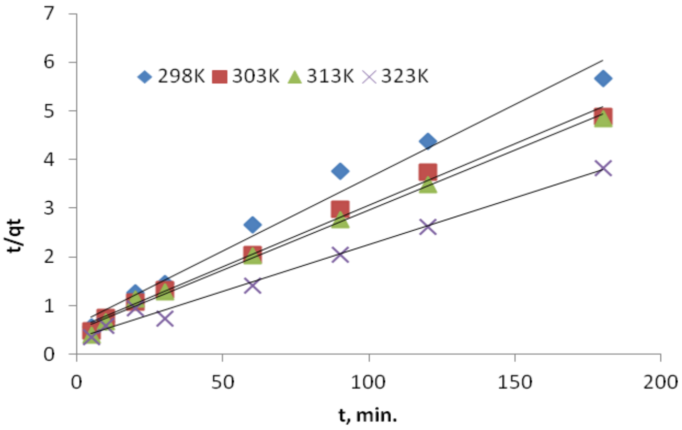

Figure 7: Pseudo second order plot of Cd(II) on CoSPT

CONCLUSION

The results obtained in this study shows that the cobalt silicate precipitation tube (CoSPT) is an effective adsorbent for the removal of Cd(II) metal ion from aqueous solution. The amount of Cd(II) ion adsorbed into the CoSPT increased with an increase in adsorbent dosage but decreased with an increase in concentration. pH 3-6 is the Cd(II) desorption region. The loading capacity was found to be 319.4 mg g^{-1}.

Cd(II) – CoSPT adsorption kinetics follow pseudo second order rate equation. Taking into consideration of the above results, it can be concluded that the CoSPT is a suitable adsorbent for the removal of Cd(II).

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