Calcium Silicate Precipitation Tubes (CaSPT) as adsorbent for the removal of Cr(III) from aqueous solution: adsorption properties, isotherm and kinetics

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Abstract- **Calcium silicate precipitation tube (CaSPT), prepared through 'silica garden' route, was investigated as Cr(III) adsorbate in aqueous medium. Batch adsorption studies were carried out with Cr(III) in the concentration range of 50-300 mg l-1 using CaSPT as adsorbent. Cr(III) loading on CaSPT was dependent on initial Cr(III) concentration. Experimental adsorption data were modelled using Freundlich and Langmuir isotherm equations. Cr(III) loading capacity of CaSPT was estimated at 290.2 mg g-1, which ranks high amongst efficient Cr(III) adsorbents. The adsorption process is endothermic and spontaneous. Adsorption kinetics follow pseudo second order model with activation energy (7.18KJ mol-1) typical for physisorption process. CaSPT was successfully tested with regard to Cr(III) removal on a real life effluent sample collected from an electroplating industry.**

Keywords – Cr(III), Calcium silicate precipitation tube(CaSPT), Adsorption, Kinetics, Desorption

I. INTRODUCTION

Gravity defying self-organized tubular structures developed through precipitation reaction of metal salt crystals with aqueous sodium silicate is popularly known as "silica garden''. "Chemical garden" or "silica garden" phenomenon is known for more than at least three centuries and a number of metal ions have been reported to produce silicate precipitation tubes[1-12] though applicability of this interesting class of compounds has remained less explored except for aluminosilicate and as adsorbent [4,10-12].

Calcium silicate precipitation tube (CaSPT) prepared through 'silica garden' route exhibits adsorption potential for heavy metal ions through typical surface properties, namely, surface area, porosity, pore volume, isoelectric point and surface charge. CaSPT was studied as multi ion adsorbent in aqueous medium. [13].

Chromium is such type of pollutant that enters the air, water and soil in the chromium(III) and chromium(VI) form through natural processes and human activities both. The main human activities that increase the concentrations of chromium(III) are steal, leather, electroplating, and textile manufacturing[14]. Chromium(III) is an essential element for humans and shortages may cause heart conditions, disruptions of metabolisms and diabetes. But the uptake of too much chromium(III) can cause health effects as well, for instances skin rashes. NIOSH, ACGIH, and OSHA has established a recommended exposure limit for chromium(III) of 0.5 mg m^{-3}. [15].

This communication reports detailed investigation on Cr(III) adsorption on CaSPT in aqueous medium along with kinetics thermodynamics and real water sample. The objective of this study was to establish adsorption as a new application area for chemical garden compounds.

II. MATERIALS AND METHODS

2.1 Adsorbent [CaSPT]
Calcium silicate precipitation tube (CaSPT) synthesized through 'silica garden' route was used as an adsorbent for the removal of chromiun(III) from aqueous solution.

2.2 Adsorbate [Cr(III)]

AR grade $Cr(NO_3)_3.9H_2O$, was used for making Cr(III) 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.

2.3 Instrumentation
Scanning Electron Microscopy (Hitachi 3400N) was used for microstructure analysis. Atomic absorption spectrometer (GBC AVANTA), equipped with an air acetylene burner was used to determine the concentration of Cr(III) ions in aqueous solution.

2.4 Adsorption experiments
All adsorption experiments were carried out in batches. 50 ml of chromium solution of desired strength (initial concentration, C_0), pH and a known weight (m) of the powdered CaSPT were taken in a stoppered conical flask and shaken in a horizontal shaker for adsorbate-adsorbent contact.
For kinetic study contact time was varied from 5 -180 min. at different temperature while for other experiments it was 60 min. Further increase in contact time has no significant effect on percentage adsorption. After shaking, contents of the conical flask were allowed to settle for 30 min., filtered and the filtrate was analyzed for Cr(III) (final concentration, C_e). Cr(III) trapped on the CaSPT surface was calculated by subtraction (C_0-C_e). All experiments were carried out at room temperature (27˚C).
Adsorption/desorption envelope of Cr(III) on CaSPT surface was developed in the pH range of 2-8. Dilute NaOH and HCl were used for making pH adjustments. For adsorption, process described above was followed in the pH range of 2-8. For desorption, Cr(III) was adsorbed over CaSPT without any pH adjustment for 60 min. This was followed by pH adjustment of the mixture in the range 2-8, 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).

III. RESULTS AND DISCUSSION

3.1 Characterization of CaSPT
Details on synthesis, characterization and surface property of CaSPT may be found elsewhere [13]. Figs. 1a, b and c show the synthesized CoSPT, scanning electron micrograph and Transmission electron micrograph of 'as grown' CaSPT. These tubes were finely crushed before using as adsorbent.
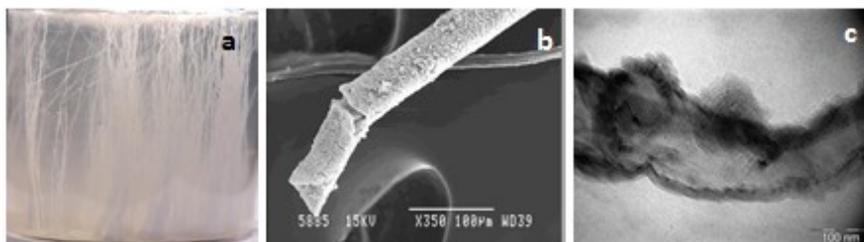

Fig.1. (a) CaSPT grown in the laboratory, (b) SEM image of 'as grown' CaSPT,
(c) TEM image of crushed particle of CaSPT at higher magnification.

3.2 Effect of pH on adsorption/desorption
Adsorption-desorption hysteresis of Cr(III) on CaSPT surface has been shown in Fig.2 in the pH range of 2-8, experimental details for which have been described in section 2.4. One may observe in Fig.2 that almost 100% adsorption could be achieved at pH 6, while at pH 2 there was no adsorption. This hysteresis clearly identifies that pH 4-7 is the region in which Cr(III) desorption from CaSPT surface is likely to occur.
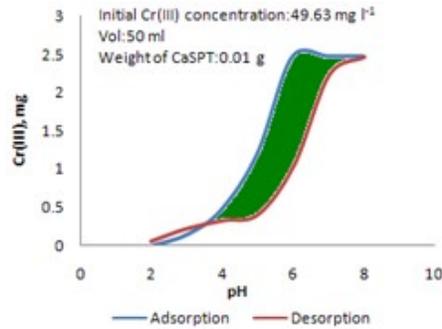
Fig.2.   Adsorption-desorption hysteresis of Cr(III) on CaSPT.

3.3 Adsorption isotherm

Experimental adsorption data were modeled with commonly used Langmuir and Freundlich isotherms, 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 Cr(III) concentration at equilibrium (mg l^{-1}), q_e is the Cr(III) adsorbed per unit weight of CaSPT 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, K_f, V_m 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.

Table 1. Freundlich and Langmuir isotherm constants for Cr(III) adsorption on CaSPT.

	Langmuir			Freundlich		
	b ml mg^{-1}	V_m mg g^{-1}	R^2	n	K_f mg g^{-1}	R^2
Solver	0.026	333.3	0.99	2.82	36.3	0.95
Linearization	0.021	290.2	0.98	3.02	40.4	0.93

It appears from Table 1 that isotherm data fit in both Langmuir models and Freundlich models using direct optimization (SOLVER) as well as linearization techniques. However between the two Langmuir fit was consistently better than Freundlich. The Langmuir and Freundlich isotherm plots obtained through SOLVER programme have been shown in Fig. 3.
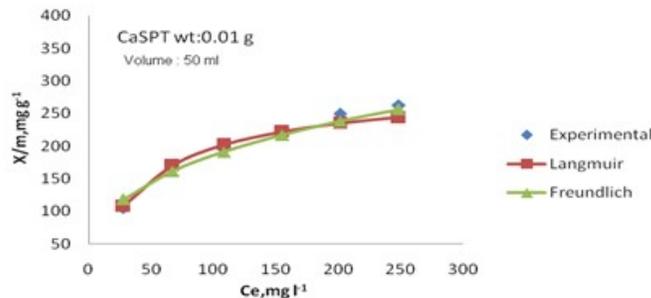

Fig.3.   Langmuir & Freundlich isotherm plot of Cr(III) adsorption on CaSPT

Cr(III) loading capacity of CaSPT as returned by Langmuir model is 290.2 mg g^{-1} which is placed in the top category of high Cr(III) loading adsorbents. Table 2 lists loading capacities of a number of Cr(III) adsorbents for comparison[14-18].

Table2. Comparison of Cr(III) loading capacity of CaSPT with some high loading adsorbents.

Adsorbent	Adsorption Loading capacity mg g^{-1}	References
Meranti sawdust	37.88	[14]
Chabazite-phillipsite	0.25	[15]
Clinoptilolite	2.4	[16]
Blast furnace sludge	9.6	[17]
Peanut husk	7.67	[18]
CaSPT	290.2	Present work

The essential characteristic of Langmuir can be expressed in terms of dimensionless separation factor R_L which is defined as,

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

b and C_e have been defined before. The R_L value between zero and one indicate favourable adsorption[20]. Our results were found to be values between zero and one in the concentration range of 50 - 300 mg l^{-1} for all concentrations. It is apparent from Table 3 that Cr(III) adsorption on CaSPT is a favourable process that moves towards irreversibility as the initial Cr(III) concentration is increased.

Table 3. RL values obtained for of Cr(III) adsorption on CaSPT using 'b' values estimated with SOLVER.

Initial Cr(III) concn., C_0 mg l^{-1}	R_L
48.9	0.628
101	0.414
147	0.304
199	0.234
251	0.190
301	0.160

3.4 Adsorption kinetics

Adsorption kinetics of Cr(III) on CaSPT surface was studied at different temperature, experimental details of which have been described in section 2.4. Lagergren first order [19] and pseudo second order [20] 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} Cr(III) solution and 0.01 g CaSPT .

Lagergren's first order rate equation:

$$\log(q_\infty - q_t) = \log q_\infty - \frac{k_L}{2.303}t \quad\quad\quad\quad (4)$$

Pseudo second order rate equation:

$$\frac{t}{q_t} = \frac{1}{k_p q_\infty^2} + \frac{t}{q_\infty} \quad\quad\quad\quad (5)$$

Where,

q_∞ = Cr(III) adsorbed per unit weight of CaSPT at equilibrium (t=∞),
q_t = Cr(III) adsorbed per unit weight of CaSPT 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. It is apparent from Table 4 that kinetic data fit is better with pseudo second order model. Specific rate constants calculated at four different temperatures were further used to calculate activation energy (E_a) of the adsorption process from Arrhenius equation,

$k = Ae^{-E_a/RT}$ ---------------------- (6)

Calculated E_a values for both first order and pseudo second order rate equations have also been listed in Table 4, which indicate that Cr(III) adsorption on CaSPT is essentially a physisorption process. Typical activation energy range of a physisorption process is 5-40 KJ mol^{-1} while in the case of chemisorption it is 40–800KJmol^{-1} [21].

Table 4.Specific rate constants kL, kP, activation energy (Ea) of Cr (III) adsorption on CaSPT at different temperatures.

Temp. (K)	Lagergren first order			Pseudo second order		
	k_L min^{-1}	R^2	E_a KJ mol^{-1}	$k_p \times 10^3$ g mg^{-1}min^{-1}	R^2	E_a KJ mol^{-1}
298	0.0207	0.93	25.6	0. 11	0.94	7.18
303	0.0230	0.92		0.08	0.94	
313	0.0284	0.91		0.06	0.96	
323	0.0345	0.88		0.05	0.98	

3.5 Adsorption thermodynamics
Cr(III) adsorption thermodynamics on CaSPT was studied following published methodology[22]. Cr(III) adsorption on CaSPT is a surface phenomenon and may be expressed by the following reaction,

$$CaSPT_{(S)} + Cr(III) \leftrightarrow CaSPT_{(s)} - Cr(III)$$ ------------(7)
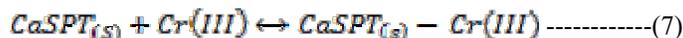
In equation 7, under condition of equilibrium,

$$k_1 . a_{Cr(III)} = k_2 . a_s$$ --------------------------------- (8)

Or,

$$\frac{k_1}{k_2} = \frac{a_s}{a_{Cr(III)}}$$ ---------------(9)

Where k_1 and k_2 are the forward and backward specific rate constants respectively, $a_{Cr(III)}$ is the activity of Cr(III) in the solution and a_s is the activity of Cr(III) in the CaSPT$_{(s)}$ – Cr(III) surface complex.
Equation 6 may be written as,

$$K_c = \frac{(f_s . C_s)}{(f_{Cr(III)} . C_{Cr(III)})}$$ ----------------- (10)

Where,
f_s and $f_{cr(III)}$ are the activity coefficients of Cr(III) in the surface complex and solution respectively. C_s is the concentration of Cr(III) in the complex (mg g^{-1}) and $C_{Cr(III)}$ is the equilibrium concentration of Cr(III) in solution(mg l^{-1}), and K_c is the equilibrium constant.
Assuming $f_{cr(III)}$ close to unity in the experimental concentration range, thus equation 7 reduces to an expression for the equilibrium constant K_c for a given condition, as shown below.

$$\lim_{, C_s \to 0} f_s \to 1, K_c = \frac{C_s}{C_{Cr(III)}}$$ ----------- (11)

Thus extrapolating C_s to zero in the plot of log ($C_s/C_{Cr(III)}$) with C_s,intercept should provide an estimate of K_c.
K_c is related to standard heat of reaction (ΔH°) and entropy (ΔS°) by the following equation,

$$lnK_c = -\left(\frac{\Delta H^°}{RT}\right) + \left(\frac{\Delta S^°}{R}\right)$$ ----- --------------- (13)

A linear plot of lnK_c with 1/T enabled calculation of ΔH° and ΔS° from the slope and intercept respectively which were further utilized for calculating ΔG° at three temperatures using equation 14.
ΔG° = ΔH°- TΔS° ---------------------- (13)

Table 5. Calculated ΔG°, ΔH° and ΔS° of Cr(III) adsorption on CaSPT.

ΔH° KJ mol^{-1}	ΔS° KJ mol^{-1}	ΔG° KJ mol^{-1}			
16.004	0.077	298K	303 K	313 K	323 K
		-6.644	-7.024	-7.784	-8.544

Table 5 lists different thermodynamic parameters calculated from equations (7-13). Shifting of ΔG° value further in the negative scale with increase in temperature confirms facilitation of the adsorption process. Positive ΔH° reconfirms endothermicity of the adsorption process.

3.6. Effluent treatment
The synthesized CaSPT was used in real life situation to remove Cr(III) from the effluent of local electroplating industry. The Cr(III) concentration in effluent was found to be 50.31 mg l^{-1}
and pH of the effluent was found to be 2.5. Table 6 shows the result of adsorption study at different pH using CaSPT. Adsorbent dose was taken as 0.2g l^{-1}, pH of the effluent was adjusted using dilute HCl or NaOH. It was observed from Table 6 that approximately 80% of Cr(III) could be removed from the effluent of electroplating industry at pH 5.8 using CaSPT. The other contaminants removed by the adsorbent CaSPT are also shown in Table 6. It is reported earlier that CaSPT is multi-ion adsorbent[14].

Table 6. Treatment of the effluent of electroplating industry using CaSPT as an adsorbent

Radical mg l^{-1}	pH 2.5		pH 4.5		pH 5.8	
	Before adsorption	After adsorption	Before adsorption	After adsorption	Before adsorption	After adsorption
Cr (III)	50.31	46.2	50.31	38.8	50.31	9.88
Zn(II)	11.31	10.27	11.28	7.5	11.65	3.5
Cu(II)	0.11	0.01	0.11	n.f	0.11	n.f

IV. CONCLUSION

The results obtained in this study shows that the calcium silicate precipitation tube (CaSPT) is an potential adsorbent for the removal of Cr(III) metal ion from aqueous solution. The amount of Cr(III) ion adsorbed into the CaSPT decreased with an increase in concentration. The loading capacity was found to be 290.2 mg g-1.
Cr(III) – CaSPT adsorption kinetics follow pseudo second order rate equation and the activation energy(7.8 KJ mol-1) indicates a physisorption process. Cr(III) – CaSPT adsorption process is spontaneous and endothermic. The synthesized adsorbent was successfully applied for the effluent treatment of electroplating industry and it was also a potential adsorbent for Zn, and Cu. The study underscores a new application area of calcium silicate precipitation tubes as adsorbents in aqueous medium.

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