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Adsorption behavior of potato starch-silica nanobiocomposite

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ABSTRACT

In continuation to our recent study on the synthesis and characterization of starch-silica nanocomposite, in the present study the nanocomposite has been evaluated for the removal of Cd(II) from the aqueous solution. The conditions for the sorption have been optimized and kinetic and thermodynamic studies were performed to understand the adsorption behaviour of the composite. Though the cadmium sorption by the nanocomposite takes place in wide pH range, pH 7.5 was found most favorable and at this pH the adsorption equlibrium data were modeled using the Langmuir and Freundlich isotherms at 10°C, 20°C, 30°C and 40 °C. At all the temperatures, the data fitted more satisfactorily to Langmuir isotherm indicating unilayer adsorption. Based on Langmuir model, Q_{max} was calculated to be 769.23 mg/g. The adsorption showed pseudo second order kinetics with a rate constant of 5.65×10^{-5} g $mg^{-1}min^{-1}$ (at 100 mg/L initial Cd(II) concentration) indicating chemisorption. The thermodynamic study revealed the endothermic and spontaneous nature of the adsorption. Effect of electrolyte on the adsorption was also studied. The nanocomposite was sucessfully recycled for six consecutive adsorption-desorption cycles with only a marginal loss in its efficiency indicating its high reusability. The composite was found to be a highly stable photoluminescent Cd(II) adsorbent which may be suitable for sensor applications in detecting the metal ions both in vivo and vitro as the material is natural polymer based. Copyright © 2010 VBRI press.

Keywords: Starch; sol-gel; silica; TEOS; composite; cadmium; sorption

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Introduction

Development of new generation environmental adsorbent based on natural nanomaterials [**1**] is the current research interest. By incorporating a natural polymer in an inorganic material [**2**], hybrid nanocomposites of increased stability can be obtained which typically exhibit synergism of the properties of the initial components. In this respect, the advantages offered by the silica matrix are chemical stability as well as large specific surface area, porosity, and mechanical strength [**3, 4**]. Composites prepared from several polysaccharides represent a new category of environmentally safe materials for the applications to explore.

Recently novel nanocomposites of vinyl modified guar gum and silica with excellent ability to bind zinc (II) [**5, 6**] and Cd(II) [**7**] have been reported by our group where saponified poly(acrylonitrile) modified guar gum and poly(acrylamide) grafted guar gum were used as templates for the ensuing silica matrix. Polysaccharides are reported to manipulate the formation of hybrid silica nanocomposites by sol-gel processes [**8-12**]. As compared to synthetic polymers, polysaccharides can be easily removed from their respective composites by calcination at temperature >500 ºC leaving behind the inorganic component. On calcination of these polysaccharide-silica nanocomposites, bioinspired hybrid silica with tailored porosity is expected. Though, polysaccharide-silica nanocomposites have been reported in the literatre [**8, 9, 12**], their use in deriving bioinspired silica adsorbents has not got much attention. The polysaccharides can adopt various conformations in solution phase and thus their presence has special impact on the silica formation from its precursor.

Starch is a group of polysaccharides, composed of glucopyranose units joined together by glycosidic linkages. Industrially, starch is broadly divided in to two types of viz, natural and modified. The characteristics of the natural starches are changed by chemical or enzymatic reaction and the products of these reactions are termed modified starches [**13**]. Starch products themselves are hardly suitable as sorbents, since they lack controllable particle size and certain wear resistance, hardness, and porosity, however the biomaterial has been used for the removal of heavy metal ions in various modified [**14**] form e.g. poly(acrylamide)-starch graft copolymer carbamoylethylated starch and starch carbamate. Water-insoluble starch phosphate [**15**] carbamate has been reported for Cu(II) removal. The effectiveness of insoluble starch xanthate [**16**] for the removal and recovery of heavy metals [Cd(II), Cu(II), Hg(II), and Ni(II)] from simulated wastewater has also been evaluated. Recently [**2**] a series of starch products (starch, starch-urea, starch-thioureas) have been encapsulated in silica in an acid catalyzed sol-gel reaction of tetraethyl orthosilicate (TEOS) to obtain composite material that sorbed Cu^{2+}, Fe^{3+}, and Al^{3+}. Sorbing capacity of this material has been compared with the other known sorbents, silica [**4**] and starch cross-linked with epichlorohydrin [**17**].

We recently reported [**18**] the synthesis of novel adsorbent bionanocomposites of soluble potato starch and silica (St-Si) in a base catalyzed sol-gel process using TEOS as silica precursor. The soluble potato starch was used as supplied and no chemical modification of the template was done before using it for the composite synthesis as we did for synthesizing [**5, 6, 7, 19**] our previous materials using guar gum. In contrast to acid catalyzed sol-gel [**20**] reactions which lead to an open network structure due to fast rate right from the first step, in base catalyzed conditions, the negatively charged transition state becomes more stable as more hydroxyl groups replace the electron donating alkoxy groups and therefore the successive steps are thus rapid, and the fully hydrolyzed species undergoes fastest condensation reactions. As a consequence, in base catalyzed reactions, highly cross-linked sol particles are initially obtained which eventually link to form gels with large pore between the interconnected particles. Thus choice of the acid and base catalysis has substantial influence on the nature of the gel which is formed. The ratio of starch: TEOS: H_2O: NH_4OH was changed to tailor the performance of the composite in terms of metal uptake from aqueous solution.

In the present study, adsorption behavior of optimum sample of potato starch-silica nanobiocomposite which was synthesized in our previous study [**18**] has been taken up. The metal ion adsorption capacity of the material was investigated using the batch technique taking cadmium ions as representative ions. To fully understand the adsorbent behavior of starch-silica nanocomposite (St-Si), kinetic isotherm and thermodynamic studies were also carried out. For easy understanding St-Si has been named as H5 in the present paper. Comparative evaluation of the nanocomposite (St-Si) was also made with control silica synthesized under identical conditions by dehydration condensation of TEOS in the absence of the starch. Its efficiency has been compared with our previously reported vinyl modified guar gum based silica nanocomposites also [**5, 6, 7**].

Experimental

Materials and methods

Soluble potato starch (CDH, LR) was used as such without purification. Tetra ethyl orthosilicate (98% TEOS; Aldrich) was used as silica precursor. NH_4OH (30% NH_3; Merck) was used. Temperature treatment of the hybrid was done in Mac (India) electric Muffle Furnace. $Cd(NO_3)_2$ (Merck) was used for preparing the stock solution. H_2SO_4 (99% Merck), NaCl (Merck), Na_2SO_4 (Merck) and NH_4OH (30% NH_3; Merck) and Cadion (Merck) were used. The pH of the solution was measured with a Digital pH meter (pHep Hanna instruments) equipped with a glassworking electrode and a reference Ag/AgCl electrode. Temperature treatment of the hybrid was done in Mac (India) Microwave Muffle Furnace. The concentration of Cd(II) was determined by microprocessor based Systronics single beam visible spectrophotometer (model T-105).

Characterization of cadmium loaded H5

Infrared (IR) spectra were recorded on a Perkin-Elmer Infrared spectrophotometer making KBr mulls in reflectance mode. X-ray diffraction (XRD) was carried out on Rigaku D/MAX-2200 X-ray powder diffractometer. Wavelength used to compute d-spacing was 1.54, 056 ºA (Cu/K-alpha-1). SEM analysis was done on EDAX, FEI Quanta 200 machine.

Preparation of silica

NH_4OH solution (12N; 3.5 mL) was added to TEOS (5 mL) dissolved in ethanol (5 mL) in a 50-mL conical flask and stirred for 14 h at room temperature followed by 3 h stirring at 80 ºC, whereupon the reaction mixture becomes completely dry. The dry product [**5**] was washed well with distilled water, filtered, and dried. The obtained silica was an amorphous white powder which was thermally treated at 40 (3 h), 60 (4 h), 70 (2 h) and 80 °C for about 2 h until a dry material was obtained. S1 thus obtained was further thermally treated inside a furnace at 250 ºC (S2), 500 ºC (S3), 700 ºC (S4), 800 ºC (S5) and 1000 ºC (S6) for 2 h each.

Preparation of composite materials

Starch (0.5 g) was dissolved in 17.5 mL of distilled water. Separately, a 1.25 mL of TEOS was also dissolved in 1.25 mL of ethanol. A third solution incorporating 0.85 mL of 12 N ammonium hydroxide was prepared separately. Afterwards, the three solutions were rapidly poured together into a reaction glass flask and kept under gentle stirring for 14 h at room temperature to grow monodisperse SiO_2 particles, within the biopolymer medium, which was subsequently washed several times with distilled water. The ensuing mixture was then subjected to slow evaporation at 40 (4 h), 60 (3 h), 70 (2 h) and 80 ºC for about 1 h until a dry material was obtained [**5, 18**], (H1) which was calcined in air inside a furnace at 250 ºC (H2), 500 ºC (H3), 700 ºC (H4), 800 ºC (H5) and 1000 ºC (H6) for 2 h each. Based on the characterization and some preliminary adsorption studies [**18**], the material calcined at 800 ºC (H5) seemed most appropriate for further adsorption studies. For understanding the adsorbent behavior of H5, removal of Cd(II) from aqueous solution was undertaken in a batch study.

Cd (II) adsorption by the composite

Adsorption batch experiments: Stock solutions of 1000 mg/L of standardized Cd(II) were prepared from $Cd(NO_3)_2$ in double distilled-deionised water. Adsorption experiments were carried out using the composite H5 as adsorbent on a temperature controlled incubator shaker set at 100 rpm maintained at 30°C for 2 h. A known amount of adsorbent was thoroughly mixed with 20 mL of respective Cd(II) solutions, whose concentrations and pH's were previously known. pH of the reaction mixture was initially adjusted using either hydrochloric acid (5 N) or sodium hydroxide (1 M). After the flasks were shaken for the desired time, the suspensions were filtered through Whatman 0.45 mm filter paper and the filtrates after suitable dilutions, were analyzed for the Cd(II) concentration. Control experiments showed that no sorption occurred on either glassware or filtration systems.

For optimizing the adsorption, one parameter was changed at a time keeping the others fixed. For pH studies, 20 mL of 100 mg/L Cd(II) solutions were adjusted to various pH ranging from 1 to 8 and the optimum pH was determined using 5 mg adsorbent dose. Various doses of the adsorbent ranging from 2.5 to 10 mg were used for studying the effect of adsorbent dose on the adsorption of the Cd(II) at 100 mg/L initial Cd(II) concentrations. The effect of temperature on the cadmium sorption was studied from 10-50°C at 100 mg/L initial Cd(II) concentration using 5 mg adsorbent dose. To study the effect of cadmium concentration, the range for different initial cadmium concentrations used were 50 to 300 mg/L (5 mg adsorbent dose; pH 7.5). In order to evaluate kinetic data, the agitation time was varied from 15 minutes to 150 min and the kinetic studies were performed at three different Cd(II) concentrations (at 100 mg/L, 150 mg/L & 200 mg/L) using 5 mg adsorbent dose at pH 7.5. Separate flasks were prepared for each time interval and only one flask was taken for desired time. Unless otherwise stated the experiments were carried out at 100 mg/L Cd(II) concentration, 5 mg adsorbent dose, 20 mL working volume, 100 rpm and 2 h shaking time. After 2 h the mixtures were filtered and the amount of the adsorbed metal ions was determined spectrophotometrically by Triton X-100 method using cadion [**21**]. The amount of metal ions adsorbed [**5**] per gram of the composite was calculated by the difference between the initial and the final readings using the following equation (**1**).

$$q_e\ (\mathrm{mg\ g^{-1}}) \quad = \quad C_{0-}C_e\ \ (\mathrm{mg\ L^{-1}})\ \mathrm{x}\ V\ (\mathrm{L}) / W(\mathrm{g}) \quad \text{------} \quad (1)$$

Where, q_e is the amount of the cadmium adsorbed (mg g^{-1}) on the adsorbent, C_o, the initial concentration of Cd(II) (mg/L), C_e, the equilibrium concentration of Cd(II) in solution (mg/L), V, the volume of the solution used (L), and W, the weight of the adsorbent used. The pH, initial concentration of Cd (II), adsorbent dose, contact time and the electrolyte amount (ionic strength) were varied, one at a time keeping the other parameters fixed. All the experiments were performed in triplicate and the results presented are the average of three where a deviation of ± 2 mg/L was observed.

Desorption studies

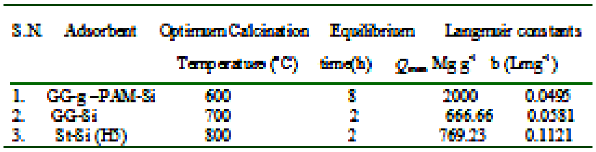
In order to determine the reusability of the St-Si adsorbent, it was recycled after stripping off Cd(II) from it using H_2SO_4. To optimize the concentration of the acid required for the quantitative stripping of the loaded Cd(II), experiments were carried out at different concentrations of H_2SO_4 ranging from 0.01 N to 1 N, where efficient desorption could be achieved using 0.05 N H_2SO_4. For the desorption, 25 mg of the Cd(II) loaded adsorbent was placed in the 20 mL of 0.05 N H_2SO_4 and stirred at 100 rpm for 2 h at 30°C. After each cycle the used adsorbent was washed well with distilled water and used in the succeeding cycle. The amount desorbed was calculated from the amount of metal ions loaded on the copolymers and the final cadmium concentration in the stripping medium. After successive leaching, the sample was used six times using 25 mg of the composite and 500 mg/L initial Cd(II) solution in total volume of 20 ml. For avoiding practical difficulty in handling the small quantity (5 mg) of the adsorbent, adsorption-desorption cycles were carried out using 25 mg adsorbent dose and accordingly 500 mg/L initial Cd(II) concentration was used for the desorption study.

Results and discussion

In our recently reported study [**18**] it was established that polycondensation of tetraethoxysilane in presence of native potato starch as template leads to the formation of hybrid nanocomposite which on calcination at 800 ºC furnishes efficient adsorbent nanocomposite (St-Si) after the loss of the template. In the synthesis of starch-silica composite material, starch was used as supplied and no modification of the template was done; neither in terms of its molecular size nor functionality, making it more economical and environment friendly. It is derived from soluble starch and silica and therefore does not have any synthetic polymeric material. pHzpc of the sorbent (7.23) indicated that at the experimental pH adsorbent had negative surface sites. At pH <7.23, the oxygens at the siloxane domains of the adsorbent biosilica and the available silanols exist in protonated state and thus are incapable of binding positive cadmium species (existing in the acidic medium), however at experimental pH (pH 7.5) which is greater than pHzpc, the sorbent has negative surface sites at which positively charged cadmium species [**22**] ($Cd(OH)^+$) are easily held. Above pH 8.0 $Cd(OH)_2$ precipitation was observed.

In general, the series of polysaccharide-silica adsorbents reported by our group are more efficient than any of the other reported biosorbents, the poly(acrylamide)-grafted guar gum-silica nanocomposite [**7**] being most efficient (Q_{max} = 2000 mg g^{-1}) amongst them. For the synthesis of guar gum-silica nanocomposite [**19**], native guar gum was used as template and the molecular size of guar template was engineered by partial depolymerization of the guar gum. Using 375 kDa guar gum as template efficient Cd(II) sorbent having Q_{max} = 666 mg/g was designed. This adsorbent had low equilibration time (2 h) in contrast to 8 h required for poly(acrylamide)-grafted guar gum-silica nanocomposite [**7**] though the later was more efficient. In our current studies, St-Si (H5) was found to be much more efficient in cadmium sorption than our previous reported guar gum based -silica nanocomposite [**19**]. Present material was also found to be superior to the material [**2**] synthesized by acid catalyzed sol-gel polymerization of TEOS in presence of starch and starch derivatives. Cd(II) binding ability of the present adsorbent has been compared with some of the adsorbents which have been previously reported by our group (**Table 1**).

Table1. Comparison of (St-Si) H5 with our previously reported similar materials.



S.N	Adsorbent	Optimum Calcination Temperature (°C)	Equilibrium time(h)	Langmuir constants Q_{max} Mg g^{-1}	b (Lmg^{-1})
1.	GG-g -PAM-Si	600	8	2000	0.0495
2.	GG-Si	700	2	666.66	0.0381
3.	St-Si (H5)	800	2	769.23	0.1121

Characterization of Cd(II) loaded H5

The Cadmium loading on the adsorbent was established by comparing the FTIR, XRD and SEM of the loaded H5 with that of H5.

FTIR: In IR spectrum (**Fig 1A**) of H5 the peaks are observed at 466 cm^{-1} (symmetric oxygen stretching vibrations of Q^3 surface silanol sites), 802 cm^{-1} (symmetric Si-O-Si stretching vibrations), 1093 cm^{-1} (LO asymmetric stretching modes) and at 1213 cm^{-1} (TO asymmetric stretching modes). SiO-H stretching is seen at 3417cm^{-1}. After cadmium loading significant change in the IR spectrum is observed in the region of silica network peaks. The LO asymmetric stretching modes and TO asymmetric stretching modes of Si-O-Si domains are seen splitted and shifted and are seen at 999 cm^{-1} and 1369 cm^{-1} respectively. Significant reduction in the intensity of symmetric Si-O-Si stretching vibrations are seen and the peak has been shifted from 802 to 790 cm^{-1} and peak intensity of oxygen ring breathing mode at 457 cm^{-1} is much reduced after cadmium loading.

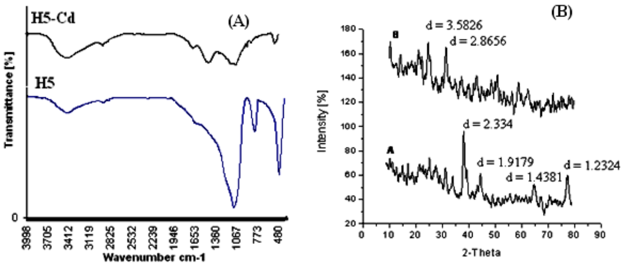


Fig. 1. (A) IR spectra of H5 and Cd(II) loaded H5; (B) XRD of H5 (A) and Cd(II) loaded H5 (B).

XRD: H5 shows crystalline peaks at 2θ 23.36 ° (d = 3.8057), 2θ 38.21 (d = 2.3534), 2θ 39.25 (d = 2.1601); 2θ 44.44 (d = 1.9179); 2θ 64.77 (d = 1.4381) and 2θ 77.37 (d = 1.2324). After Cd(II) loading significant change in XRD pattern of H5 was noticed (**Fig 1B**). In the loaded sample new peaks appeared at 2θ 24.6 ° and 31.4º while original diffraction peak (at 2θ 38.21º) of the H5 disappeared.

SEM: H5 is a porous material having strand like structures made up of agglomerated spherical particles (**Fig. 2A**). The cadmium loaded material has altogether changed surface topology where the pores are seen stuffed with the deposited cadmium metal (**Fig. 2B**). EDAX spectrum of the cadmium loaded composite further supports cadmium adsorption where significant amount of cadmium has been adsorbed. The porous structure of H5 explains the metal ion binding (**Fig. 2C**) by the material.

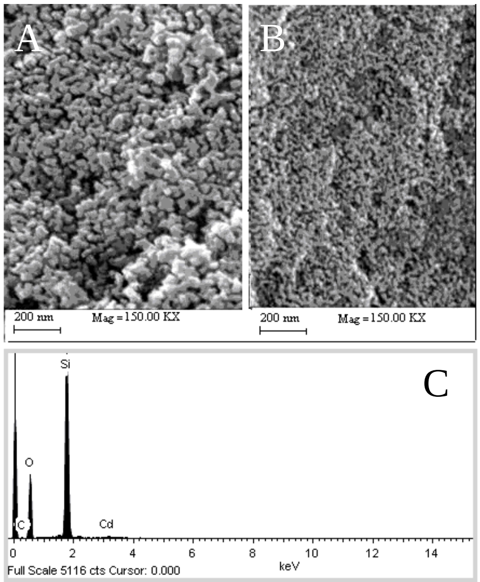
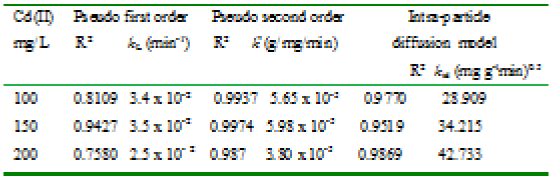


Fig. 2. SEM picture of H5 (A), Cadmium loaded composite (B), EDAX of cadmium loaded H5 (C).

Cadmium adsorption batch experiments

Sorption kinetics: % Removal of Cd(II) at a fixed adsorbent dose was monitored with time. The kinetics of Cd(II) removal by H5 indicated rapid binding of Cd(II) to the sorbent during first few minutes, followed by a slow increase until a state of equilibrium in 2 h was reached. No change in the uptake capacity was observed with further increase in equilibration time up to 2.5 h. The initial rapid phase may be due to increased number of vacant sites available at the initial stage, as a result there was an increased concentration gradient between adsorbate in solution and adsorbate on the adsorbent [**23**]. Generally, when adsorption involves a surface reaction process, the initial adsorption is rapid. Then, a slower adsorption would follow as the available adsorption site gradually decreases. Kinetics [**24**] of sorption was modeled by the pseudo first order equation, the pseudo-second-order equation and the intraparticle diffusion [**25**] models at three different initial Cd(II) concentrations (100, 150 and 200 mg/L) (**Fig. 3**). Rate equations for the pseudo first order, pseudo second order and intra particle diffusion models are shown below as Eqs. (**2**)–(**4**), respectively.

Table 2. Constants of kinetic models for Cd(II) adsorption on St-Si (H-5) at different Cd(II) concentration, pH 7.5, temperature 30^{0}C and rpm 100.



Cd(II) mg/L	Pseudo first order		Pseudo second order		Intra-particle diffusion model	
	R^2	k_L (min^{-1})	R^2	k' (g/mg/min)	R^2	k_{id} (mg g^{-1}min)$^{0.5}$
100	0.8109	3.4×10^{-2}	0.9937	5.65×10^{-2}	0.9770	28.909
150	0.9427	3.5×10^{-2}	0.9974	5.98×10^{-2}	0.9519	34.215
200	0.7580	2.5×10^{-2}	0.987	3.80×10^{-2}	0.9869	42.733

$$\mathrm{Log}\,(q_e - q_t) = \mathrm{Log}\,q_e - k_L \times t/2.303 \text{ ---------}(2)$$

$$t/q_t = 1/k' q_e^2 + t/q_e \text{ ----------------------------}(3)$$

$$q_t = k_{id} \cdot t_{0.5} \text{ ---}(4)$$

where, K_L is the pseudo first order rate constant of adsorption (min^{-1}); k' is the pseudo-second-order rate constant of adsorption (g mg^{-1} min^{-1}) and K_{id} is the intraparticle diffusion rate constant (g mg^{-1} min^{-1}); qe and qt were the amounts of Cd(II) adsorbed (mg g^{-1}) at equilibrium and at time t, respectively.

The adsorption kinetic data fitted best in pseudo-second-order model, where linear plots of t *vs* t/qt was obtained. The correlation coefficients (R^2) and the rate constants for H5 are summarized in **Table 2** these results suggest that adsorption is not diffusion controlled but is chemisorption.

Adsorption isotherms: Adsorption data were fitted to the Langmuir and Freundlich isotherms [**26**]. The Langmuir isotherm is valid for monolayer sorption due to a surface of a finite number of identical sites and expressed in the linear form as under

$$C_e/q_e = \mathrm{b}/Q_o + Ce/Q_o \text{ --------------------------- (5)}$$

where, C_e is the equilibrium concentration (mg L^{-1}) and q_e the amount adsorbed at equilibrium (mg g^{-1}). The Langmuir constants Q_o (mg g^{-1}) represent the monolayer adsorption capacity and b (L mg^{-1}) relates the heat of adsorption. The essential feature of the Langmuir adsorption can be expressed by means of R_L, a dimensionless constant referred to as separation factor or equilibrium parameter for predicting whether an adsorption system is favorable or unfavorable. R_L is calculated using the following equation.

$$R_L = 1/\ (1 + bC_0) \text{ --------------------------- (6)}$$

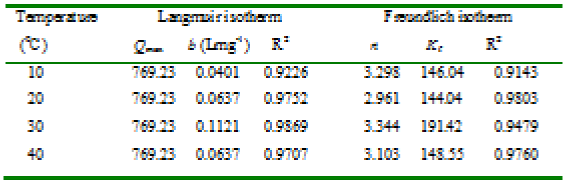
where, C_0 is the initial Cd(II) concentration (mg/L). If R_L values lies between 0 and 1, the adsorption is favorable [**27**]. The Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption and is expressed in linear form as:

$$\mathrm{In}\ q_e = \mathrm{In}\ K_f + 1/\mathrm{n}\ \mathrm{In}\ C_e \text{ --------------------------- (7)}$$

where, K_f indicates adsorption capacity (mg g^{-1}) and ‘n’ an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the adsorbent. The greater the value of the ‘1/n’ better is the favorability of the adsorption.

Adsorption of Cd(II) by H5 was modeled by Langmuir (**Fig 4I**) and Freundlich adsorption (**Fig 4II**) equations where the data fitted better to Langmuir adsorption isotherm (**Table 3**) indicating unilayer adsorption.

Table 3. Langmuir and Freundlich constants for the adsorption of Cd(II) by St-Si (H5).



Temperature (°C)	Langmuir isotherm Q_{max}	b (Lmg^{-1})	R^2	Freundlich isotherm n	K_f	R^2
10	769.23	0.0401	0.9226	3.298	146.04	0.9143
20	769.23	0.0637	0.9752	2.961	144.04	0.9803
30	769.23	0.1121	0.9869	3.344	191.42	0.9479
40	769.23	0.0637	0.9707	3.103	148.55	0.9760

Points of zero charge: The comprehensive influence of all functional groups determines pHpzc, the pH at which the net charge on the adsorbent surface is zero. At pH < pH_{PZC}, the adsorbent surface has a net positive charge, whereas at pH>pH_{PZC}, the surface has a net negative charge. Based on the pH drift tests [**22, 25**], pH_{PZC} value of the composite was calculated to be 7.23 (Figure not shown). The pH_{PZC} value indicated that at the experimental pH (pH 7.5), the surface of composite had consistently net negative charged.

Optimization of adsorption conditions: Adsorption conditions were optimized by varying one adsorption parameter at a time while keeping the others fixed. The optimization of the adsorption conditions has been depicted in **Fig. 5**.

Effect of adsorbent dose: The removal of Cd(II) increases from 63.89 mg/L to 97.21 mg/L on increasing the adsorbent dose from 2.5 mg to 10 mg in 20 mL of 100 mg/L initial Cd (II) concentration at 30°C, rpm 100, pH 7.5 and contact time 2 h (**Fig. 5B**). This increase is due to the availability of extra binding sites at higher doses of the composite.

Effect of Cd(II) concentration: With the increase in the initial Cd(II) concentration from 50 to 300 mg/L (at pH 7.5, 100 rpm, 5 mg adsorbent dose, contact volume 20 mL, contact time 2 h, temperature 30°C), an initial sharp increase in the adsorption was observed due to the availability of the extra Cd(II). Thereafter the adsorption slowly stagnates on the saturation of the adsorption sites at the adsorbent (**Fig. 5C**).

Effect of temperature: The effect of temperature on the adsorption was studied in the range of 10-50 ºC at 100 mg/L initial Cd(II), pH 7.5, 100 rpm, 5 mg adsorbent dose, contact volume 20 mL, contact time 2h. Initial increase in the adsorption with the increase in the temperature (up to 30 ºC), indicated that the adsorption is endothermic in nature. However at temperature >30 ºC, a nominal decrease in adsorption was observed which indicated some desorption is taking place at high temperatures (**Fig. 5D**).

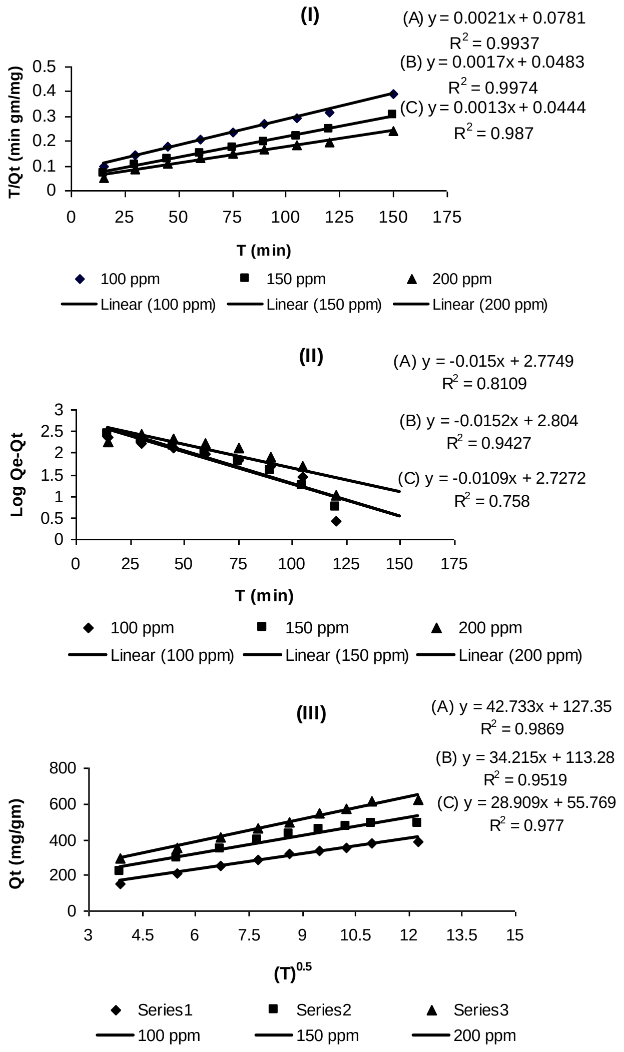


Fig. 3. (I) .Pseudo second order (II) Pseudo first order (III) Intra-particle diffusion model for the adsorption at 100 (A), 150 (B) and 200 mgL^{-1}(C) initial Cd(II) concentrations using 5mg adsorbent dose, pH 7.5, temperature 30 ºC, rpm 100.

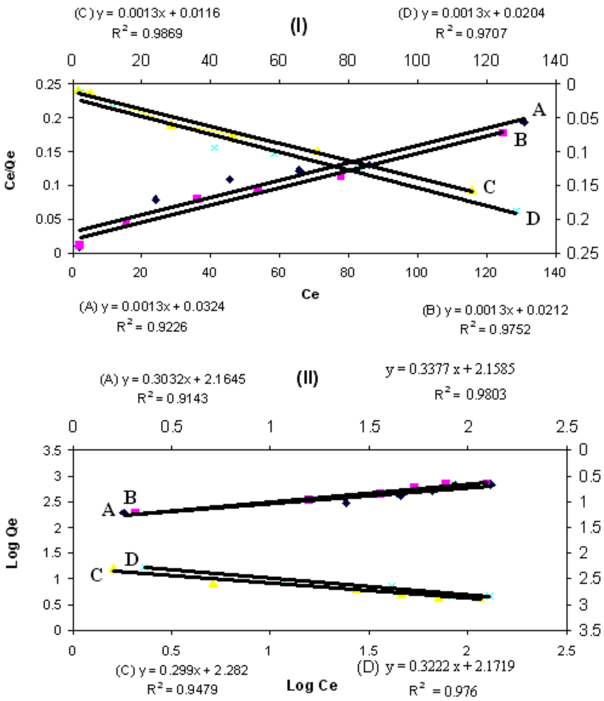


Fig. 4. (I) Langmuir isotherms models for Cd(II) adsorption on H5 at different temperatures (A) 10ºC (B) 20ºC (C) 30ºC (D) 40ºC. (II) Freundlich isotherms for Cd(II) adsorption on H5 at different temperatures (A) 10ºC (B) 20ºC (C) 30ºC (D) 40ºC.

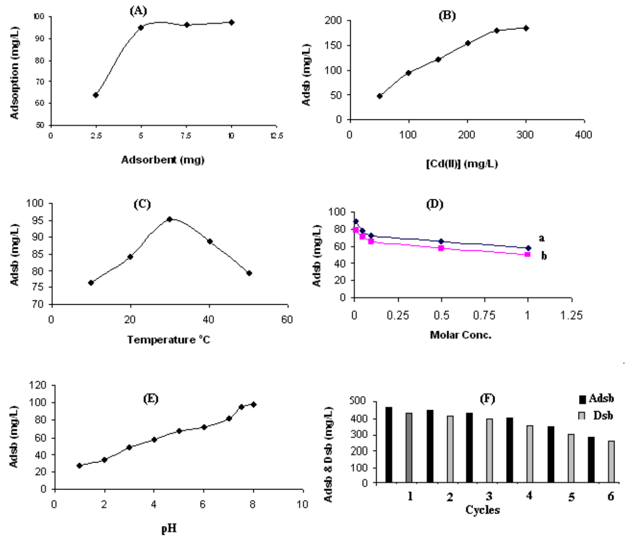


Fig. 5. Optimization of adsorption of cadmium by St-Si (H5) (A) Effect of adsorbent dose at pH 7.5, initial Cd(II) 100 mg/L, 100 rpm, contact volume 20 mL, contact time 2 h, temperature 30°C; (B) Effect of initial Cd(II) concentrations at pH 7.5, 100 rpm , 5 mg adsorbent dose, contact volume 20 mL, contact time 2h, temperature 30°C; (C) Effect of temperature at 100 mg/L initial Cd(II), pH 7.5, 100 rpm, 5 mg adsorbent dose, contact volume 20 mL, contact time 2h; (D) Effect of electrolytes (A) NaCl, (B) Na_2SO_4 on the adsorption at 100 mg/L initial Cd(II), pH 7.5, 100 rpm, 5 mg adsorbent dose, contact volume 20 mL, contact time 2h, temperature 30°C; (E) Effect of pH on the adsorption at 100 mg/L initial Cd(II), 5 mg adsorbent dose, 100 rpm, contact volume 20 mL, contact time 2 h, temperature 30ºC; (F) Adsorption desorption cycles.

Effect of electrolytes: The presence of salts may interfere with the cadmium adsorption. To understand the effect of some interfering ions on Cd(II) binding, NaCl and Na_2SO_4 were added to the aqueous synthetic solution of cadmium. With increase in concentration of both NaCl and Na_2SO_4 from 0.01M to 1.0 M, removal decreases from 89.27 mg/L to 79.22 mg/L and from 79.22 mg/L to 49.87 mg/L respectively from 20 mL of 100 mg/L Cd(II) solution at pH 7.5, temperature 30°C, rpm 100 and contact time 2 h (**Fig. 5E**). The decrease in the removal on increasing the electrolyte concentration may be due to the competition between ionic species furnished by the electrolytes on the binding sites of the adsorbent.

Effect of pH on Cd (II) adsorption: Cd(II) removal by the adsorbent increased with the increase in the pH and was maximum at pH 7.5 (**Fig. 5A**). At 100 mg/L initial Cd(II), 5 mg adsorbent dose, 100 rpm, contact volume 20 mL, contact time 2 h, temperature 30 ºC, Cd(II) removal increased from 27.97 mg/L to 95.13 mg/L with the increase in the pH from 1.0 to 7.5. Further increase in the pH resulted into $Cd(OH)_2$ precipitation which decreased the adsorption. In acidic medium cadmium exists as Cd^{2+}, $Cd(H_2O)_6^{2+}$, $Cd(H_2O)_4^{2+}$ while at pH 7.5, cadmium existed [**28**] mainly as $Cd(OH)^+$. pHpzc of the adsorbent (7.23) indicated that at the experimental pH (pH 7.5), surface sites of the adsorbent were negative to which $Cd(OH)^+$ species get attracted. To avoid $Cd(OH)_2$ precipitation, studies were not performed >pH 8.

Desorption studies

To make the sorbent economically competitive, the prepared composite material should be reused for 'n' number of cycles. 93.83 % of the Cd(II) was removed in the 1st cycle. Adsorbed Cd^{2+} could be easily stripped off by introducing protons that competed with metal ions for the binding sites. The used composite was treated with 0.05 N H_2SO_4 which resulted in to 94.55 % stripping of Cd (II). The adsorption ability was almost completely resumed after the regeneration of acid-treated sorbent. In the second cycle the material could now remove 90.94 % Cd (II) that could be desorbed up to 92.09 %. In the third cycle 86.47 % adsorption and 91.88 % desorption was possible (**Fig. 5F**). The removal decreased nominally per cycle up to six cycles suggesting high efficiency of the adsorbent. In the last cycle 57.93 % adsorption was feasible.

Adsorption thermodynamics

The values of thermodynamic parameters are relevant for the practical application of adsorption process [**29**]. Isotherm data related to adsorption of Cd(II) onto the composite at various temperatures ranging from 10 to 30 ◦C were analyzed to obtain the values of thermodynamic parameters. The values of thermodynamic functions Δ*S* and Δ*H* were evaluated using Vant Hoff's equation [**30**] which is expressed by equations **8** & **9**.

$$\ln b = \left(\frac{\Delta S}{R}\right) - \left(\frac{\Delta H}{RT}\right) \quad \text{------------------} (8)$$

$$\Delta G = \Delta H - T\Delta S \quad \text{------------- ------}(9)$$

where, Δ *G* change in Gibbs free energy (J mol^{-1}), *R* universal gas constant (8.314 JK^{-1} mol^{-1}), T temperature (Kelvin), Δ*H* change in enthalpy (J mol^{-1}), *b* is Langmuir constant at temperature *T*, Δ*S* change in entropy (J mol^{-1} K^{-1}).

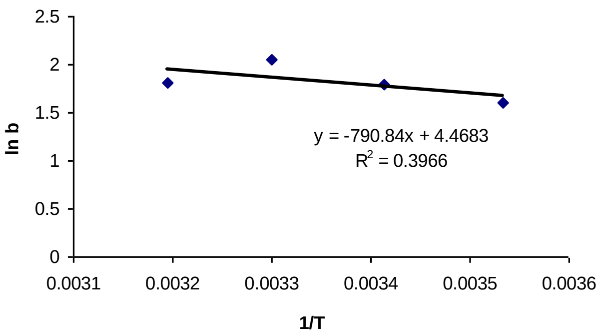
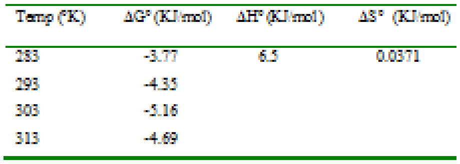


Fig.6. Thermodynamic simulation of the adsorption of Cd(II) by H5.

ln b was plotted with 1/T (**Fig. 6**) and Δ*S* and Δ*H* were calculated from the intercept and slope respectively. Negative values of Δ*G* indicated that the adsorption process was favorable and spontaneous in nature (**Table 4**). Thus adsorption of Cd(II) onto the composite was increased at higher temperature. The positive value of enthalpy change (Δ*H*) confirmed chemisorption and the endothermic nature of the adsorption process. Positive values of Δ*S* suggested good affinity of the metal ion towards the adsorbent and increased randomness at the solid-solution interface during the fixation of the metal ion on the active sites of the adsorbent.

Table 4. Thermodynamic parameters of the adsorption by (St-Si) H5



Temp (°K)	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (KJ/mol)
283	-3.77	6.5	0.0371
293	-4.35		
303	-5.16		
313	-4.69		

Conclusion

Starch derived novel nanocomposite reported in the present investigation has excellent Cd(II) binding ability and the adsorption by the composite showed pseudo second order kinetics indicating chemisorption. The adsorption was unilayer and thermodynamic study indicated endothermic nature of the adsorption**.** The adsorbent was more efficient than most of the reported cadmium adsorbents. The high stability, reusability and simple preparation procedure are its added advantages making it an environment friendly material with potential to be used in wastewater remediation and many other industrial applications. Being photoluminescent, the material may be useful in designing sensor for the metal ion detection.

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