

Cadmium (II) removal from aqueous solution using guar gum-silica nanocomposite

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Received: 26 February 2015, Revised: 18 April 2015 and Accepted: 19 April 2015

ABSTRACT

In present communication we report on Cd(II) adsorption using our recently reported material, the guar gum-silica nanocomposite. The equilibrium, thermodynamics and kinetics of Cd(II) adsorption onto composite from aqueous solution were investigated. Optimum experimental parameters were determined to be pH 8, contact time 2 hours, Cd(II) concentration 100 mg/L, temperature 30°C and adsorbent dose 10 mg. The sorption equilibrium data were modeled using the Langmuir and Freundlich isotherms where the data fitted better to Langmuir model indicating unilayer sorption, the Q_{\max} being 666 mg/g. The kinetic data indicated chemisorption in the rate-controlling step as the pseudo second order model was best suited (rate constant of $2.79 \times 10^{-4} \text{ gmg}^{-1}\text{min}^{-1}$ at 100 mg/L Cd^{2+}). The calculated thermodynamic parameters (ΔG^0 , ΔS^0 , ΔH^0) showed the adsorption to be exothermic and spontaneous with decreased randomness at the solid-solution interface. The adsorbent could be recycled for six successive cycles with 31% loss in its efficiency. Copyright © 2015 VBRI Press.

Keywords: Guar gum; nanocomposite; cadmium adsorption.

Introduction

The presence of highly toxic cadmium ions in many industrial aqueous wastes is a complex example of pollution which affect aquatic life and in extreme cases, human life [1]. Most of these residual waters are acidic; however in some chemical manufacturing processes it is not rare to find aqueous solutions whose pH varies even in a range between 7 and 10 with the possible existence of many dissolved heavy metals. Ionic cadmium is released into the environment by wastewater from electroplating, pigments, plastic, battery and zinc refining industries. Conventional physicochemical methods for removing heavy metals from waste streams include chemical reduction, electro-chemical treatment, ion exchange, precipitation and evaporative recovery. These processes have significant disadvantages, such as incomplete metal removal, high reagent or energy requirements, generation of toxic sludge or other waste products and are generally very expensive. Among the available remedial technologies, adsorption is most popular because of its low cost and simplicity [2].

Polysaccharides are abundant, renewable and biodegradable materials, which being multifunctional can potentially link (physically or chemically) to a wide variety of molecules [3-7]. Polysaccharide based materials have widely used as biosensor [8] and hydrogel [9,10], which have potential applications in water retention, dyes removal and drug release [11, 12]. Removal of toxic compounds

using the polysaccharide based macromolecular adsorbents [13, 14] has been the area of current research interest and the availability of voluminous literature reflects the importance of such adsorbents [15, 16].

Polysaccharides are the attractive biopolymers for templating the sol-gel processes in deriving silica based hybrid hydrogels [17-22]. Simple calcination of the dried hydrogels removes the templating biopolymer to result porous adsorbents. The secondary structures adopted by polysaccharide molecules in solution influence the silica sol polymerization to result adsorbents of novel architecture and tailored porosity. Several polysaccharides have been used for the synthesis of hybrid materials [18, 20, 22] but the porous adsorbents derived from these hybrids are still to be focused. Vinyl modified guar gum-silica nanocomposites having excellent ability to bind zinc (II) [23,24] and Cd(II) [25] are reported earlier by our research group, where saponified poly(acrylonitrile) modified guar gum and poly(acrylamide) grafted guar gum were used as templates for tetraethyl orthosilicate polymerization.

Though abundant and multifunctional, being water miscible, guar gum (GG) cannot be usefully exploited as adsorbent in aqueous systems; however its hybridization with silica has resulted water insoluble porous material (GX) having high surface area [26] and multifunctionality. This hybridization was done by guar gum (molecular weight 375 KDa) templated and ammonia catalyzed

polymerization of tetraethyl orthosilicate (TEOS), followed by controlled calcination (at 700°C) of the dried hydrogel. In view of the high toxicity of cadmium contaminated water and conducive characteristics of GX for adsorbent applications, in the current study, GX has been evaluated for Cd(II) removal from aqueous solution using batch adsorption technique at room temperature. To fully understand the sorption; kinetics, isotherms and thermodynamic studies were also carried out. GX is not only environment friendly but is more cost effective than our previously reported materials [27, 28] as in its synthesis the vinyl modification step of the guar gum has been fully eliminated and adsorbent of nearly similar performance was developed by tailoring the molecular size of the guar gum template. Under optimum sorption conditions for GX, comparative evaluation vinyl modified guar gum silica nanocomposites [23-25] has also been carried out to highlight the performance of this material.

Experimental

Materials

Tetraethyl orthosilicate (98% TEOS; Aldrich) was used as silica precursor. NH_4OH (30% NH_3 ; Merck), H_2SO_4 (99% Merck), HCl (G.R, Merck, 35%); $\text{Cd}(\text{NO}_3)_2$ (99% Merck), Rochelle salt (99% Qualigens), KOH (84% Merck), Absolute alcohol (99.9% A.R., China), formaldehyde (37-41% Merck), ascorbic acid (99-100% Qualigens), Triton-X-100 (Himedia) were used. Commercial sample of guar gum (Merck) after purification was used. BaCO_3 (Merck) and Cadion (Merck) were used.

Schott AVS 470 viscometer was used for viscosity measurements. Temperature treatment of the hybrid was done in Mac (India) electric Muffle Furnace. The concentration of Cd(II) was determined by microprocessor based Systronics single beam visible Spectrophotometer model T-105. Systronics Digital pH meter model 335 was used for pH measurement. The pH values were adjusted by the addition of 5 N HCl or 5 M NaOH.

Determination of pH_{ZPC}

A solution of 0.005M CaCl_2 was boiled to remove dissolved CO_2 and then cooled to room temperature. The pH was adjusted to a value between 2 and 10 using 5N HCl or 5M NaOH. GX (0.03 g) was added into 20 mL of the pH adjusted solution in a capped vial and equilibrated for 24 h. The final pH was measured and plotted against the initial pH. The pH at which the curve crosses the pH initial/ pH final line is taken as pH_{ZPC} .

Purification of the guar gum

The guar gum (GG) was purified by barium complexing as described elsewhere [26]. The pure gum was finally washed successively with different concentrations of ethanol (70, 80, 90, 95% (v/v)) and then dried.

Hydrolysis of the guar gum

For partial hydrolysis, the purified GG sample was refluxed [27, 28] with 0.01N H_2SO_4 . The hydrolysis was allowed for 80 minutes and the resulting hydrolyzate after neutralization with barium carbonate was precipitated in

excess of 95% ethanol to obtain GG sample (GG375) of molecular weight 375 KDa [26].

Preparation of composite materials

General procedure for the preparation of guar gum-silica nanocomposite material is shown in Fig. 1.

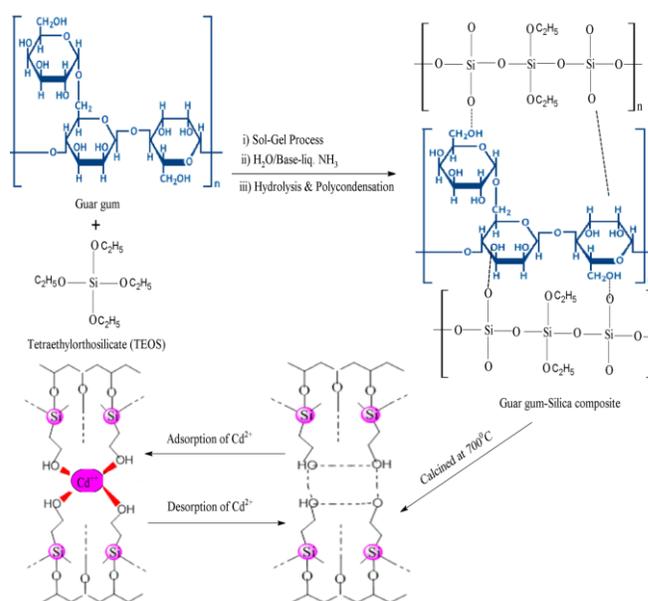


Fig. 1. Proposed mechanistic pathway for synthesis of Guar gum-Silica nanocomposite and removal of Cd^{2+} from aqueous solution.

To the solution of GG375 (1.0 g/10 mL distilled water), 2.5 mL TEOS dissolved in 2.5 mL ethanol and 1.75 mL of 12 N ammonium hydroxide were poured rapidly with constant stirring. Afterwards, the reaction mixture was kept under gentle stirring for 18 h at room temperature. The ensuing mixture was then subjected to slow evaporation at 40°C (3h), 60°C (4h), 70°C (2h) and 80°C until dry material was obtained [18], which was calcined in air inside a electric muffle furnace at 700°C for 2 h to obtain GX which was coded as H4 in our recently reported paper [26] and for convenience we are renaming it as GX in this study.

Preparation of the control silica

To 10 mL of distilled water, 2.5 mL TEOS dissolved in 2.5 mL ethanol and 1.75 mL of 12N ammonium hydroxide were poured rapidly with stirring. Afterwards, the solution was kept under gentle stirring for 18 h at room temperature. The ensuing mixture was then subjected to slow evaporation at 40°C (3h), 60°C (4h), 70°C (2h) and 80°C until dry material was obtained [18], which were calcined in air inside a furnace at 700°C for 2 h to obtain the control silica (CS).

Adsorption batch experiments

Stock solutions of 1000 mg/L of standardized Cd(II) were prepared by dissolving 2.75 g $\text{Cd}(\text{NO}_3)_2$ in 1 L of distilled-deionized water. The cadmium solutions were prepared in distilled water by gradually diluting the stock solution to the desired concentrations. Cd(II) concentration was determined by Triton X-100 method (Triton X-100 is used as solubilizing agent) using p-

Nitrobenzenediazoaminobenzene-p-azobenzene (cation) [29]. Stock solution of Cadion (0.02%) was prepared by dissolving Cadion in 0.02M potassium hydroxide in alcohol. Mixed Cadion solution was prepared by mixing the following in a 50 mL standard flask just before use and making up to the mark with distilled water: 1 mL of 20 % Rochelle salt solution, 12 mL of 4 M potassium hydroxide, 20 mL of 95 % ethyl alcohol, 1 mL of 10 % Triton X-100 solution and 10 mL of 0.02 % cadion solution.

Adsorption experiments were carried out in a temperature controlled incubator shaker set at 100 rpm maintained at 30°C for 2h. A known amount of adsorbent was thoroughly mixed with 20 mL of respective Cd(II) solutions, whose concentrations and pH values were previously known. Either hydrochloric acid (5N) or sodium hydroxide (5M) was used to initially adjust the pH of the reaction mixture. After the flasks were shaken for the desired time, the suspensions were filtered through whatman 0.45 mm filter paper and the filtrates, were analyzed for the Cd(II) concentration after suitable dilution. Control experiment was performed with 2 mL aliquot from a solution (25 mL) containing 5 mL of 0.004 % mixed cadion solution, 50 mg ascorbic acid, 2 mL of 20 % Rochelle salt, 3 drops saturated KOH and 1 mL formalin (1:1).

Unless otherwise stated the experiments were carried out at 100 mg/L Cd(II) concentration, 10 mg adsorbent dose, 20 mL working volume, 100 rpm, 30°C and 2 h shaking time. After 2 h the mixtures were filtered and the amount of the adsorbed metal ions was determined. The amount of metal ions adsorbed [30] per gram of the sorbent was calculated by the difference between the initial and the final readings using the following equation.

$$Q_e \text{ (mg/g)} = (C_0 - C_e) \text{ (mg/L)} \times V \text{ (L)} / W \text{ (g)} \quad (1)$$

where q_e is the amount of the cadmium adsorbed (mg/g) on the adsorbent; C_0 , 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.

Blank experiments (without adsorbents) under optimum conditions indicated that there is no change in the metal concentration during 2 h contact time. For optimizing the adsorption, one parameter was varied at a time while keeping the others fixed. Experiments were always carried out in duplicates to check the accuracy of results.

Desorption

In order to determine the reusability of the adsorbent, Cd(II) was stripped off from the used adsorbent using H_2SO_4 and reused. To optimize the concentration of the acid required for the quantitative stripping of the loaded Cd(II), experiments were carried out with varying concentrations of H_2SO_4 ranging from 0.001 to 1M, where efficient desorption could be achieved using 0.01N H_2SO_4 in 4 h. Composite loaded with Cd(II) (50 mg) were placed in the 20 mL of 0.01N H_2SO_4 and stirred at 100 rpm for 4 h at 30°C and centrifuged. The final Cd(II) concentration

was determined in the centrifugate. After each cycle the used adsorbent was washed well with distilled water and reused in the succeeding cycle, where the sorption experiments were performed at 500 mg/L initial Cd(II) concentration using contact volume 20 mL, pH 8, rpm 100, sorbent dose 50 mg, contact time 2h. The amount desorbed was calculated from the amount of metal ions loaded on the GX and the final cadmium concentration in the stripping medium. After successive leaching, the adsorbent was used six times. To ensure the accuracy and precision in the desorption experiments and for avoiding the handling of very small sorbent doses, five times higher sorbent doses (50 mg) were used for the sorption-desorption cycles than it were used for the optimization experiments (10 mg) and accordingly the higher initial Cd(II) concentration (500 mg/L) was chosen for the desorption experiments, while spectroscopic determinations were performed on suitably diluted solutions.

Table 1. Cd(II) adsorption by guar gum silica nanocomposite (GX), control silica (CS), poly(acrylamide) grafted guar gum silica nanocomposite (PAN-g-GSi) and poly(acrylonitrile) grafted guar gum silica nanocomposite (PAM-g-G-Si).

Sample	Cd adsorption in mg/g	Reference
PAN-g-GSi	186	[15]
PAM-g-G-Si	190	[17]
GX	182	Present study
CS	76	Present study

Results and discussion

Characterization of our recently reported material, the guar gum-silica nanocomposite [26] had revealed that the material possess suitable characteristics for adsorption application. The material (GX) was synthesized by polycondensation of tetraethyl orthosilicate in presence of depolymerized guar gum template of molecular size 375 KDa (GG375), followed by controlled calcination (at 700°C in air) of the hybrid gel. On a preliminary level, the material showed promising results in zinc adsorption from Zn(II) solution. However to compare the present material with vinyl modified guar gum-silica composites, cadmium removal using this material has been undertaken.

In a batch adsorption study, GX (10 mg) could remove 182 mg/g Cd (II) from aqueous solution in 2 h at 30°C from 100 mg/L Cd(II) at pH 8 and 100 rpm. Comparative evaluation of the Cd adsorption (mg/g) by GX, control silica and of our previously reported materials are performed in the present investigation and results are summarized in **Table 1**. GX could adsorb 1.6 times more Cd(II) than the uncalcined control silica (CS) synthesized in an identical manner, indicating the role of polysaccharide templating on the silica matrix. However the adsorption by CS700 (control silica calcined at 700°C) was much lower than CS, this is explainable as silica xerogel shrinks on calcination due to condensation polymerization across the pores. Under the optimum conditions for the GX, our previously reported composites, PAN-g-GSi [23] and PAM-g-G-Si [25] adsorbed 186 mg/g and 190 mg/g Cd(II)

respectively, however GX has the advantage of being more cost effective and environment friendly due to the absence of the vinyl moiety in the template. All the guar templated materials prepared by our group are much more efficient than most of the reported cadmium adsorbents [25].

Characterization of GG-silica hybrids

The adsorbent was characterized using FTIR, XRD, SEM, TEM, PL and BET as described elsewhere [26]. Brief description of FTIR, SEM and BET are given here.

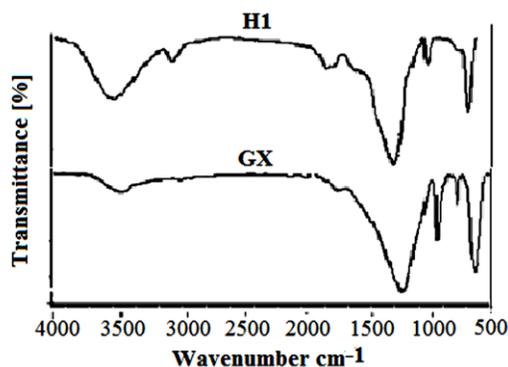


Fig. 2. FTIR spectra of guar gum silica composite (H1) and composite calcined at 700 °C.

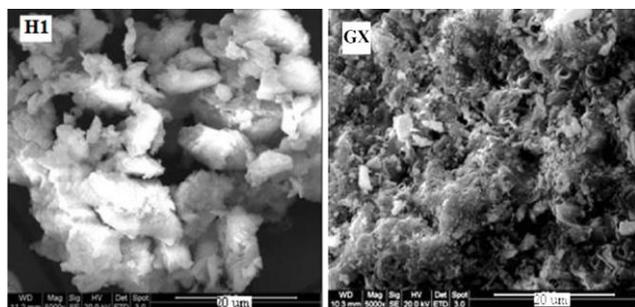


Fig. 3. SEM picture of guar gum silica composite (H1) and composite calcined at 70000C (GX).

Infra red spectroscopy

In IR spectrum of the H1 (**Fig. 2**), the inorganic component can be identified from the Si–O–Si modes observed below 1250 cm^{-1} . Peaks at 797 cm^{-1} (symmetric Si–O–Si stretching vibrations), 970 cm^{-1} (assigned to Si–OH stretching), 1104 cm^{-1} and 1218 cm^{-1} (are due to LO and TO Si–O–Si asymmetric stretching modes) are seen merged as a sharp peak. A broad SiO–H absorption band is visible at 3429 cm^{-1} which showed reduction in the heated hybrid samples (GX) due to less availability of silanol groups after the dehydration condensation. Detail investigation of effect of calcination temperature over composite has already been discussed in our previously reported article [26].

Scanning electron microscopy

In the SEM picture (**Fig. 3**) of guar gum silica composite (H1), templating effect of the polysaccharide is evident; here silica is seen deposited around the macromolecules due to dehydroxylation condensation polymerization of the silica precursor [26]. The specimen heated to 700 °C shows almost equidimensional particles in the order of 5–20 nm as

a result of transformation. The densification of the silica matrix is seen upon calcining the hybrid to 700 °C, where upon gradual loss of the polysaccharide porous silica matrix results (GX). The images at higher magnification give an idea of the morphology and size of the particles.

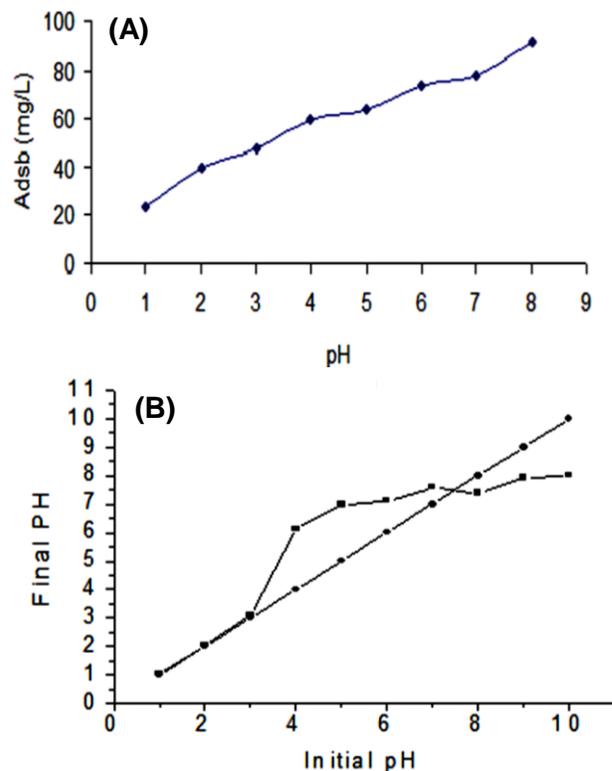


Fig. 4. Cd (II) adsorption by GX with change in pH at 20 mL of 100 mg/L initial Cd(II) solution, 10 mg adsorbent dose, 100 rpm, 2h contact time, 30 °C temperature (A) and determination of the points of zero charge (pHpzc) of the GX (B).

BET surface area and mesopore size distribution

Nitrogen adsorption–desorption isotherm of GX corresponds to type-II adsorption–desorption isotherm. Total pore volume was determined to be 0.2968 cc/g for pore size smaller than 31917.2 Å (diameter). The specific surface area for GX was shown to be 264 m^2/g from BET curve [26]. The correlation coefficient of the nitrogen adsorption measurement is 0.999057, which indicates the very high accuracy of the measurement. The porous nature and high surface area of HX, justifies the efficient adsorption of Cd(II). Pore size and surface area of composite can be controlled during synthesis and thermal curing.

Optimization of adsorption of Cd(II) on to the composite

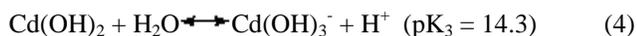
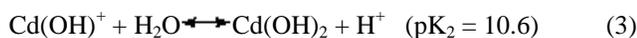
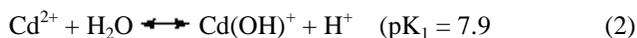
For optimizing the adsorption conditions, one adsorption parameter was varied at a time keeping all the others fixed (**Fig. 4** and **5**).

Effect of pH on Cd(II) adsorption

At 100 mg/L initial Cd(II) concentration and 10 mg adsorbent dose, Cd(II) removal increased from 23 mg/L to 91 mg/L with the increase in pH from 1.0 to 8.0 (**Fig. 4A**).

Increase in Cd(II) removal with the increase in pH can be explained in terms of pH_{pzc} (point of zero charge) of the adsorbent and metal speciation taking place in the solution. The comprehensive influence of all functional groups determines pH_{pzc} of a sorbent; the pH at which the net charge on the adsorbent surface is zero. At $pH < pH_{pzc}$, the surface of the adsorbent is positively charged and thus a decrease in the removal of positively charged metal ions species was observed. At $pH > pH_{pzc}$, the adsorbent is negatively charged and the adsorbate species are positively charged. Such a situation enhanced the electrostatic attraction between the positively charged sorbate species and the negatively charged adsorbent surface, which ultimately resulted in increase in the adsorption of metal ions. **Fig. 4B** shows the pH drift tests [31], from which the pH_{pzc} value of 7.4 was obtained for the sorbent. The pH_{pzc} value indicated that at the experimental pH (pH 8), the sorbent had negative surface sites.

Another aspect that must be considered is the metal speciation in solution, which is also pH dependent. The concentration of the hydrolyzed cadmium species depends on the cadmium concentration and the solution pH. The distribution of various hydrolyzed cadmium species can be calculated from the following stability constants (Eqs. 2-4).



In acidic medium at $pH < pH_{pzc}$, siloxane oxygens of the nanohybrid remain in the protonated form and are incapable of binding positive cadmium species (Cd^{2+} , which exists in the hydrated forms e.g. $Cd(H_2O)_6^{2+}$, $Cd(H_2O)_4^{2+}$). Moreover such complexes find difficult to approach the porous network of silica matrix.

The effect of pH on the sorption indicated polar interaction between the negative sites in the siloxane domains (oxygen) of the hybrid and $Cd(OH)^+$ (positively charged cadmium species existing in the alkaline medium) which gets trapped inside the porous network of the hybrid silica. At pH 8, cadmium exists [32] mainly as $Cd(OH)^+$ and is thus adsorbed at negatively polarized surface sites of the siloxanes. pH_{pzc} of the adsorbent (7.4) indicated that at the experimental pH (pH 8.0), $Cd(OH)^+$ species are attracted to the surface sites of the adsorbent, which are negative. To avoid the possible precipitation of $Cd(OH)_2$, pH studies were not performed at $pH > 8$. Control experiments revealed that at pH 9, precipitation of Cd(II) initiates, though it was not very conspicuous.

Effect of adsorbent dose

In 20 mL solution of 100 mg/L Cd(II) at 30°C, pH 8, 100 rpm and 2 h contact time, the removal of Cd(II) was found to increase from 57 mg/L to 91 mg/L on increasing the adsorbent dose from 5 mg to 10 mg (**Fig. 5A**). Further increase in the adsorbent dose did not much affect the adsorption (only 2 % increase was witnessed on increasing the dose from 10 mg to 25 mg), Thus 10 mg dose was chosen for further optimization. It appears that at low sorbent dosage, the metal ions were competing for sorption

at limiting sorption sites. However, as the quantity of sorbent was increased, the availability of binding sites increased due to increased surface area resulting in greater percentage removal of the metal ions. At dosage higher than 10 mg there was little increase in the uptake of Cd (II), although excess metal binding sites were present as the available Cd(II) ions present in solution was limited at the fixed concentration of 100 mg/L.

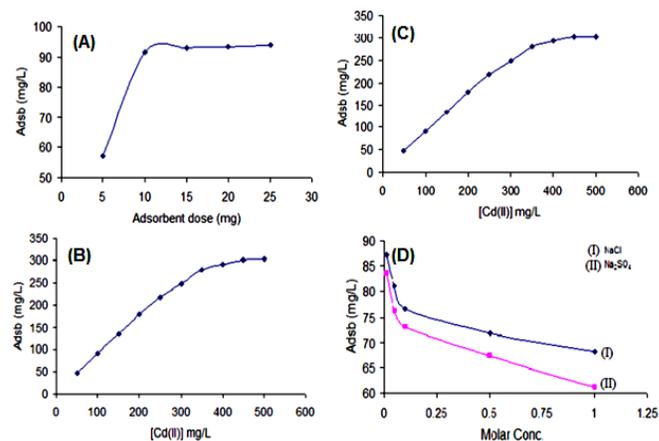


Fig. 5. Optimization of adsorption conditions (A) Adsorption at various adsorbent dose (20 mL of 100 mg/L Cd(II) solution, pH 8, 2 h contact time, 30°C temp, 100 rpm), (B) Adsorption at various concentration (10 mg adsorbent dose, pH 8, 2 h contact time, 30°C temp, 100 rpm), (C) Adsorption at various temperature (20 mL of 100 mg/L Cd(II) solution, 10 mg adsorbent dose, pH 8, 2 h contact time, 100 rpm) and (D) Adsorption under the influence of different concentration of NaCl (I) and Na_2SO_4 (II) (20 mL of 100 mg/L Cd(II) solution, 10 mg adsorbent dose, pH 8, 2 h contact time, 30 °C temp, 100 rpm).

Effect of Cd(II) concentration

With the increase in the initial concentration of Cd(II) from 50 to 500 mg/L, there was a increase in the sorption from 48 mg/L to 302 mg/L due to the availability of extra cadmium for the binding. On increasing the initial Cd(II) concentration, the sorption sharply increased in the beginning and thereafter slowly decreased and reached the saturation level. On increasing the concentration from 450 to 500 mg/L initial Cd(II), there was enhancement of only 1 mg/L sorption. Thus it appears that almost all the sorbent sites at the hybrid are occupied at 450 mg/L initial Cd(II), leading to saturation (**Fig. 5B**).

Effect of temperature

The effect of temperature on the sorption was studied in the temperature range of 10-50°C (**Fig. 5C**) using 100 mg/L Cd(II) concentration and 10 mg sorbent dose. The increase in the sorption from 72 mg/L to 91 mg/L on increasing the temperature from 10°C to 30°C is explainable since at higher temperature better interaction between the metal ions and the sorbent takes place due to increased collisions between them as the viscosity of the medium decreases. However further increase in the temperature led to decrease in sorption, indicative of some desorption taking place. Thus for deriving thermodynamic parameters, isotherm studies were performed at two suitable temperatures (10°C and 30°C).

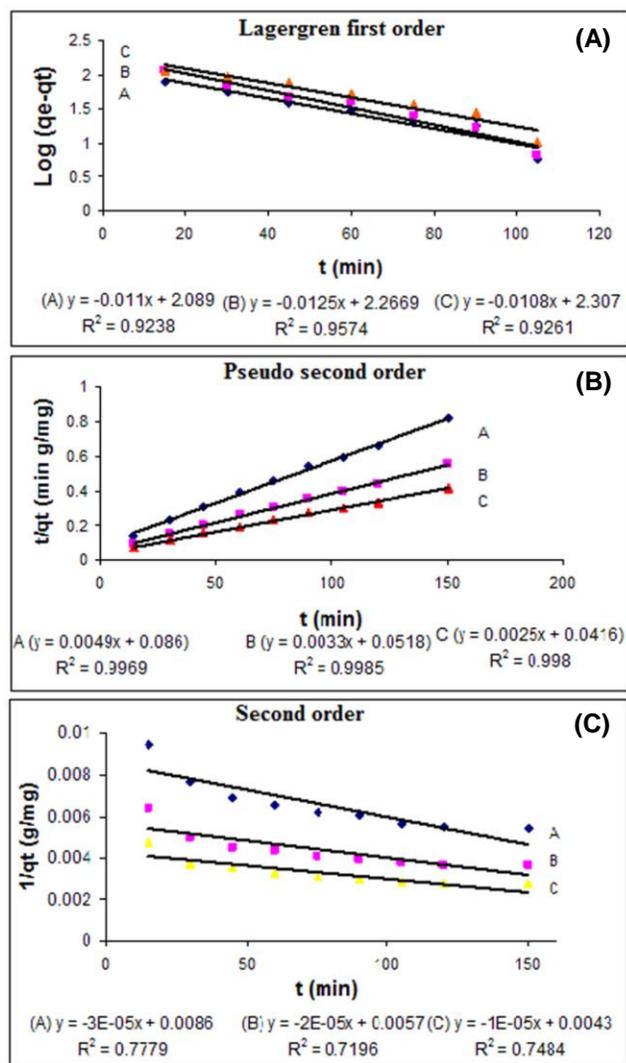


Fig. 6. Kinetic modelling of Cd(II) adsorption by GX; Lagergren First order, Pseudo second order and Second order for the adsorption at 100 mg/ L (A), 150 mg/ L (B) and 200 mg/ L and (C) initial Cd(II) concentrations.

Effect of electrolyte

The presence of salts may interfere with the Cd(II) adsorption. To understand the effect of some interfering ions on cadmium binding, NaCl and Na₂SO₄ were added to the aqueous synthetic solution of cadmium. With increase in concentration of both NaCl and Na₂SO₄ from 0.01 M to 1.0 M, removal decreased from 87 mg/L to 68 mg/L and from 83 mg/L to 61 mg/L respectively from 20 mL of 100 mg/L Cd(II) solution at pH 8, temperature 30°C, rpm 100 and contact time 2h (**Fig. 5D**). The decrease in the removal on increasing the electrolyte concentration may be due to competition between cadmium species and Na⁺ for the binding sites of the hybrid matrix, where sodium ion can be electrostatically held on the silicon atoms.

Sorption kinetics

The kinetics of Cd(II) removal by the composite indicated that binding of Cd(II) to the sorbent was rapid initially. Thereafter the binding shows a slow increase until a state of equilibrium (in 2h) reached. No change in the uptake

capacity was observed further 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 in the adsorbent [33].

Table 2. Kinetic model (A), Langmuir and Freundlich constant (B) and Thermodynamic parameters (C) of Cd(II) adsorption by guar gum silica nanocomposite.

(A) Pseudo second order, second order and lagergren kinetic model								
Cd(II) mg/L	Pseudo second order			Second order			Lagergren	
	R ²	k'(g/mg.min)	qe (mg/g)	R ²	k ₂ (g/mg.min)	qe (mg/g)	R ²	k _L (min ⁻¹)
100	0.9969	2.79 × 10 ⁻⁴	204	0.7779	3.0 × 10 ⁻⁵	116	0.9238	2.5 × 10 ⁻²
150	0.9985	2.1 × 10 ⁻⁴	303	0.7196	2.0 × 10 ⁻⁵	175	0.9574	2.87 × 10 ⁻²
200	0.9980	1.5 × 10 ⁻⁴	400	0.7484	1.0 × 10 ⁻⁵	232	0.9261	2.48 × 10 ⁻²

(B) Langmuir and Freundlich adsorption isotherm						
Temperature (°C)	Langmuir isotherm			Freundlich isotherm		
	Q _{max}	b (L/mg)	R ²	n	K _f	R ²
30	666	0.058	0.9971	2.4265	86	0.9385
10	666	0.021	0.9150	2.5627	68	0.8558

(C) Thermodynamic parameters			
Temperature (°K)	ΔG ⁰ (KJ/mol)	ΔH ⁰ (KJ/mol)	ΔS ⁰ (KJ/mol)
283	-3.11	18.2	75.3
303	-4.44		74.7

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. At equilibrium (under optimum conditions), 182 mg/g Cd(II) sorption was observed from 100 mg/L Cd(II) solution containing 200 mg/g cadmium. Kinetics of the sorption was modeled by the first order Lagergren equation, pseudo-second-order equation [34] and the second order equation [35] shown below as Eqs. (5) – (7), respectively (**Fig. 6**).

$$\text{Log}(q_e - q_t) = \text{Log} q_e - k_L \times t/2.303 \quad (5)$$

$$t/q_t = 1/k' \times q_e^2 + t/q_e \quad (6)$$

$$1/q_t = 1/q_e + k_2 t \quad (7)$$

where k_L is the Lagergren rate constant of adsorption (min⁻¹); k' the pseudo-second-order rate constant (g/mg.min) of adsorption and k_2 the second order rate constant (g/mg.min); q_e and q_t are the amounts of metal ion adsorbed (mg/g) at equilibrium and at time t , respectively. Kinetic data of Cd(II) sorption by the composite was best fitted in to pseudo second order kinetic equation, where linear plot of t/q_t vs t was obtained with the correlation coefficient (R^2) being 0.9993 and rate constant 2.79×10^{-4} at 100 mg/L initial Cd(II) concentration. Kinetics was studied at three different initial Cd(II) concentrations and the R^2 values and the rate constants for all the three models are listed in **Table 2A**, indicating that rate of adsorption was higher at 100 mg/L Cd(II) concentration. The equilibrium rate constant of pseudo second-order, k' decreases with the

increase in various initial cadmium (II) concentrations, similar observations have been published [36]. The decrease in the k' with increasing Cd(II) concentrations may be explained by changing the eq. (6) into eq. (8) expressed as below.

$$k' = \frac{F}{q_e(1-F)t} \quad \text{----- (8)}$$

where F is the fraction of q_t/q_e , and t is the time to reach q_t , so k' can be expressed as a function of uptake fraction F (q_t/q_e) and t . Eq.(6) indicates that k' is inversely related to t , and therefore, the decrease of k' with increasing initial concentrations of cadmium only suggests that a longer period of time will be needed for a higher concentration cadmium to realize the specific uptake fraction, while the adsorption rate (dq_t/dt) at contact time t still increases as the initial concentration of cadmium increases.

Adsorption isotherm studies

Adsorption data were fitted to the Langmuir [37] and Freundlich isotherms. 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 below.

$$C_e/q_e = 1/bQ_0 + C_e/Q_0 \quad (9)$$

Where C_e is the equilibrium concentration (mg/L) and q_e the amount adsorbed at equilibrium (mg/g). The Langmuir constants Q_0 (mg/g) represent the monolayer adsorption capacity and b (L/mg) relates the heat of adsorption. The essential feature of the Langmuir adsorption can be expressed by means of RL , a dimensionless constant referred to as separation factor or equilibrium parameter for predicting whether an adsorption system is favorable or unfavorable. RL is calculated using the following equation.

$$RL = 1/(1 + bC_0) \quad (10)$$

Where C_0 is the initial Cd(II) concentration (mg/L). If RL values lies between 0 and 1, the adsorption is favorable. This model can be written in non-linear form as follows [38].

$$q_e = Q_0 b C_e / (1 + b C_e) \quad (11)$$

Where q_e is the equilibrium metal ion concentration on the sorbent (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/L), Q_0 is the monolayer sorption capacity of the sorbent (mg/g), and b is the Langmuir sorption constant relating the free energy of sorption. The Freundlich isotherm is expressed in linear form as:

$$\ln q_e = \ln K_f + 1/n \ln C_e \quad (12)$$

Where K_f indicates adsorption capacity and n an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the adsorbent. The greater the values of the $1/n$, better is the favorability of the adsorption. The higher fractional value of $1/n$ ($0 < 1/n < 1$)

signifies that the surface of the adsorbent is heterogeneous in nature [39].

For isotherm studies, adsorption equilibrium data were obtained at different initial Cd(II) concentrations ranging from 50 mg/L to 500 mg/L at 10 mg adsorbent dose, 20 mL contact volume, 2h contact time, 100 rpm at 10°C and 30°C. The equilibrium data fitted to Langmuir model better than Freundlich model indicating surface homogeneity of the adsorbent and unilayer adsorption. From Langmuir isotherm Q_0 was calculated to be 666 mg/g indicating that the adsorbent had a significantly high capacity to remove Cd(II) ions (Fig. 7). The values of Langmuir and Freundlich constants are presented in Table 2B. The Langmuir constant "b" increased with increasing temperature from 10°C to 30°C implying that the adsorption process was endothermic in nature and Cd(II) exhibited higher affinity for the adsorbent at higher temperature than at lower temperature [40]. At 30°C for 100 mg/L Cd(II), RL was calculated to be 0.1468, indicative of the adsorption as being favorable.

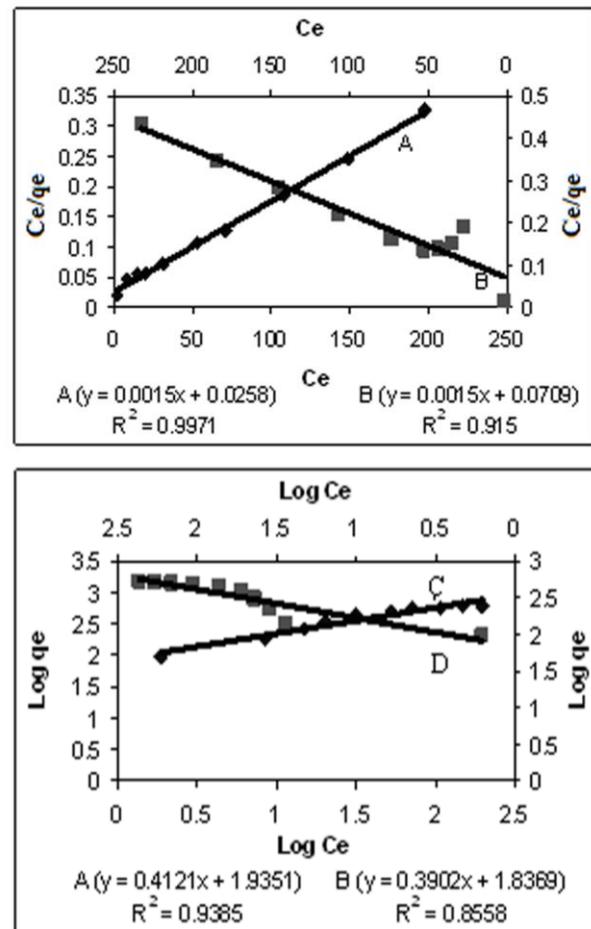


Fig. 7. Langmuir isotherms at 10 °C (A), at 30 °C (B) and Freundlich isotherms at 10 °C (C), at 30 °C and (D) for Cd(II) adsorption by GX using 10 mg adsorbent dose, 8 pH, 100 rpm, 2h contact time.

Adsorption thermodynamics

The values of thermodynamic parameters are relevant for the practical application of adsorption process [41]. Isotherm data related to adsorption of Cd(II) on to the sorbent at 10°C and at 30°C were analyzed to obtain the

values of thermodynamic parameters. Change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) for the adsorption process were calculated using the Eqs. (13) – (15) [42] and computed values are listed in **Table 2C**.

$$\Delta G = -RT \ln b \quad (13)$$

$$(\ln b_2 / \ln b_1) = -\Delta H/R (1/T_2 - 1/T_1) \quad (14)$$

$$\Delta G = \Delta H - T\Delta S \quad (15)$$

Where ΔG , change in Gibbs free energy (J/mol); R, universal gas constant (8.314 J/K.mol); T, T_1 and T_2 temperatures (K); ΔH , change in enthalpy (J/mol); b_1 and b_2 are Langmuir constants at temperatures T_1 and T_2 , respectively; ΔS , Change in entropy (J/mol.K). Negative values of ΔG indicated that the adsorption process was favorable and spontaneous in nature. It may be noted that with the increase in temperature from 10°C to 30°C the value of ΔG_0 decreased from -3.11 kJ mol⁻¹ to -4.44 kJmol⁻¹. Thus adsorption of Cd(II) onto the composite was increased at higher temperature. The positive value of enthalpy change (ΔH_0) confirmed the endothermic nature of the adsorption process. Positive values of ΔS_0 suggested good affinity of the metal ion toward the adsorbent and increased randomness at the solid-solution interface during the fixation of the metal ion on the active site of the adsorbent.

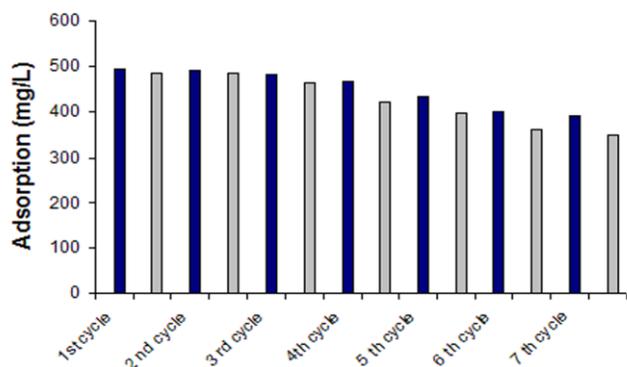


Fig. 8. Adsorption-desorption cycles for Cd(II) by GX at 20 mL of 500 mg/L initial Cd(II) concentration, 8 pH, 100 rpm, 50 mg adsorbent dose, 30°C temp, 100 rpm.

Regeneration and reuse of the adsorbent

To make the adsorbent economically competitive, it should have the potential of regeneration for repeated use. This feature of the material is of crucial importance in commercial/field applications for heavy metal removal from wastewaters. 94.5 % of the Cd(II) was removed in the first cycle. Adsorbed Cd (II) could be stripped by the introduction of protons that compete with metal ions for binding sites. The used sorbent was treated with 0.05 N H₂SO₄ which resulted in to 97% stripping of Cd(II). In the second cycle the material could remove 92.7 % Cd(II) that could be desorbed up to 93.2 %. In the third cycle 89.5 % adsorption and 91.3 % desorption was possible (**Fig. 8**). The removal decreased only nominally per cycle up to sixth cycle suggesting a very high efficiency of the sorbent. In the last sixth cycle, 61.7 % sorption was feasible.

These experimental results have thus shown that the sorption ability was almost completely resumed after the

regeneration with acid during the successive adsorption-desorption cycles.

Considering the very high concentrations of Cd(II) sorbed in each cycle, the high performance of the material could be of well exploited in the treatment of industrial waste water with high metal contents.

Conclusion

The Cd(II) adsorption by the nanocomposite showed unilayer adsorption which followed pseudo second order kinetics indicating that chemisorptions was the rate-controlling step. Besides being cost effective, very efficient Cd(II) sorption and high reusability of the adsorbent makes it a very appealing candidate for wastewater remediation technologies. Almost complete recovery of Cd(II) from the cadmium-loaded composite, and the reusability of desorbed-composite in six repeated adsorption-desorption cycles, showed that the material can be efficiently used for metal sorption. Compared to our previously synthesized materials, this material does not involve the vinyl modification step which makes it a green and environment friendly product and hence has potential in sensor applications too. It can be concluded from the reported observations that this material can be successfully used as a low-cost environment-friendly bio sorbent for the removal of heavy metals even from heavily contaminated waters.

Acknowledgements

The authors are thankful to Council of Scientific & Industrial Research, New Delhi, for the financial support to carry out this work.

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