**Cassia grandis** seed gum-*graft*-poly(acrylamide)-silica hybrid: An excellent cadmium (II) adsorbent

Vandana Singh\(^1\)*, Stuti Tiwari\(^1\), Sadanand Pandey\(^1\), Preeti\(^1\), Rashmi Sanghi\(^2\)

\(^1\)Department of Chemistry, University of Allahabad, Allahabad 211 002, India
\(^2\)Indian Institute of Technology Kanpur, Kanpur 208016, India

*Corresponding author. Tel: (+91) 9415310942; E-mail: singhvandanasingh@rediffmail.com

Received: 28 July 2014, Revised: 11 September 2014 and Accepted: 24 October 2014

**ABSTRACT**

This study puts forward the synthesis of an excellent cadmium adsorbent having unprecedented high capacity \(Q_{\text{max}} = 5000 \text{ mg g}^{-1}\) to capture cadmium ions from synthetic cadmium solution. To synthesize the adsorbent \((A_{700})\), base catalyzed polymerization of tetraethylorthosilicate (TEOS) was conducted under the sacrificial templation effect of poly(acrylamide) grafted *Cassia grandis* seed gum (CG) while using \(\text{H}_2\text{O}, \text{TEOS and EtOH in 8:1:1: ratio (v/v)}.\) The CG inspired adsorbent was characterized by FTIR, XRD and SEM, both before and after cadmium adsorption. The adsorption parameters for the synthesized adsorbent were optimized by performing the batch adsorption studies under different pH, initial cadmium concentration, adsorbent dose, and contact time. The adsorption showed pseudo second order kinetics with a rate constant of \(1.55 \times 10^{-4} \text{ g mg}^{-1} \text{min}^{-1}\) at 450 mg mL\(^{-1}\) Cd(II) concentration. The thermodynamic study showed that the adsorption is endothermic and spontaneous. The adsorbent could be successfully reused for three cycles. The present adsorbent is not only very efficient in cadmium uptake; it is greener than the contemporary porous silica adsorbents derived through templation of pure synthetic polymers or surfactants. Moreover the source polysaccharide used for its synthesis is abundant and cheap. This hybrid can utilized as versatile and sustainable adsorbent for cadmium recovery from industrial wastes. Copyright © 2015 VBRI Press.

**Keywords**: Tetraethylorthosilicate; *Cassia grandis*-graft-polyacrylamide; Cd(II) adsorbent.

---

**Vandana Singh** is Associate Professor of Chemistry at Department of Chemistry, University of Allahabad, India. She has >20 years of teaching experience and her research interest is polysaccharide based macromaterials. She could evolve greener methods for polysaccharide transformations such as methylation, hydrolysis and grafting. She has been ranked first among the top ten world scientists working on Guar gum. She is editor of *Green Chemistry for Environmental Remediation* and has authored over ten book chapters in book series of international repute. She has published seventy eight (78) research papers in international journals which include one review article in Progress in Polymer Science. She is recipient of AML medal 2011. She is a fellow of many professional societies in India and has been an elected sectional "Recorder” of chemical sciences section of Indian Science Congress, India.

**Preeti** is pursuing doctorate degree at University of Allahabad, India. Her present research work is on synthesis and characterization of polysaccharide based macromolecular materials. She graduated with a first class degree in chemistry from University of Allahabad. She is recipient of JRF, C.S.I.R, India. Her research interest is the fabrication of carrier matrices for enzyme immobilization.

**Rashmi Sanghi** is currently working as consultant in Ganga River Basin Management Plan (GRBMP), a project running at Indian Institute of Technology Kanpur. Her research interest is Environment, Bioremediation and green chemistry. He has published more than ninety (>90) research papers and is editor of a number of books. She is recipient of CHEMRAWN VII Prize for Atmospheric and Green Chemistry.

**Introduction**

The development and applications of new organic/inorganic hybrid materials prepared by the sol–gel approach is rapidly becoming a fascinating new field of research in materials science [1]. The biomineralization processes regulated by proteins and polysaccharides
leading to silica synthesis are widely spread in nature [2]. Hybrids with organic and inorganic interface are of special interest to researchers as they are multifunctional materials with tailored properties. Such bioinspired materials with organic-inorganic interface possess properties such as good permeability, selectivity, mechanical strength, and thermal and chemical stability.

Seed gums are galactomannan polysaccharides having a backbone of \( \beta-D(1\rightarrow4) \) mannopyranosyl units attached to \( \alpha-D \)-galactopyranosyl units as the side chains [3-5]. The galactomannans [6] in their native and derived form find use in various industries and many of them are popular as industrial gums e.g. guar gum [6,7]. The repeating units of these seed gums differ from each other in having different galactose to mannose ratios and molecular weights. Their chemical properties may be utilized towards the development of various versatile materials for commercial use. The properties of these gums have been enhanced by chemical modifications, grafting of polymeric units and by incorporating inorganic components, depending upon the application in question. Since the ratio difference of the component monosaccharides can drastically affect the properties of the seed gums, the scope of utilization of these gums is endless. Many of the vinyl modified polysaccharide materials have been used as efficient flocculators [5, 8, 9] and adsorbents for heavy metal ions [10,11]. Recently our group reported lead removal from waste water using methylmethacrylate grafted Cassia grandis seed gum [12].

Functionalized porous silicas [13] are known to behave as heavy metal ion adsorbent. Ideally a chemically active adsorbent with high stability and capacity should possess very low solubility in water; sufficient thermal stability, sterically compact geometry and sufficient chemical stability to retain activity during the operation and regeneration. Careful planning and execution of templated silicas can be used as a method of choice in deriving highly selective chemically active adsorbents [14].

The ribbon like conformation of the galactomannans and their copolymers can potentially modify the sol gel process to result into silica hybrids with novel microstructures and morphologies. So far, no attempt has been made towards the preparation of silica adsorbent materials using the copolymeric polysaccharides as templates except by our own group [15, 16] on the novel nanocompositional hybrids derived from vinyl modified guar gum and silica. The materials showed promising results for Zn(II) or/and Cd(II) uptake from aqueous solutions. The vinyl grafts at the polysaccharide played an important role in deciding the adsorbent’s performance. The use of poly(acrylamide) grafted guar in place of saponified poly(acrylonitrile) guar gum as template during the sol gel hybrid synthesis from TEOS resulted into exceptionally good Cd(II) adsorbent (\( Q_{\text{max}} 2000 \text{ mg g}^{-1} \)) [17].

The focus of this work was to design an efficient cadmium adsorbent from sol gel polymerization of tetra ethyloxy silicate (TEOS) under the sacrificial templatation effect of Cassia grandis seed gum-graft-poly(acrylamide) (CG-g-PAM). Cassia grandis is a nonconventional source of seed gum in which galactose and mannose are present in 1:3 molar ratio [18]. The seed gum differs from guar gum in its molecular weight and in galactose to mannose ratio, which is 1:2 for the guar gum [15]. The fine structural difference between the two seed gums can be manipulated for tailoring the adsorbent behavior of the silica hybrids derived from them. The hybrid was calcined at various temperatures [14] for a better understanding on the role of the polysaccharide’s fine structure in controlling the adsorbent microstructure and performance. The adsorbent behavior of the prepared hybrids was compared and evaluated by taking Cd(II) as representative heavy metal ion where the Cd(II) adsorption capacity of the optimum performance material was investigated using batch adsorption technique.

Present cadmium adsorbent is important as its synthesis utilized a nonconventional galactomannan polysaccharide (Cassia grandis seed gum) which is much cheaper and abundant [19] than the pure polymeric or surfactant templates. This is first study of this kind where a copolymer of nontraditional galactomannan polysaccharide has been used as template to develop a porous silica adsorbent for metal ion removal.

**Experimental**

**Materials**

Tetraethylorthosilicate (98% TEOS; Aldrich, USA) was used as silica precursor. \( \text{NH}_2\text{OH} \) (30% \( \text{NH}_3 \); Merck, India) was used. Acrylamide (Merk, India) was recrystallized twice from methanol (GR) and dried in vacuum. Ascorbic acid and potassium persulfate (BDH, India Analar Grade) were used without further purification. \( \text{AgNO}_3 \) (Merk, India) was used. \( \text{Cd(NO}_3)_2 \) (Merk, India) was used for preparing stock Cd(II) solution. Cassia grandis seed gum was supplied by Himani seed stores, Dehradun, India and identified by systematic botanist at Botanical Survey of India, Allahabad.

**Instrumentations**

The pH of the solution was measured with a Digital pH meter (pHep Hanna instruments) equipped with a glass working electrode and a reference Ag/AgCl electrode (Systronics model T-105). Infrared (IR) spectra were recorded on a Perkin-Elmer Infrared spectrophotometer making KBr mulls in reflectance mode. XRD was carried out on Rigaku D/MAX-2200 X-ray powder diffractometer. SEM analysis was done on EDAX, FEI Quanta 200 machine. Temperature treatment of the hybrid was performed in Mac (India) electric Muffle Furnace in air. The adsorbed metal ions were determined by titration with 0.01M EDTA using Xylenol Orange as indicator. The amount of metal ions adsorbed per gram of the polymer was calculated by difference between the initial and final concentration of the metal ion in the solutions.

**Isolation and purification of the seed gum**

Cassia grandis (CG) seeds (1 kg) were exhaustively extracted with light petroleum followed by EtOH to remove fatty and coloring materials and then suspended in 1% aqueous acetic acid overnight. The filtrate of the 1% solution was precipitated with 95% EtOH. The seed gum was reprecipitated thrice from 1% aqueous solution to...
obtain a white amorphous product that was purified as described elsewhere [5].

Grafting of the seed gum

To 25 mL of CG gum solution (4g L\(^{-1}\)), calculated amount of acrylamide (11x 10\(^{-3}\) M), ascorbic acid (2.3 x 10\(^{-2}\) M) and AgNO\(_3\) (8 x 10\(^{-5}\) M) (as a catalyst) were added and the reaction mixture was thermostated on thermostat water bath at 35 ± 0.2 ºC [20]. After 30 min, K\(_2\)SO\(_4\) (30 x10\(^{-3}\) M) was added and this time of addition of persulfate was taken as zero time. Graft copolymerization was allowed for 1 h. Grafted CG gum sample was separated from the reaction mixture by pouring into excess of MeOH: H\(_2\)O (7:3). The copolymer sample was finally extracted with MeOH: H\(_2\)O in a soxhlet apparatus for 4 h to dissolve all the homopolymer and was finally dried under vacuum at 50 ºC for >24 h to a constant weight for obtaining Cassia grandis-g-poly(acrylamide) (CG-g-PAM) (%G 110; % E 56).

Preparations of CG-g-PAM-silica hybrid

CG-g-PAM (1.0 g) was dissolved in 20 mL of distilled water. Separately a definite amount of TEOS was also dissolved in a known volume of ethanol. A solution incorporating a known volume of ammonium hydroxide (12 N) was prepared separately. Afterwards, the three solutions were rapidly poured together into a reaction glass flask and kept under gentle stirring for 18 h at room temperature. The mixture was then subjected to slow evaporation at 60 ºC for about 6 h and then 4 h at 80 ºC until a dry material was obtained [16]. A series of hybrids (H\(_{X - Y}\) H\(_{g}\)) were obtained by changing the H\(_2\)O: TEOS: EtOH ratios, keeping the amount of CG-g-PAM and NH\(_2\)OH fixed.

The cadmium binding capacity of the prepared hybrid materials was evaluated in batch adsorption experiments under optimized parameters: adsorbent dose 25 mg, 450 mg mL\(^{-1}\) Cd(II) concentration, pH 8, rpm 60 at 35 ºC. The hybrid (H\(_{g}\)) synthesized using H\(_2\)O:TEOS:EtOH in 8:1:1 ratio at fixed amount of CG-g-PAM and catalyst showed maximum binding. To understand the effect of the thermal sintering on the adsorption behavior, H\(_g\) was treated by heating at 80, 250, 500, 700, 800 ºC for 2 h and the adsorbents so obtained were named A\(_{80}\), A\(_{250}\), A\(_{500}\), A\(_{700}\), A\(_{800}\) respectively.

Preparations of control silica

To evaluate the role of polysaccharide, dehydroxylation polymerization of TEOS was allowed in absence of the polysaccharide template. In a manner similar to H\(_g\), the reaction mixture was then subjected to slow evaporation at 60 ºC for about 5-6 h and then 3-4 h at 80 ºC until a dry material was obtained. This was further heated treated inside furnace at 250 ºC, 500 ºC, 700 ºC and 800 ºC for 2 h at each temperature to obtain control adsorbents devoid of polysaccharide (C\(_{80}\), C\(_{250}\), C\(_{500}\), C\(_{700}\), C\(_{800}\) respectively).

Adsorption batch experiments

The Cd(II) binding capacities of both, heat treated hybrids (A\(_{80}\), A\(_{250}\), A\(_{500}\), A\(_{700}\), A\(_{800}\)) and control silicas (C\(_{80}\), C\(_{250}\), C\(_{500}\), C\(_{700}\), C\(_{800}\)) were evaluated by batch adsorption studies from synthetic aqueous solutions.

Stock solutions of standard Cd(II) (1000 mg mL\(^{-1}\)) were prepared from Cd(NO\(_3\))\(_2\) in distilled-deionised water. Adsorption experiments were carried out using the synthesized materials in a temperature controlled incubator shaker set at 60 rpm maintained at 35 ºC for 2.5 h. A known amount of adsorbent was thoroughly mixed with 50 mL of respective Cd(II) solutions, whose concentrations and pH values were previously known. pH of the reaction mixture was initially adjusted using either hydrochloric acid (1 M) 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 were analyzed for the Cd(II) concentration by titration with 0.01M EDTA using Xylenol Orange as indicator [21].

The amount of metal ions adsorbed [17] per gram of the adsorbent was calculated by the difference between the initial and the final readings using the following equation.

\[ q_e \ (mg \ g^{-1}) = \frac{C_0 - C_e \ (mg \ L^{-1}) \times V \ (L)}{W \ (g)} \quad (1) \]

Where \(q_e\) is the amount of the cadmium adsorbed (mg g\(^{-1}\)) on the adsorbent, \(C_0\), the initial concentration of Cd(II) (mg L\(^{-1}\)), \(C_e\), the equilibrium concentration of Cd(II) in solution (mg L\(^{-1}\)), \(V\), the volume of the solution used (L), and \(W\), the weight of the adsorbent used.

The adsorption was optimized using the optimum performance sample (A\(_{250}\)). The pH, initial concentration of Cd (II), adsorbent dose, contact time and the electrolyte amount (ionic strength) were varied, one at a time while keeping the other parameters fixed.

For pH studies, 50 mL of 450 mg mL\(^{-1}\) Cd(II) solutions were adjusted to various pH ranging from 1 to 12 and the optimum pH was determined using 25 mg adsorbent dose. To study the effect of initial Cd(II) concentration, the range for different initial cadmium concentrations used were 225 mg mL\(^{-1}\) to 2023 mg mL\(^{-1}\) at 25 mg adsorbent dose. Effect of adsorbent dose on the adsorption was studied in the range of 25-125 mg. In order to evaluate kinetic data, the agitation time was varied from 30 minutes to 150 min and the kinetic studies were performed at 450 mg mL\(^{-1}\) initial Cd(II) concentration using 25 mg adsorbent dose. 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 450 mg mL\(^{-1}\) Cd(II) concentration, 25 mg adsorbent dose, 50 mL working volume, 60 rpm and 2.5 h shaking time.

Desorption studies

In order to determine the reusability of the A\(_{250}\), Cd(II) was stripped off from the spent A\(_{250}\) using 2 M H\(_2\)SO\(_4\) and reused. For the stripping, the Cd(II) loaded A\(_{250}\) was placed in the 2 M H\(_2\)SO\(_4\) and stirred at 130 rpm for 2 h at 30 ºC and the final Cd(II) concentration was determined. 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 adsorbent and the final cadmium concentration in the stripping medium. After successive
leaching, the adsorbent was used two more times using 25 mg of the composite and 450 mg mL$^{-1}$ initial Cd(II) solution in total volume of 50 mL, 60 rpm, 35 °C.

**Results and discussion**

The hybrid (H$_k$) (Table 1) synthesized using H$_2$O:TEOS:EtOH in 8:1:1 ratio at fixed amount of CG-g-PAM and catalyst showed maximum cadmium binding (Scheme 1). H$_k$ hybrid along with the control silica was dried and calcined in air at 80°C, 250 °C, 500 °C, 700 °C and 800 °C for 2 h at each temperature. The calcined materials were evaluated for batch adsorption and reusability studies (Table 2).

Scheme 1. A plausible explanation for Cd(II) binding by CG-g-PAM-Si in comparison to GG-g-PAM-Si.

**Table 1.** Cd(II) adsorption by different hybrids synthesized at pH 8, 450 mgL$^{-1}$ Cd(II) initial concentration, adsorbent dose 25 mg, rpm 60, temperature 35 °C, adsorbent dose 50 mg.

<table>
<thead>
<tr>
<th>Hybrid</th>
<th>CG-g-PAM (g)</th>
<th>H$_2$O (mL)</th>
<th>TEOS (mL)</th>
<th>EIOH (mL)</th>
<th>H$_2$O/TEOS:EIOH</th>
<th>Ads in [Cd(II)] mgL$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_k$</td>
<td>1.0</td>
<td>10</td>
<td>1.5</td>
<td>1.5</td>
<td>6:6:1:1</td>
<td>370.92</td>
</tr>
<tr>
<td>H$_k$</td>
<td>1.0</td>
<td>15</td>
<td>1.5</td>
<td>1.5</td>
<td>10:1:1</td>
<td>377.66</td>
</tr>
<tr>
<td>H$_k$</td>
<td>2.0</td>
<td>20</td>
<td>1.5</td>
<td>1.5</td>
<td>13:3:1:1</td>
<td>386.66</td>
</tr>
<tr>
<td>H$_k$</td>
<td>1.0</td>
<td>25</td>
<td>1.5</td>
<td>1.5</td>
<td>16:6:1:1</td>
<td>388.90</td>
</tr>
<tr>
<td>H$_k$</td>
<td>1.0</td>
<td>20</td>
<td>1.0</td>
<td>1.5</td>
<td>20:0:6:6:1</td>
<td>382.16</td>
</tr>
<tr>
<td>H$_k$</td>
<td>1.0</td>
<td>20</td>
<td>2.5</td>
<td>1.5</td>
<td>8:1:6:1:1</td>
<td>413.63</td>
</tr>
<tr>
<td>H$_k$</td>
<td>1.0</td>
<td>20</td>
<td>3.0</td>
<td>1.5</td>
<td>6:6:2:1</td>
<td>409.14</td>
</tr>
<tr>
<td>H$_k$</td>
<td>1.0</td>
<td>20</td>
<td>2.5</td>
<td>1.0</td>
<td>8:2:2:5:1</td>
<td>409.14</td>
</tr>
<tr>
<td>H$_k$</td>
<td>1.0</td>
<td>20</td>
<td>2.5</td>
<td>1.5</td>
<td>8:1:6:1:1</td>
<td>413.63</td>
</tr>
<tr>
<td>H$_k$</td>
<td>1.0</td>
<td>20</td>
<td>2.5</td>
<td>2.0</td>
<td>8:1:25:1:1</td>
<td>427.12</td>
</tr>
<tr>
<td>H$_k$</td>
<td>1.0</td>
<td>20</td>
<td>2.5</td>
<td>2.5</td>
<td>8:1:1:1</td>
<td>445.14</td>
</tr>
</tbody>
</table>

It is evident from Table 2, that calcinations up to 700 °C to enhanced the adsorption potential of the hybrids, while further increase in calcination temperature decreased the adsorption which can be attributed to the decrease in porosity of the hybrid as a result of transverse condensation within the siloxane domains.

The cadmium adsorption by A$_{700}$ was optimized by varying the process parameters of the batch adsorption experiments. The maximum Cd$^{2+}$ adsorption that could be reached was 98.8 % using 25 mg adsorbent dose, 450 mg mL$^{-1}$ initial cadmium concentration, 60 rpm, 2.5 h contact time, 50 mL contact volume at 35 °C. The poly(acrylamide) grafted CG gum offered appropriate templating environment for the ensuing porous siloxane network.

**Table 2.** Adsorption of Cd(II) using the composite and silica calcinated at different temperatures at 450 mg L$^{-1}$ initial Cd(II) concentration, pH = 8, adsorbent dose 25 mg, rpm 60, contact time 2.5 h, total volume 50 mL at 35 °C.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>1st cycle (mg L$^{-1}$)</th>
<th>2nd cycle (mg L$^{-1}$)</th>
<th>3rd cycle (mg L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>292.24</td>
<td>291.12</td>
<td>289.43</td>
</tr>
<tr>
<td>250</td>
<td>325.96</td>
<td>322.71</td>
<td>322.59</td>
</tr>
<tr>
<td>500</td>
<td>359.68</td>
<td>357.86</td>
<td>355.75</td>
</tr>
<tr>
<td>700</td>
<td>445.14</td>
<td>442.86</td>
<td>441.17</td>
</tr>
<tr>
<td>800</td>
<td>438.36</td>
<td>436.11</td>
<td>434.99</td>
</tr>
</tbody>
</table>

To the best of our knowledge, the adsorption capacity of A$_{700}$ was found to be far superior to any of the previously reported cadmium adsorbents. More over the adsorbent attained equilibrium in just 2.5 h and its performance was 2.5 times higher than the similarly derived guar-graft-poly(acrylamide)-silica nanocomposite synthesized [17] by our group (Table 3). The huge difference in adsorption capacities of similarly derived nano-hybrids may be attributed to different structure of the repeating units of the two polysaccharides (Fig. 1). The repeating unit structure (Fig. 1) of the two polysaccharides indicates that *Cassia grandis* seed gum has galactose side chains after every two mannose units at the mannose main chain, while the guar gum has galactose branching at every alternate mannose units. More frequent branching in the guar gum is likely to diminish the association between the mann hydroxyls at the backbone with the surface silanols of silica matrix (Scheme 1) due to steric reasons. It appears that due to stronger association, CG-g-PAM escaped in small pieces, leaving back few tightly associated fragments attached to the hybrid pore wall to offer extra sites for the metal ion binding but this assumption needs further study and experimental evidences. The weaker association of GG-g-PAM with silanols at the ensuing silica matrix might have allowed an easy escape of GG-g-PAM from the siloxane network structure on calcination.

**Table 3.** Comparison of silica hybrids synthesized from Guar-g-PAM and CG-gum-g-PAM (A$_{700}$).

<table>
<thead>
<tr>
<th>Composite</th>
<th>Gal: Man</th>
<th>Ratio of the seed gum</th>
<th>H$_2$O:TEOS:EIOH</th>
<th>b (mg g$^{-1}$)</th>
<th>Q$_{max}$ (mg g$^{-1}$)</th>
<th>R$_{at 100}$ (mg mL$^{-1}$)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>GG-g-PAM-Si</td>
<td>1:2</td>
<td>16:2:1</td>
<td>0.0495</td>
<td>2000</td>
<td>0.6688</td>
<td>17</td>
<td>Current study</td>
</tr>
<tr>
<td>GG-g-PAM-Si</td>
<td>1:3</td>
<td>8:1:1</td>
<td>0.03223</td>
<td>5000</td>
<td>0.2367</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Optimization of adsorption conditions

Cd(II) adsorption conditions for A_{700} has been optimized by changing the various parameters of the batch experiment, one at a time while keeping the others fixed (Fig. 2).

Effect of pH on Cd (II) adsorption

The effect of pH on Cd (II) adsorption was studied in the range of pH 1-12 using 25 mg adsorbent dose, 450 mg mL\(^{-1}\) initial Cd(II) concentration, 60 rpm, 2.5 h contact time, 50 mL contact volume at 35 ºC. It was observed that the extent of Cd(II) removal by A_{700} increased (from 112 to 445 mg mL\(^{-1}\)) with the increase of pH and was maximum at pH 8 (445 mg mL\(^{-1}\)), which again decreased as the pH was further increased (from 445 to 415 mg mL\(^{-1}\)). This decrease can be explained by the precipitation of Cd(OH)\(_2\) at pH>8. Effect of pH on Cd\(^{2+}\) adsorption is summarized in Fig. 2(A).

Effect of concentration of Cd\(^{2+}\).

The effect of initial Cd(II) concentration was studied at pH 8, 60 rpm, 2.5 h contact time, 25 mg adsorbent dose at 35 ºC. It was observed that with the increase in the initial concentration of Cd\(^{2+}\) from 250 mg mL\(^{-1}\) to 2023 mg mL\(^{-1}\), the adsorption increased (from 225 mg mL\(^{-1}\) to 1821 mg mL\(^{-1}\)). At higher initial Cd\(^{2+}\) concentration, more Cd(II) is available for the binding on the binding sites at the adsorbent, which are fixed. The effect of initial Cd (II) concentration on the adsorption has been shown in the Fig. 2(B).

Effect of adsorbent dose on Cd\(^{2+}\) adsorption

The effect of adsorbent dose on Cd\(^{2+}\) removal was studied in the range of 15-100 mg per 50 mL at 450 mg mL\(^{-1}\) initial cadmium concentration. The percentage Cd(II) removal by A_{700} increased on increasing the dose from 15-25 mg (from 402 mg mL\(^{-1}\) to 445 mg mL\(^{-1}\)) and further increase in the adsorbent dose did not affect the adsorption much therefore 25 mg dose was chosen for the optimization of the adsorption (Fig. 2C).

Effect of rpm on Cd\(^{2+}\) adsorption

Variation in rpm was studied in the range of 60-200 at 450 mg mL\(^{-1}\) initial Cd(II) concentration, pH 8, 2.5 h contact time, 25 mg adsorbent dose at 35 ºC, where optimum adsorption was seen at 60 rpm (445 mg mL\(^{-1}\)) and therefore all the studies were performed at 60 rpm. Increasing the rpm beyond 130, decreased the adsorption. The adsorption decreased from 421 to 395 mg mL\(^{-1}\) on increasing the rpm from 130 to 200, which indicated some desorption taking place at high rpm (Fig. 2D).

Effect of electrolytes

The effect of electrolyte (NaCl and Na\(_2\)SO\(_4\)) on the Cd (II) removal by A_{700} was studied (Figure not shown). With increase in concentration of both NaCl and Na\(_2\)SO\(_4\) (from 0.01M to 1.0 M), the removal decreased from 427 to 391 mg mL\(^{-1}\) and from 422 to 382 mg mL\(^{-1}\) respectively from 50 mL of 450 mg mL\(^{-1}\) Cd(II) solution at pH 8, temperature 30 ºC, rpm 60 and contact time 2.5 h. The decrease in the removal on increasing the electrolyte concentration may be due to the competition between cadmium species and SO\(_4^{2-}\)/Cl\(^-\) at the binding sites of silica matrix, where SO\(_4^{2-}\)/Cl\(^-\) ion can be electrostatically held on silicon atom.

Adsorption isotherm studies

Adsorption data were fitted to the Langmuir and Freundlich isotherms [17].

The Langmuir isotherm is expressed in the linear form as under.

\[
\frac{C}{q_e} = \frac{1}{bQ_o} + \frac{C}{Q_o}
\]

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:

\[
R_L = 1 + \frac{1}{bC_0}
\]  

(3)

Where \( C_0 \) is the initial Cd(II) concentration (mg L\(^{-1}\)). If \( R_L \) values lie between 0 and 1, the adsorption is favorable. The Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption and is expressed in linear form as:

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e
\]  

(4)

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 values of the \( 1/n \), better is the favorability of the adsorption.

The equilibrium data fitted to Langmuir model and Freundlich models at 35 and 15 °C where the data fitted better in Langmuir isotherm indicating surface homogeneity of the adsorbent and unilayer adsorption (Fig. 3).

![Langmuir isotherm](image)

**Fig. 3.** Langmuir isotherm (A) at 35 °C and (B) at 15 °C and Freundlich isotherm (A') at 35 °C at 15 °C.

At both the temperatures, \( Q_0 \) was calculated (from Langmuir isotherm) to be 5000 mg g\(^{-1}\) indicating that the adsorbent had a very high capacity to remove Cd (II) ions (Fig. 3). The \( R_L \) value was 0.0645 (at 450 mg L\(^{-1}\) Cd(II)) indicating the adsorption to be favorable. The Langmuir constant \( b \) (and Freundlich constant \( K_f \)) increased with increasing temperature from 15 to 35 °C implying that the adsorption process was endothermic in nature. The value of Langmuir constant \( b \) increased with temperature thereby suggesting that the Cd(II) exhibited higher affinity for the adsorbent at higher temperature than at lower temperature. The value of \( n \) is found to be >1, that indicated that the adsorption of Cd(II) onto the composite was favorable. The \( Q_{max} \) for the composite was found 2.5 time higher than the material derived from guar-g-poly(acrylamide) where the optimum sorbent was obtained by using H\(_2\)O:TEOS:EtOH in 16:2:1 ratio and sintering the composite to 600 °C the two hybrids have been compared in **Table 4**. It is also higher than other reported adsorbents (Table 5).

**Sorption kinetics**

Cd(II) adsorption was monitored with time. The kinetic study revealed that the adsorption was initially rapid which attained a state of equilibrium within 2.5 h and thereafter no adsorption took place up to 4 h. The initial rapid adsorption can be attributed to the large number of available vacant sites which generated an increased concentration gradient between adsorbate in solution and adsorbate in the adsorbent [22]. Gradually the adsorption sites decreased which in turn resulted into decreased adsorption. Initial rapid adsorption indicated a surface reaction process is taking place. Kinetics [23] of the adsorption was modeled by the first order Lagergren equation, the pseudo-second-order equation and the second-order rate equation shown below as Eqs. (5)–(7), respectively (Fig. 4).

\[
\frac{\ln (q_e - q_t)}{q_t} = \frac{1}{k_1q_e^2 + k_2t}
\]  

(5)

\[
\frac{qt}{q_e} = \frac{1}{k_1q_e^2 + k_2t}
\]  

(6)

\[
1/(q_e - q_t) = 1/q_e + k_2t
\]  

(7)

Where \( K_f \) is the Lagergren rate constant of adsorption (min\(^{-1}\)); \( k_1 \) the pseudo-second-order rate constant of adsorption (g. mg\(^{-1}\). min\(^{-1}\)) and \( k_2 \) the second-order rate constant (g. mg\(^{-1}\).min\(^{-1}\)). If \( q_e \) and \( q_t \) are the amounts of metal ion sorbed (mg g\(^{-1}\)) at equilibrium and at time \( t \), respectively. Kinetic data of Cd(II) adsorption by A\(_{700}\) fitted best in to pseudo second order kinetic equation, where linear plot of \( qt \) vs \( t \) was obtained with the correlation coefficient \( R^2 \), being 0.9999 and rate constant 1.282 × 10\(^{-4}\) at 450 mg mL\(^{-1}\) Cd(II) concentration (Fig. 4).

**Characterization of the composite**

The optimum performance sample A\(_{700}\) has been characterized using FTIR, XRD and SEM techniques.

**Fourier transform spectroscopy**

In the IR of CG-g-PAM, merged amide I and amide II peak is seen as broad intense peak at 1663 cm\(^{-1}\) along with the O-H, C-H stretchings at 3412 and 2929 cm\(^{-1}\) respectively as in CG gum (spectra not shown). However in A\(_{700}\) the incorporation of inorganic component can be identified from the Si-O-Si modes observed below 1250 cm\(^{-1}\) (Fig. 5a). Peak is visible at 459 cm\(^{-1}\)(due to oxygen ring breathing mode, involving four membered rings (cyclic tetrasiloxanes) or a symmetric oxygen stretching vibrations of Q\(^1\) surface silanol sites [25], at 792 cm\(^{-1}\) (symmetric Si-
O-Si stretching vibrations). LO and TO Si-O-Si asymmetric stretching modes are seen as merged broad peak at 1091 cm\(^{-1}\). A broad Si-OH absorption band is visible at 3429 cm\(^{-1}\).

IR of the cadmium loaded hybrid showed Si-O-Si stretching modes at 1201 cm\(^{-1}\), oxygen ring breathing mode at 464 cm\(^{-1}\), symmetric Si-O-Si stretching vibrations at 798 cm\(^{-1}\), Si-OH stretching, Si-O-Si asymmetric stretching modes as merged broad peak at 1091 cm\(^{-1}\) and a broad Si-OH absorption band at 3411 cm\(^{-1}\).

IR spectra of the Cd(II) loaded sample with the adsorbent balls on to the surface of the composite. Cd loading on to the hybrids. Cd loading on to the hybrids. Fig. 5a. IR spectra of (A) A\(_{700}\) (B) A\(_{700}\)-Cd; (b) XRD of A\(_{700}\) and A\(_{700}\)-Cd.

Certain amount of peak shifts are visible in the cadmium loaded hybrid, being major for Si-OH modes (from 3439 to 3411 cm\(^{-1}\)), indicating their involvement in the cadmium binding.

X-ray diffraction

The X-ray diffraction pattern (Fig. 5b) showed that the hybrids retained their amorphous characters even on thermal treatment until 700 °C (A\(_{700}\)) and showed a broad hollow, typical of amorphous material, however the Cd (II) loaded adsorbent show crystalline peaks in the region of 2- theta 23.6, 30.35, 49.8, that give concrete evidence for cadmium sorption on to the hybrids.

Scanning electron microscopy

The cadmium loading on to A\(_{700}\) is confirmed by morphological changes observed in the SEM picture. In the loaded samples the cadmium deposits are seen as small balls on to the surface of the composite. Cd loading on to the adsorbent is further evidenced by comparing EDX spectra of the Cd(II) loaded sample with the adsorbent (Fig. 6).

**Conclusion**

The composite synthesized from Cassia grandis seed gum-graft-poly(acrylamide) templated polymerization of TEOS on calcination at 700 °C furnished an adsorbent which showed unprecedented Cd(II) adsorption (Q\(_{max}\) of 5000 mg g\(^{-1}\)) at pH 8. The composite can be distinguished by its high adsorption capability, reusability, stability and versatile applicability. The reusability of the bioinspired adsorbent was tested for three consecutive cycles where almost negligible loss in its adsorption capacity was witnessed. The present adsorbent showed 2.5 times higher Qmax and 3.2 times shorter equilibrium time than our previously reported adsorbent that was similarly derived from guar gum. The composite synthesized from Cassia grandis seed gum-graft-poly(acrylamide) templated polymerization of TEOS on calcination at 700 °C furnished an adsorbent which showed unprecedented Cd(II) adsorption (Q\(_{max}\) of 5000 mg g\(^{-1}\)) at pH 8. The composite can be distinguished by its high adsorption capability, reusability, stability and versatile applicability. The reusability of the bioinspired adsorbent was tested for three consecutive cycles where almost negligible loss in its adsorption capacity was witnessed. The present adsorbent showed 2.5 times higher Qmax and 3.2 times shorter equilibrium time than our previously reported adsorbent that was similarly derived from guar gum. This indicates that other than the calcination temperature and TEOS:H\(_2\)O ratio, the polysaccharide’s structure plays an important role in deciding the microstructure and performance of the synthesized adsorbents. Thus the adsorbent is economical and industrially viable and lucrative material for the removal of cadmium ions from industrial waste and mining discharges.

**Acknowledgements**

Authors acknowledge Department of Science and Technology, New Delhi, India for the financial support to carry out the present work.

**Reference**


32. Singh, V.; Tiwari, S.; Pandey, S.; Sanghi, R. Indian patent TIFAC Ref L&S Ref.: PD001432IN-SC.