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A new guar gum-based adsorbent for the removal of Hg(II) from its aqueous solutions

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ABSTRACT

Modification of biopolymers by oxidation is an easy process to develop effective adsorbents for the removal of toxic metal ions from their aqueous solutions. In the present study, guar gum (GG) was crosslinked with epichlorohydrin and then oxidized to the polydialdehyde form (GG-*cl*—PDA). The latter was converted to a Schiff-base, GG-*cl*—CH=N—$(CH_2)_6$—N=CH—GG, by reaction with hexamethylenediamine. Different forms of the modified GG were characterized by SEM, FTIR and XRD and investigated as adsorbents for the removal of Hg(II) ions from their aqueous solutions. The adsorption process was carried out through the variation of time, temperature, pH and initial concentration of Hg(II) ions. GG-*cl*—CH=N—$(CH_2)_6$—N=CH—GG was observed to be an efficient adsorbent with a maximum adsorption capacity of 41.13 mg/g. It is reusable up to five cycles at the optimum conditions obtained for the maximum ions uptake. The kinetic data generated fit the Freundlich isotherm and pseudo-second order kinetics.

1. Introduction

Water pollution from toxic metal ions is a serious environmental issue. Mercury (Hg) is one of the most toxic metals and its removal from the contaminated water is imperative to make water fit for the human consumption. Recently, it has been identified as one of the most dangerous toxic metals and there is a call from the international community to check its use (UNEP, 2013). The consumption of methylmercury by human being is reported to damage the central nervous system (Parks et al., 2013). Hence, the treatment of Hg contaminated water is crucial to render it fit for human consumption. Adsorption is one of the preferred methods for the removal of metal ions from the wastewater as it is effective as well as cost-effective (Li, Zhai, Zhang, Wang, & Zhou, 2007). Biomass itself and polysaccharides are natural adsorbents for the removal of toxic metal ions from the polluted water. Adsorption of the metal ions on biomass or polysaccharides is facilitated by the presence of functional groups such as —OH. However, their capacity to partition metal ions from the solution phase to the adsorbent phase is limited due to the low accessibility of the ions to the active sites. This limitation can be overcome by the chemical modification of biomass or polysaccharides. The crosslinking and attachment of functional groups such as, $-NH_2$, —OH, —NHOH, $-CO_2H$ or $-SO_3H$ on polysaccharides increase their efficacy manifold in the removal of metal ions from the aqueous solutions (Becker, Schlaak, & Strasdeit, 2000). There are many reports in the literature on the modification of biopolymers by various polymer analogous reactions to increase their efficacy in the metal ion uptake (Chauhan, Chauhan, Kumar, & Kumari, 2008; Chauhan, Jaswal, & Verma, 2006; Chauhan, Singh, Chauhan, Verma, & Mahajan, 2005; Chauhan, Singh et al., 2006). The porous cellulose modified with poly(ethyleneimine) (Navarro, Sumi, Fujii, & Matsumura, 1996) and polyaniline-coated sawdust (Ansari & Raofie, 2006) have been reported for the selective removal of Hg(II) ions. Polyamines derived from cellulose and starch through the dialdehyde formation (Masri & Friedman, 1972) and polyacrylamide grafted cellulose (Bicak, Sherrington, & Senkal, 1999) have been reported to be efficient and selective adsorbents of Hg(II) ions from their aqueous solutions. However, one of the most promising modifications of the polysaccharides, to render these effective adsorbents for Hg(II) ions, is to their corresponding Schiff-bases where an aldehyde or ketone is converted to an imine or azomethine group. Apart from being effective metal ion complexing agents they also exhibit biological activities. Thus, two important properties required in the water purification technology are inherent in these materials.

Polysaccharide-based Schiff-bases have been reported as effective adsorbents for the uptake of Hg(II) ions from their aqueous solutions (Donia, Atia, & Elwakeel, 2008; Gavilan et al., 2009;

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Monier, 2012; Wang et al., 2010). Two strategies are employed to synthesize Schiff-bases from polysaccharides. One, the amino group present on the polysaccharide, such as chitosan, is reacted with a dialdehyde. Two, the aldehyde groups are generated on the polysaccharide backbone and subsequently reacted with a diamine.

In the present work, the latter strategy was employed using guar gum as the starting material. Gaur gum is a high molecular weight hydrocolloidal heteropolysaccharide composed of galactan and mannan units. It is an attractive starting material to develop effective adsorbents for the heavy metal ions including Hg(II). A guar gum based resin, guar triazine aspartic hydroximate, has been reported to be an efficient adsorbent for the removal of toxic metal ions via selective ion exchange technique (Loonker & Sharma, 2011). In earlier works we reported modified guar gum-based smart hydrogels as drug delivery devices (Dharela, Raj, & Chauhan, 2012; Thakur, Chauhan, & Ahn, 2009) and as Cu(II) adsorbents (Chauhan, Chauhan, & Ahn, 2009). In the latter study, guar gum was crosslinked with *N*,*N*-methylenebisacrylamide and subsequently its primary hydroxyl groups at C-6 were oxidized to the carboxylic groups. The presence of the carboxylic groups imparted cation exchange properties to the guar gum. In the present study, a new adsorbent was synthesized from guar gum by first crosslinking it with epichlorohydrin and subsequently the crosslinked guar gum was converted to its dialdehyde by periodate oxidation at the C-2 and C-3 positions. The latter was reacted with hexamethylene diamine (HMDA) to generate an effective adsorbent for Hg(II) ions. It has high maximum adsorption capacity and is effectively reusable up to five cycles.

2. Experimental

2.1. Materials

Guar gum (courtesy Lucid Colloids, Jodhpur, India), epichlorohydrin, potassium periodate, iso-propanol, sodium hydroxide, (Merck, Schuchardt, Germany), hexamethylene diamine (S.D Fine, Mumbai, India), mercuric acetate, sodium acetate, acetic acid 100%GR, Michler's thioketone (4,4′-bis-(dimethylamino)-thiobenzophenone), 1-propanol LiChrosolv (Merck), all analytical grade, were used as received. The concentration of Hg(II) ions was determined with Photolab 6600 UV89. Visible programmable spectrophotometer and pH values were measured with a pH meter (Eutech 20).

2.2. Modification of guar gum

Guar gum (5.0 g) was dissolved in 2.5 M NaOH and to the resultant solution was added 3% epichlorohydrin. The contents were then stirred for 24 h at room temperature. The crosslinked guar gum, GG-*cl*—, was extracted with *iso*-propanol and repeatedly washed with water. GG-*cl*— was suspended in 100 mL of distilled water and 0.015 M potassium periodate was added to it (Kim & Kuga, 2001). The beaker containing the mixture was wrapped in black sheet of paper and the contents were stirred at room temperature for 72 h. Thereafter a large amount of ethylene glycol was added to terminate the reaction. The crosslinked dialdehyde guar gum, GG-*cl*—PDA, was separated from the reaction mixture and washed with *iso*-propanol. The dried GG-*cl*—PDA was mixed with hexamethylenediamine (HMDA) in a 1:2 weight ratio. The contents were thoroughly stirred and kept at 60 °C for 48 h. The Schiff-base, GG-*cl*—CH=N—$(CH_2)_6$—N=CH—GG, was separated and washed with ethanol and dried at 40 °C.

In the overall synthetic Scheme 5.0 g of guar gum yielded 4.03 g of GG-*cl*—CH=N—$(CH_2)_6$—GG. The overall substitution efficiency was calculated as follows:

$$\%\text{Substitution efficiency} = \frac{\text{Yield of the final product (g)}}{\text{Amount of guar gum taken (g)}} \times 100$$

A high degree of substitution (0.94) was obtained from the yield of the GG-*cl*—CH=N—$(CH_2)_6$—GG obtained and the theoretical yield taken as 4.31 g expected for the 100% conversion in the reaction of dialdehyde, GG-*cl*—PDA, and HMDA as follows:

$$\text{Degree substitution (DS)} = \frac{\text{Yield of the final product (g)}}{\text{Theoretical yield (g)}}$$

2.3. Characterization of different forms of modified guar gum

GG and its modified forms were characterized by scanning electron microscopy (SEM), Fourier transformed infrared (FTIR) and X-ray diffraction (XRD) to obtain evidence of modification at each synthetic stage. Elemental analysis (C, H, N) of GG-*cl*—CH=N—$(CH_2)_6$—GG was recorded on Elementar Vario EL GmbH. SEM was recorded on SEM Quanta 250 D9393. The samples were mounted onto stubs, sputter coated with gold in a vacuum evaporator, and micrographs were recorded. FTIR spectra were recorded on Nicolet 5700 in transmittance mode in KBr. XRD was recorded on PANanalytic XPERT-PRO X-ray diffractrometer.

2.4. Adsorption procedure for Hg(II) ions

Guar gum and its modified forms (0.01 g) were separately immersed in 10.0 mL solution of Hg(II) ions of a known concentration. After the specified time, polymers were removed from this solution by centrifugation. The filtrate from each adsorption experiment was analyzed for the concentration of the unadsorbed Hg(II) ions by the addition of Michler's thioketone that was dissolved in acetate buffer medium. A red complex was formed which absorbs at 560 nm. The concentration of Hg(II) ions was recorded directly from the Photolab 6600 UV–vis spectrophotometer. The adsorption capacity was evaluated as a function of time from the final concentration of Hg(II) ions obtained by the photometric method as described above. Since GG-*cl*—CH=N—$(CH_2)_6$—N=CH—GG afforded the best efficiency among the three adsorbents, it was selected for the optimization of other adsorption parameters such as temperature, pH, and concentration of ions. The effect of temperature was studied by variation of temperature from 20 to 40 °C and using 25 ppm of Hg(II). The effect of pH of the solution on the Hg(II) ions removal was studied at pH 2.0, 3.0, 5.0, 7.0 and 9.0. The pH stabilization was carried out with HCl and NaOH solutions. The pH was monitored with a digital pH meter.

The maximum adsorption capacity (MAC) of the polymer was determined by repeated treatments of the same sample using 50 ppm of Hg(II) ions at the conditions obtained for the maximum ions uptake. The reusability studies were also carried out to assess the regeneration of the adsorbent by stripping-off the adsorbed ions with 0.1 N HCl.

Adsorption capacity was calculated after every batch experiment by following the same procedure as stated in the preceding paragraph. Adsorption capacity (q) is expressed as follows:

$$\text{Adsorption capacity } (q)\left(\frac{\text{mg}}{\text{g}}\right) = \frac{[(C_o - C_t)V]}{m}$$

where q is the amount of Hg(II) ions adsorbed onto unit dry mass of the polymer (mg/g), C_o and C_t, respectively, are the concentration of ions in the feed solution and in the aqueous phase after treatment for a certain period of time t, V (mg/L) is the volume of the aqueous phase (L) and m is the weight of the dry adsorbent (g).

2.5. Kinetics of Hg(II) ions uptake

Pseudo-first order and pseudo-second order kinetic models were applied to understand the adsorption of Hg(II) ions on GG-*cl*—CH=N—$(CH_2)_6$—N=CH—GG. The pseudo-first order rate model is expressed as (Ho, 2004):

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

where q_e and q_t are amounts of Hg(II) adsorbed per g of adsorbent (mg/g) at equilibrium and at time t (min), respectively. k_1 is the pseudo-first-order rate constant for the adsorption process (min^{-1}). Plot of $\ln(q_e - q_t)$ vs. t gives a straight line for the first order adsorption kinetics and the pseudo-first order rate constant k_1 can be calculated from the slope, and intercept gives the value of $\ln q_e$. Pseudo-second order model is based on the adsorption capacity of the solid phase and is expressed as (Ho, 2006):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{t}{q_e}$$

where K_2 ($\text{g mg}^{-1}\ \text{min}^{-1}$) is the rate constant of the pseudo-second order adsorption process and is determined from the experimental data by plotting t/q_t vs. t. The Langmuir and Freundlich isotherms are used to describe the adsorption equilibrium over the entire concentration range studied (Ho, Malarvizhi, & Sulochana, 2009). In Langmuir model, adsorption is assumed to occur uniformly on the active sites of the adsorbent assuming monolayer adsorption. Once the active sites are occupied by the adsorbate, the adsorption process naturally gets terminated (Barkat, Nibou, Chearouche, & Mellah, 2009; Langmuir, 1918). The linear form of the Langmuir isotherm is expressed as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m}$$

where q_e (mg/g) is the amount of Hg(II) adsorbed and C_e (mg/L) is Hg(II) concentration at equilibrium. The Langmuir constants q_m (mg/g) and b (L/mg) are related to the maximum adsorption capacity and energy of adsorption, respectively. If the data yields a linear plot C_e/q_e vs. C_e then it follows the Langmuir isotherm. Freundlich adsorption isotherm is an empirical model that describes equilibrium on heterogeneous surfaces and it allows multilayer adsorption on the adsorbent (Greluk & Hubicki, 2009). The linear form of Freundlich sorption isotherm can be represented as:

$$\ln q_e = \ln K_F + \ln \frac{C_e}{n}$$

where K_F ($\text{mg}^{1-n}\,\text{L}^n\,\text{g}^{-1}$) and $1/n$ indicate adsorption capacity and adsorption intensity, respectively. q_e (mg/g) is the amount of the adsorbate on the adsorbent and C_e is aqueous concentration of adsorbate at equilibrium (mg/L). The linear plot of $\ln q_e$ vs. $\ln C_e$ gives slope $1/n$ and an intercept $\ln K_F$. Larger value of n and smaller value of $1/n$ implies strong interactions between the adsorbent and metal ions. When $1/n$ equals 1 it indicates linear adsorption leading to identical adsorption energies for all the active sites.

3. Results and discussion

3.1. Synthesis and characterization of modified guar gum

In the present work, guar gum (GG) was crosslinked with epichlorohydrin to make it water insoluble. Subsequently it was oxidized to the dialdehyde form, GG-*cl*—PDA, by the periodate oxidation. The overall high substitution efficiency (80.6%) and substitution degree (0.94) was calculated from the expressions used in Section 2.2. The high conversion efficiency was supported from the elemental analysis (CHN) data. Elemental analysis revealed the presence of C, H and N in the ratio 46:36:09 in GG-*cl*—CH=N—$(CH_2)_6$—N=CH—GG. The ratio of C:N theoretical [144:28 (5.14:1)] and that obtained from the elemental analysis [46:9 (5.1:1)] are very close. The aldehyde functional groups present on GG-*cl*—PDA were reacted with hexamethylenediamine, HDMA, to generate Schiff base, GG-*cl*—CH=N—$(CH_2)_6$—N=CH—GG. The modification of GG to GG-*cl*—CH=N—$(CH_2)_6$—N=CH—GG is presented in Scheme 1.

The resultant adsorbent is expected to be more stable than the Schiff-bases reported in the literature due to the long hydrophobic chain of the base, HMDA. Furthermore, intense crosslinking results in the generation of numerous sites for the adsorption of Hg(II) than the conventional Schiff-bases. All the three materials synthesized in this work were characterized by different physical methods and further investigated for the adsorption of Hg(II) ions. Characterization studies were carried out by SEM, XRD, and FTIR spectroscopy to obtain evidence of modification of GG. The FTIR spectra of the respective polymers are presented in Fig. 1. In the case of GG, important peaks can be observed at 3365.5 cm^{-1}, 2928.5 cm^{-1}, 1015 cm^{-1}, and 1152 cm^{-1} due to the stretching vibration of O—H, C—H, C—O single bond and C—O—C groups, respectively (not presented). In the spectrum of GG-*cl*—PDA additional peaks can be observed at 2849.5 cm^{-1} and near 1700 cm^{-1}, respectively, due to the C—H and C=O bond stretching of the aldehyde groups. In the spectrum of GG-*cl*—CH=N—$(CH_2)_6$—N=CH—GG a peak at 1664.8 cm^{-1} corresponds to the C=N vibration characteristic of imine groups formed by the reaction of —NH_2 groups of HMDA and —CHO groups present on the GG backbone. Apart from the presence of new absorption peaks, the change in the intensity and the position of absorption peaks due to the GG backbone 208 can also be observed in these spectra. In the modification process many of the primary hydroxyl groups react to form new bonds. That results in the loss of intermolecular hydrogen bonding between the hydroxyl groups. Hence, the peak due to the O—H stretching is sharp in the spectra presented in Fig. 1.

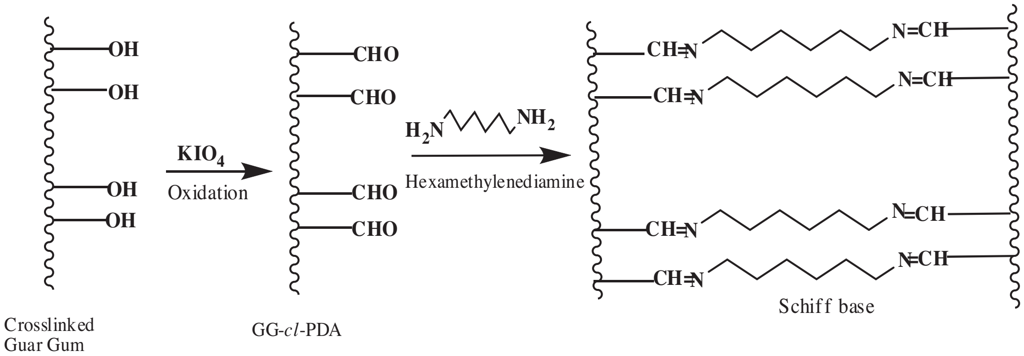
Surface morphology provides strong evidence of modification of GG and formation of Schiff-base. In the present study all the materials have porous morphology which is a positive feature of an effective adsorbent (Fig. 2). The SEM of GG-*cl*—PDA reveals a highly porous surface (Fig. 2a). However it can be observed from the micrograph of GG-*cl*—CH=N—$(CH_2)_6$—N=CH—GG that it has surface morphology which is smooth yet dotted with pores (Fig. 2b). Such morphology is manifestation of the extensive crosslinking due to the reaction of —CHO groups of GG-*cl*—PDA with —NH_2 groups of the bifunctional HMDA. Such contrast in morphology provides evidence of modification of GG-*cl*—PDA to GG-*cl*—CH=N—$(CH_2)_6$—N=CH—GG.

The XRD patterns of GG-*cl*—, GG-*cl*—PDA and GG-*cl*—CH=N—$(CH_2)_6$—N=CH—GG are presented in Fig. 3.

GG is of amorphous nature. However, GG-*cl*—PDA has crystalline nature due to the close alignment of the —CHO groups of different chains. Furthermore, GG-*cl*—CH=N—$(CH_2)_6$—N=CH—GG has an amorphous nature as close packing of chains is not possible due to the presence of long hydrophobic segment —$(CH_2)_6$— which acts as bridge between the two GG chains. Such morphology suggests a highly crosslinked matrix which is formed by the reaction of both the end groups of HDMA.

3.2. Adsorption studies of Hg(II) ions

Adsorption studies were carried out as a function of time, temperature, pH and Hg(II) concentration. Effect of time was studied at 20 °C and 5.0 pH using 25 ppm of Hg(II) ions. It was observed that q values increased with time and equilibrium was attained at 2 h (Fig. 4). The rate of adsorption was initially rapid as about half of the Hg(II) ions were adsorbed within the first 30 min.



Scheme 1.

Under these conditions the maximum q value of 15.27 mg/g was observed for GG-*cl*—CH=N—$(CH_2)_6$—N=CH—GG. The temperature variation (20–40 °C) resulted in decrease in q values from 15.27 to 9.9 mg/g. Further studies were carried out at the optimum operating conditions of 2 h and 20 °C with GG-*cl*—CH=N—$(CH_2)_6$—N=CH—GG.

The pH of the solution is a significant factor to be studied in the evaluation of the efficacy of a metal ion adsorbent. It is reported in the literature that pH 2.6 is the lower limit for the effective Hg(II) binding to an adsorbent (Bicak et al., 1999). In the present study pH of the solution was varied from 2.0 to 9.0. The results of pH variation on the adsorption capacity are presented in Fig. 5.

The q values were observed to increase with pH. A large difference in q values was observed as pH of the solution was changed from 3.0 to 5.0. At a lower pH protonation of adsorbent surface takes place which results in lower Hg(II) ions uptake and q value

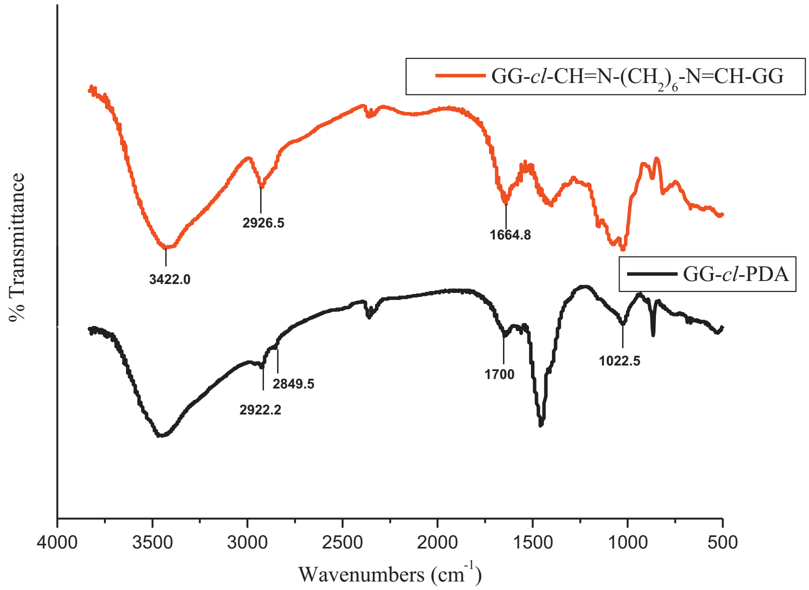


Fig. 1. FTIR spectra (from bottom) of GG-*cl*—PDA and GG-*cl*—CH=N—$(CH_2)_6$—N=CH-GG.

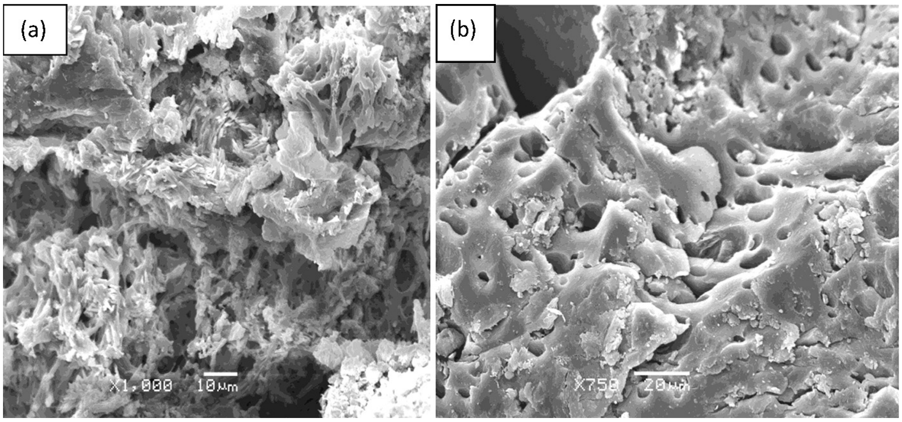


Fig. 2. SEM images (from left to right) of GG-*cl*—PDA and GG-*cl*—CH=N—$(CH_2)_6$—N=CH—GG.

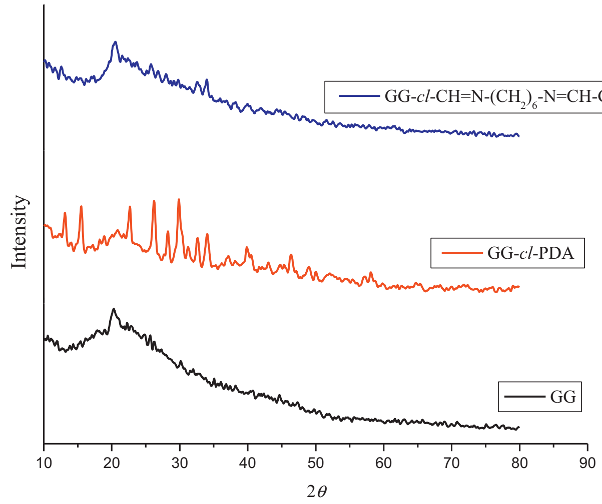


Fig. 3. XRD patterns of (from bottom) of GG, GG-*cl*—PDA, and GG-*cl*—CH=N—$(CH_2)_6$—N=CH—GG.

is subsequently reduced. At a higher pH more active sites, specifically the imine groups, are available on the adsorbent for Hg(II) ions adsorption. Hence q values increased with pH (Ansari & Raofie, 2006). A low affinity for Hg(II) in the acidic condition (pH 4.0) has also been reported for poly(ethyleneimine)-attached poly(2-hydroxyethylmethacrylate) gel beads. An increase in adsorption above pH 4.0, between pH 5.0 and 7.0, has been reported elsewhere (Denizli, Senel, Alsancak, Tuzmen, & Say, 2003). Further studies were carried out at pH 5.0 as q_e value increased sharply at pH 5.0. Furthermore, opalescence or precipitation generally takes place above pH 6.0 due to the formation of $Hg(OH)_2$ (Kyzas & Deliyanni, 2013).

On the variation of Hg(II) ions concentration, in the range 1–100 ppm, q_e values were observed to increase from 0.424 to 74.67 mg/g over the entire range of Hg(II) ions concentration studied. Hence, the modified GG is efficient in removing Hg(II) ions even from their very dilute to a highly concentrated aqueous solution.

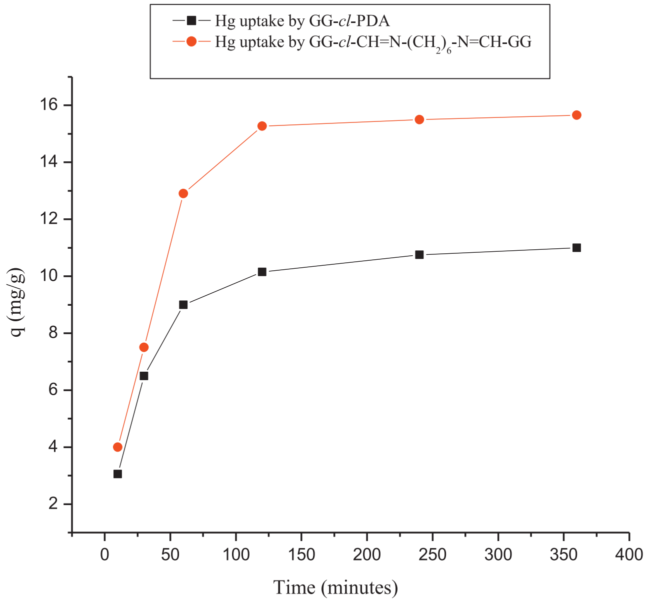


Fig. 4. Adsorption of Hg(II) ions by GG-*cl*—PDA and GG-*cl*—CH=N—$(CH_2)_6$—N=CH—GG as a function of time.

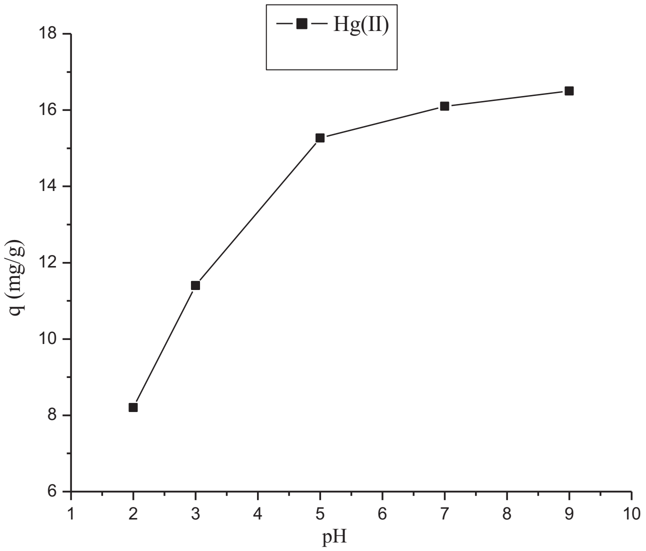


Fig. 5. Adsorption of Hg(II) ions as a function of pH.

3.3. Evaluation of maximum adsorption capacity and reusability

Maximum adsorption capacity (MAC) studies were carried out with GG-*cl*—CH=N—$(CH_2)_6$—N=CH—GG up to six feeds using 50 ppm concentration of Hg(II) ions in each feed (Fig. 6a).

It was observed that q values increased with successive feeds and the maximum q value of 41.13 mg/g was obtained after the sixth feed. At a higher concentration of 100 ppm a high MAC of 74.67 mg/g was obtained in a single feed. But lower concentration was used in batch experiments to evaluate the MAC. Reusability studies were carried out by the elution of the adsorbed Hg(II) from the GG-*cl*—CH=N—$(CH_2)_6$—N=CH—GG and subsequent reuse of the regenerated adsorbent (Fig. 6b). The successful reuse of the adsorbent for five cycles is a strong indicator that the synthetic strategy employed in the present study stabilized the adsorbent for multiple uses.

3.4. Kinetics and adsorption isotherm

The kinetics of Hg(II) adsorption was studied using different kinetic rate expressions. The rate constant, K_1 and K_2, with values

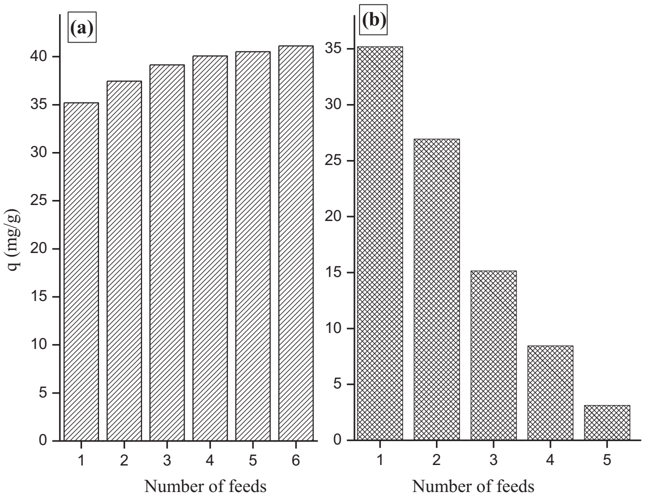


Fig. 6. (a) Maximum adsorption capacity evaluation as a function of q vs. number of feeds at 50 ppm and (b) reusability studies plot of q vs. number of feeds.

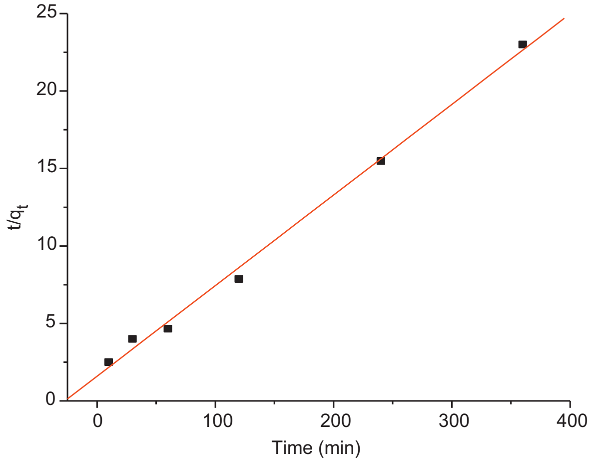


Fig. 7. Pseudo-second order plot for Hg(II) adsorption.

of $1.959 \times 10^{-2}\,\text{min}^{-1}$ and $2.15 \times 10^{-3}\,\text{g}\,\text{mg}^{-1}\,\text{min}^{-1}$ and the corresponding correlation coefficients, R^2 of 0.952 and 0.997, were obtained from the pseudo-first order and pseudo-second order kinetic models, respectively. The correlation coefficients of the pseudo-second order kinetic model are very close to 1.0. Hence the adsorption process followed pseudo-second order kinetics (Fig. 7).

The isotherm plot indicates that adsorption of Hg(II) follows the Freundlich isotherm. The values of Freundlich constants K_F (0.745), n (0.710) and R^2 (0.995) were obtained from the plot of $\ln Q_e$ vs. $\ln C_e$. Langmuir isotherm constants q_m (22.97), b (0.0352) and R^2 (0.90) were obtained from the plot of C_e/Q_e vs. C_e. It can be stated that the Freundlich model fits well with the experimental values more than the Langmuir model supporting the multi-layered and complex adsorption process (Fig. 8). The imine groups, —C═N, are active sites for the Hg(II) adsorption (Donia et al., 2008). However, the heterogeneity of the adsorption mechanism originates from the fact that apart from the adsorption at the imine groups Hg(II) ions are also adsorbed, to a smaller amount, on other functional groups of the GG backbone. The later aspect of the adsorption process is supported by the fact that an adsorption capacity of 7.55 mg/g was obtained with the pure form of GG.

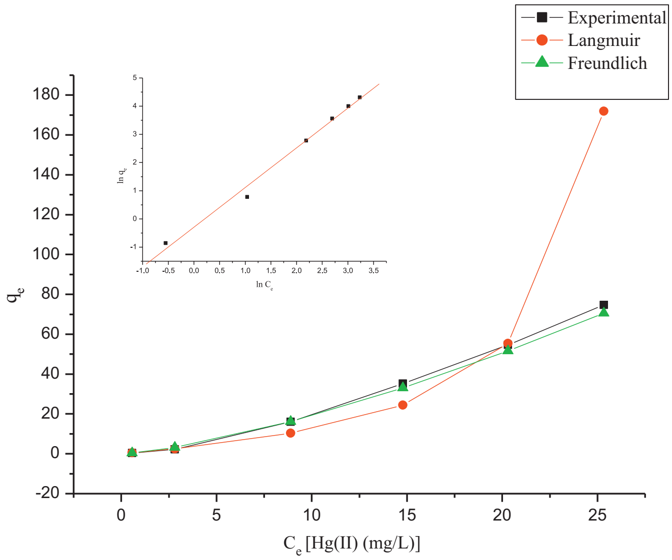


Fig. 8. Correlation of Langmuir and Freundlich isotherms with the experimental data (inset linear fit form of Freundlich adsorption isotherm).

4. Conclusions

Guar gum crosslinked with epichlorohydrin was oxidized by periodate oxidation to the polydialdehyde stage and subsequently reacted with hexamethylenediamine to synthesize a new Schiff-base. The later was used as adsorbent for the removal of Hg(II) from its aqueous solutions. High maximum adsorption capacity of 41.13 mg/g was obtained using 50 ppm of Hg(II) as the initial feed concentration. The adsorbent is also reusable up to five cycles. Thus, the adsorbent is efficient and reusable for the removal of Hg(II) ions from their aqueous solutions and can also be useful in the pre-concentration processes.

References

Ansari, R., & Raofie, F. (2006). Removal of mercuric ion from aqueous solutions using sawdust coated by polyaniline. *e-Journal of Chemistry*, *3*(1), 35–43.

Barkat, M., Nibou, D., Chearouche, S., & Mellah, A. (2009). Kinetics and thermodynamics studies of chromium(VI) ions adsorption onto activated carbon from aqueous solutions. *Chemical Engineering and Process*, *48*(1), 38–47.

Becker, T., Schlaak, M., & Strasdeit, H. (2000). Adsorption of nickel(II), zinc(II) and cadmium(II) by new chitosan derivatives. *Reactive and Functional Polymers*, *44*(3), 289–298.

Bicak, N., Sherrington, D. C., & Senkal, B. F. (1999). Graft copolymer of acrylamide onto cellulose as mercury selective sorbent. *Reactive and Functional Polymers*, *41*(1–3), 69–76.

Chauhan, G. S., Chauhan, S., Kumar, S., & Kumari, A. (2008). A study in the adsorption of Fe^{2+} and on pine needles based hydrogels. *Bioresource Technology*, *99*(14), 6464–6470.

Chauhan, K., Chauhan, G. S., & Ahn, J. H. (2009). Synthesis and characterization of novel guar gum hydrogels and their use as Cu^{2+} sorbents. *Bioresource Technology*, *100*(14), 3599–3603.

Chauhan, G. S., Jaswal, S. C., & Verma, M. (2006). Post functionalization of carboxymethylated starch and acrylonitrile based networks through amidoximation for use as ion sorbents. *Carbohydrate Polymers*, *66*(4), 435–443.

Chauhan, G. S., Singh, B., Chauhan, S., Verma, M., & Mahajan, S. (2005). Sorption of some metal ions on cellulosic-based hydrogels. *Desalination*, *181*(1), 217–224.

Chauhan, G. S., Singh, B., Sharma, R. K., Verma, M., Jaswal, S. C., & Sharma, R. (2006). Use of biopolymers and acrylamide-based hydrogels for sorption of Cu^{2+}, Fe^{2+} and Cr^{6+} ions from their aqueous solutions. *Desalination*, *197*(1), 75–81.

Denizli, A., Senel, S., Alsancak, G., Tuzmen, N., & Say, R. (2003). Mercury removal from synthetic solutions using poly(2-hydroxyethylmethacrylate) gel beads modified with poly(ethyleneimine). *Reactive and Functional Polymers*, *55*(2), 121–130.

Dharela, R., Raj, L., & Chauhan, G. S. (2012). Synthesis, characterization, and swelling studies of guar gum-based pH, temperature, and salt responsive hydrogels. *Journal of Applied Polymer Science*, *126*(S1), E260–E265.

Donia, A. M., Atia, A. A., & Elwakeel, K. Z. (2008). Selective separation of mercury(II) using magnetic chitosan resin modified with Schiff's base derived from thiourea and glutaraldehyde. *Journal of Hazardous Materials*, *151*, 372–379.

Gavilan, K. C., Pestov, A. V., Garcia, H. M., Yatluk, Y., Roussy, J., & Guibal, E. (2009). Mercury sorption on a thiocarbamoyl derivative of chitosan. *Journal of Hazardous Materials*, *165*(1–3), 415–426.

Greluk, M., & Hubicki, Z. (2009). Sorption of SPADNS azo dye on polystyrene anion exchangers: Equilibrium and kinetics studies. *Journal of Hazardous Materials*, *172*(1), 289–297.

Ho, Y. S. (2004). Citation review of Lagergren kinetic rate equation on adsorption reactions. *Scientometrics*, *59*(1), 171–177.

Ho, Y. S. (2006). Review of second-order models for adsorption systems. *Journal of Hazardous Materials*, *136*(3), 681–689.

Ho, Y. S., Malarvizhi, R., & Sulochana, N. (2009). Equilibrium isotherm studies of methylene blue adsorption onto activated carbon prepared from Delonix Regia pods. *Journal of Environmental Protection Science*, *3*, 111–116.

Kim, U. J., & Kuga, S. (2001). Thermal decomposition of dialdehyde cellulose and its nitrogen-containing derivatives. *Thermochimica Acta*, *369*(1–2), 79–85.

Kyzas, G. Z., & Deliyanni, E. A. (2013). Mercury(II) removal with modified magnetic chitosan adsorbents. *Molecules*, *18*, 6193–6214.

Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, *40*(9), 1361–1403.

Li, Q., Zhai, J., Zhang, W., Wang, M., & Zhou, J. (2007). Kinetic studies of adsorption of Pb(II), Cr(III) and Cu(II) from aqueous solution by sawdust and modified peanut husk. *Journal of Hazardous Materials*, *141*(1), 163–167.

Loonker, S., & Sharma, S. K. (2011). Studies of newly synthesized GT-AAH resin derived from guar. *International Journal of Basic and Applied Chemical Sciences*, *1*(1), 29–36.

Masri, M. S., & Friedman, M. (1972). Mercury uptake by polyamine–carbohydrates. *Environmental Science and Technology*, *6*(8), 745–746.

Monier, M. (2012). Adsorption of Hg^{2+} Cu^{2+} and Zn^{2+} ions from aqueous solution using formaldehyde cross-linked modified chitosan-thioglyceraldehyde Schiff's base. *International Journal of Biological Macromolecules*, *50*(3), 773–781.

Navarro, R. R., Sumi, K., Fujii, N., & Matsumura, M. (1996). Mercury removal from waste water using porous cellulose carrier modified with polyethyleneimine. *Water Research*, *30*(10), 2488–2494.

Parks, J. M., Johs, A., Podar, M., Bridou, R., Hurt, R. A., Smith, S. D., et al. (2013). The genetic basis for bacterial mercury methylation. *Science*, http://dx.doi.org/10.1126/science.1230667

Thakur, S., Chauhan, G. S., & Ahn, J. H. (2009). Synthesis of acryloyl guar gum and its hydrogel materials for use in the slow release of L-DOPA and L-tyrosine. *Carbohydrate Polymers*, *76*(4), 513–520.

UNEP. (2013). *Global Mercury Assessment 2013: Sources, emissions, releases and environmental transport*. Geneva, Switzerland: UNEP Chemicals Branch.

Wang, L., Xing, R., Liu, S., Cai, S., Yu, H., Feng, J., et al. (2010). Synthesis and evaluation of a thiourea-modified chitosan derivative applied for adsorption of Hg(II) from synthetic wastewater. *International Journal of Biological Macromolecules*, *46*(5), 524–528.