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Adsorption of mercury(II), methyl mercury(II) and phenyl mercury(II) on chitosan cross-linked with a barbital derivative

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ABSTRACT

The sorption behavior of glutaraldehyde cross-linked chitosan (G-Chitosan) and barbital-glutaraldehyde cross-linked chitosan (BG-Chitosan) was investigated for the sorption of Hg(II), $CH_3Hg(II)$ and $C_6H_5Hg(II)$. The pH_{Zpc} values were found to be 7.5 and 7.9 for G-Chitosan and BG-Chitosan respectively. Batch experiments were conducted to study the effect of adsorption under different pH (1–10), temperature (30–70 °C) and contact time (20–180 min) conditions. The optimum pH was found to be 4.5 and 6–8 for Hg(II), $CH_3Hg(II)$ and $C_6H_5Hg(II)$ respectively in case of G-Chitosan while in case of BG-Chitosan it was >8 for $CH_3Hg(II)$ and 7 for Hg(II) and $C_6H_5Hg(II)$. Adsorption was found to be endothermic in the case of Hg(II) and exothermic for $CH_3Hg(II)$ and $C_6H_5Hg(II)$. FT-IR analysis showed the possibility of metal binding to amino groups and free aldehyde groups of G-Chitosan and amide N and O of BG-Chitosan.

1. Introduction

Conventional treatments to remove Hg^{2+} from contaminated sources are often inadequate to reduce Hg^{2+} concentrations to the acceptable regulatory standards. Current interests are focused on sorption due to the diversity of the available sorbent materials. Some of the biosorbents used are fungal or bacterial biomass, substituted celluloses (Muzzarelli, 1966) and biopolymers like chitosan or alginated polymers obtained as byproducts of marine industries (Gwen et al., 2007; Krishnaiahbburi, Jonathanl, & Edgard, 2003). Chitosan was described as a suitable biopolymer for removal of metal ions from waste water (Arguelles & Peniche, 1993; Choong, 2005; Choong & Holl, 2003; Fei, Shaoguang, & Yue, 2008; Guibal, 1998; Karol, Guibal, Francisco, Ly, & Holger, 2007; Koyama, Taniguchi, & Haung, 1986; Kurita, Sannan, & Iwakura, 1979; Li & Renbi, 2002; Meng-Wei, Chi-Chuan, Buenda, & Maria, 2010; Merrifield, Davids, MacRae, & Amirbahman, 2004; Muzzarelli & Isolati, 1971; Muzzarelli & Rocchetti, 1974; Nan, Renbi, & Changkun, 2005; Oshita, Oshima, Gao, Lee, & Motomizu, 2002; Peniche, Alvarez, & Arguelles, 2003; Vieira & Beppu, 2005; Wan & Fatinathan, 2008; Zhang et al., 2009).

Thanks to its amino groups, chitosan is reactive towards many chemicals: this results in a number of chitosan derivatives having a wide range of uses, and in particular transition metal chelates (Choong, 2005; Choong & Holl, 2003; Guibal, 1998; Merrifield et al., 2004; Muzzarelli & Tubertini, 1969; Oshita, Oshima, Gao, Lee, & Motomizu, 2002; Vieira & Beppu, 2005; Zhang et al., 2009).

Chitosan is soluble in all organic and mineral acids and has reduced diffusivity of sorbate due to its low porosity and high crystallinity. Derivatization can enlarge the space between the chitosan chains improving the accessibility of functional groups for metal ions (Koyama et al., 1986; Kurita et al., 1979).

The ability of mercury (II) to form a complex with barbital (5,5′-diethyl barbituric acid) has been used as the basis for the separation and determination of barbiturates where barbital was treated with excess mercury (II) to form a chloroform extractable complex (Padmaja, 1994). Advantage was taken of the ability of mercury to form mercury barbital complex for the determination of mercury (Curry, 1964). Our group has also studied the adsorption of inorganic, methyl and phenyl mercury using barbital immobilized chitosan (Kushwaha, Sreedhar, & Padmaja, 2010). The aim of this work was to study the sorption of Hg^{2+}, CH_3Hg^{2+} and $C_6H_5Hg^{2+}$ ions on cross-linked chitosan using glutaraldehyde (G-Chitosan) and barbital glutaraldehyde cross-linked chitosan (BG-Chitosan). For the preparation of BG-Chitosan initially glutaraldehyde was condensed with barbital to form 5-(2,4,6-trioxo-tetrahydro-pyrimidin-5-ylidene)-pentanal which was then cross-linked with chitosan (Scheme 1).

The chemical structure and physical properties of the adsorbents were characterized by FT-IR, SEM and XRD. Potentiometric technique was also used to determine pH_{Zpc} of the adsorbents

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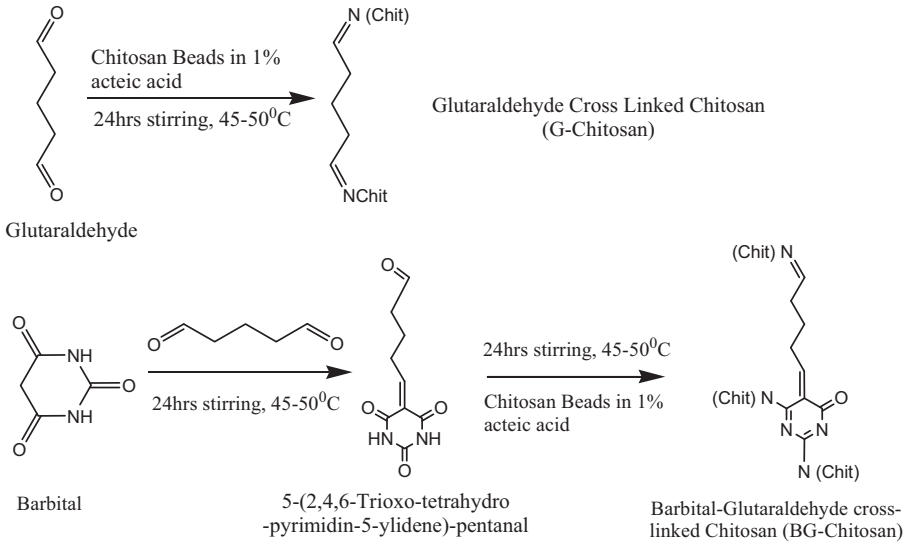

Scheme 1. Cross-linking with glutaraldehyde and barbital with glutaraldehyde.

under study. Studies have been conducted on the optimization of various experimental conditions like pH, adsorbent dose, temperature, time, the determination of sorption isotherms, and kinetics.

2. Experimental

2.1. Sorbent preparation

Chitosan flakes (87.6% deacetylated and molecular weight 5.5×10^5 g/mol) from Sigma Aldrich were used for the experiments. 1% (w/v) chitosan solution was prepared by dissolving chitosan flakes in 1% (v/v) acetic acid solution at room temperature and homogenizing the mixture for 48 h. A 100 mL of 0.1% solution of glutaraldehyde was added to 100 mL of 1% solution of chitosan in 1% acetic acid and allowed to react for 24 h at 45–50 °C to form an imine [G-Chitosan] through a Schiff's base reaction between aldehyde ends of glutaraldehyde and amine moieties of Chitosan. G-Chitosan was then filtered, washed with double distilled water until neutral and then left for air drying.

BG-Chitosan was formed by initial condensation of glutaraldehyde and barbiturate moiety followed by cross-linking with chitosan. A 100 mL of 0.1% solution of glutaraldehyde was mixed with 100 mL of 0.1% solution of freshly prepared sodium barbiturate and were allowed to react at 45–50 °C for 24 h (TTPP). This solution was added to 100 mL of 1% solution of chitosan in acetic acid and stirred for 24 h at 50 °C, filtered, washed with double distilled water until neutral and then left for air drying. The barbital glutaraldehyde condensation product (5-(2,4,6-trioxo-tetrahydro-pyrimidin-5-ylidene)-pentanal) undergoes cross-linking with chitosan resulting in the formation of BG-Chitosan. BG-Chitosan was found to be less soluble, hard and had greater swelling capacity compared to G-Chitosan.

Scanning electron micrograph of G-Chitosan displays a open porous and heterogeneous structure (Fig. 1). Cross-linking with BG-Chitosan is seen to bring about conspicuous textural and morphological changes with BG-Chitosan forming a more compact and rigid structure. The pores are in the range 100 μm in G-Chitosan which reduce in BG-Chitosan to 50 μm.

2.2. Sorption experiments

A series of metal sorption experiments were conducted to study the effect of pH, dose and temperature. For each experiment 25 mL of Hg^{2+}, CH_3Hg^{2+} and $C_6H_5Hg^{2+}$ solution of known initial concentration and pH were taken in a 100 mL stoppered conical flask. A suitable adsorbent dose is added to the solution and the mixture was shaken at a constant speed. The supernatant was separated from the adsorbent by filtration and analyzed for the presence of unadsorbed mercury by CVAAS (MA-5840 analyser ECIL). All the experiments were conducted in triplicate and the average results are reported. The mercury uptake by the chitosan was calculated as follows:

$$q_e = \frac{C_i - C_e}{m}$$

where C_i is the initial concentration of metal ion mg/L; C_e is equilibrium concentration of metal ion mg/L; m is mass of adsorbent g/L; and q_e is the amount of metal ion adsorbed per gram of adsorbent. The experiments done without adsorbent were treated as blanks and they showed no precipitation of metal ions occurred under the conditions selected.

2.3. Sorption kinetics

In order to investigate the sorption process of Hg^{2+}, CH_3Hg^{2+}, $C_6H_5Hg^{2+}$ pseudo first order rate equation, pseudo second order rate equation and Intraparticle diffusion equation were used as kinetic models.

Pseudo first order model. The sorption kinetics can be defined by a pseudo-first-order.

$$\frac{dq}{dt} = K_1'(q_e - q_t)$$

where q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g); q_t is the amount of solute adsorbed at any time (mg/g) and K_1' is the adsorption constant and equation can be linearized as the function of time.

$$\log(q_e - q_t) = \log q_e - \frac{K_1' t}{2}.303$$

Plots for the linearized equation were made and the constants were calculated from the slopes and intercept of the plots of $\log(q_e - q_t)$ vs. time.

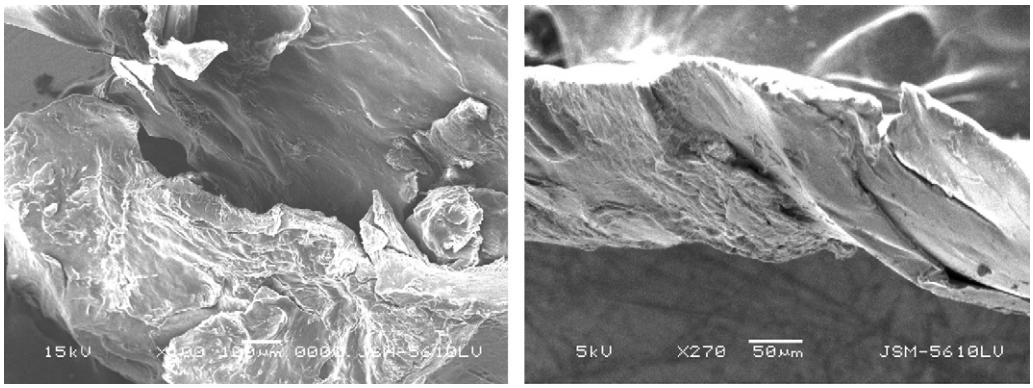

Fig. 1. Scanning electron micrograph of G-Chitosan and BG-Chitosan.

Pseudo second order model. This model based on the solid capacity has been presented for the kinetics of sorption of divalent metal ions

$$q_t = \frac{q_e^2 K'^t_2}{1 + q_e K t}$$

where K'_2 is the pseudo second order rate constant (g/mg min), the above equation can be rearranged to obtain the linearized form which is shown as follows:

$$\frac{t}{q_t} = \frac{1}{q_e^2 K'_2} + \frac{t}{q_e}$$

The pseudo second order constants can be determined experimentally by plotting t/q_t vs. t.

Intraparticle diffusion study. Equation for the Weber Morris intraparticle diffusion model

$$q_t = K_i t^{0.5}$$

where k_i is the intraparticle diffusion rate constant (mg/g min$^{0.5}$).

The results of the sorption experiments were analyzed using Freundlich, Langmuir models to determine the parameters associated with sorption.

3. Instrumental analysis

The surface morphology and topographic analysis of the adsorbent samples was examined by Scanning Electron Microscope (JEOL, Model JSM-5610LV). Samples were mounted onto metal holders using a conducting substrate. The scanning electron micrographs enable the direct observation of the changes in the surface microstructures between the two biosorbents G-Chitosan and BG-Chitosan that are due to the chemical surface modifications.

Powder-XRD of the ingredients was taken by holding in place on quartz plate for exposure to CuKα radiation of wavelength 1.5406 Å. The sample was analyzed at room temperature over a range of 10–70° 2θ with sampling intervals of 0.02° 2θ and scanning rate of 2°/min.

Estimation of particle size by the use of Scherrer's equation revealed the crystallite size (Khanna, Priyesh, Jagdish, & Bharate, 2009).

$$\text{Size} = \frac{k\lambda}{\beta \cos\theta}$$

where $k = 0.9$, wavelength used λ is 0.154 nm, θ is the peak maxima and β is full width at half maxima in radian.

Spectra for biosorbent and the metal-loaded biosorbents were obtained using a Perkin Elmer RX1 model within the wave number range of 400–4000 cm^{-1}. Specimens of samples were first mixed with KBr and then ground in a mortar at an appropriate ratio of 1/100 for the preparation of the pellets. Resulting mixture was pressed at 10 tons for 5 min sixteen scans and 8 cm^{-1} resolution were applied in recording spectra. The background obtained from the scan of pure KBr was automatically subtracted from the sample spectra.

Potentiometric experiments were carried out according to reported procedure (Chen & Yang, 2006). Adsorbent mass of 0.1 g was suspended in 50 mL of 0.01 M KNO_3 solution, and the suspension was purged with N_2 for 30 min to dissipate CO_2 and then left for 24 h for equilibrating the solution in electrolyte. The suspensions were acidified to pH 3.5 using 0.1 M HNO_3 and then titrated to pH 11 using 0.1 M NaOH. All experiments were conducted in triplicate in a glass vessel with a lid as part of a Spectralab AT-38C Automatic potentiometric titrator. The temperature was recorded with a temperature sensor; the error of the temperature probe was 0.1 °C. The pH electrode was three-point calibrated with buffers (pH 4, 7, and 10) before each experiment, and the slope did not deviate more than 1% from the Nernst value. The Titrator unit was programmed with a step volume dose mode for the titration, which adds 0.001 mL of titration solution according to the pH changes.

4. Results and discussion

4.1. Uptake studies

Batch sorption studies were carried out using temperature controlled shaking bath to investigate number of variables affecting the sorption of Hg^{2+}, CH_3Hg^{2+}, $C_6H_5Hg^{2+}$ like agitation time, pH variation, temperature variation, etc.

4.2. pH optimization

Effect of pH was studied as a function of % uptake of the adsorbate under study (Hg^{2+}, CH_3Hg^{2+}, $C_6H_5Hg^{2+}$) in the range of pH 1–10, using metal ion concentration of 0.8 mg/L with an adsorbent dose of 4 g/L for G-Chitosan and BG-Chitosan. Fig. 2 shows the effect of pH on sorption of inorganic and organic mercury onto G-Chitosan and BG-Chitosan. Inorganic Hg uptake was found to increase with increase in pH and reach equilibrium at pH 4 and 7 in case of G-Chitosan, BG-Chitosan respectively. Organic Hg uptake also was found to increase with increase in pH. Methyl mercury was found to reach equilibrium at pH 5, >8 in case of G-Chitosan, BG-Chitosan respectively while phenyl mercury was found to reach equilibrium at pH 6–8, 7 in case of G-Chitosan, BG-Chitosan respectively. This is in contrast to what is observed in general that adsorption of mercury decreases from pH 6 onwards due to precipitation (Ahmed,

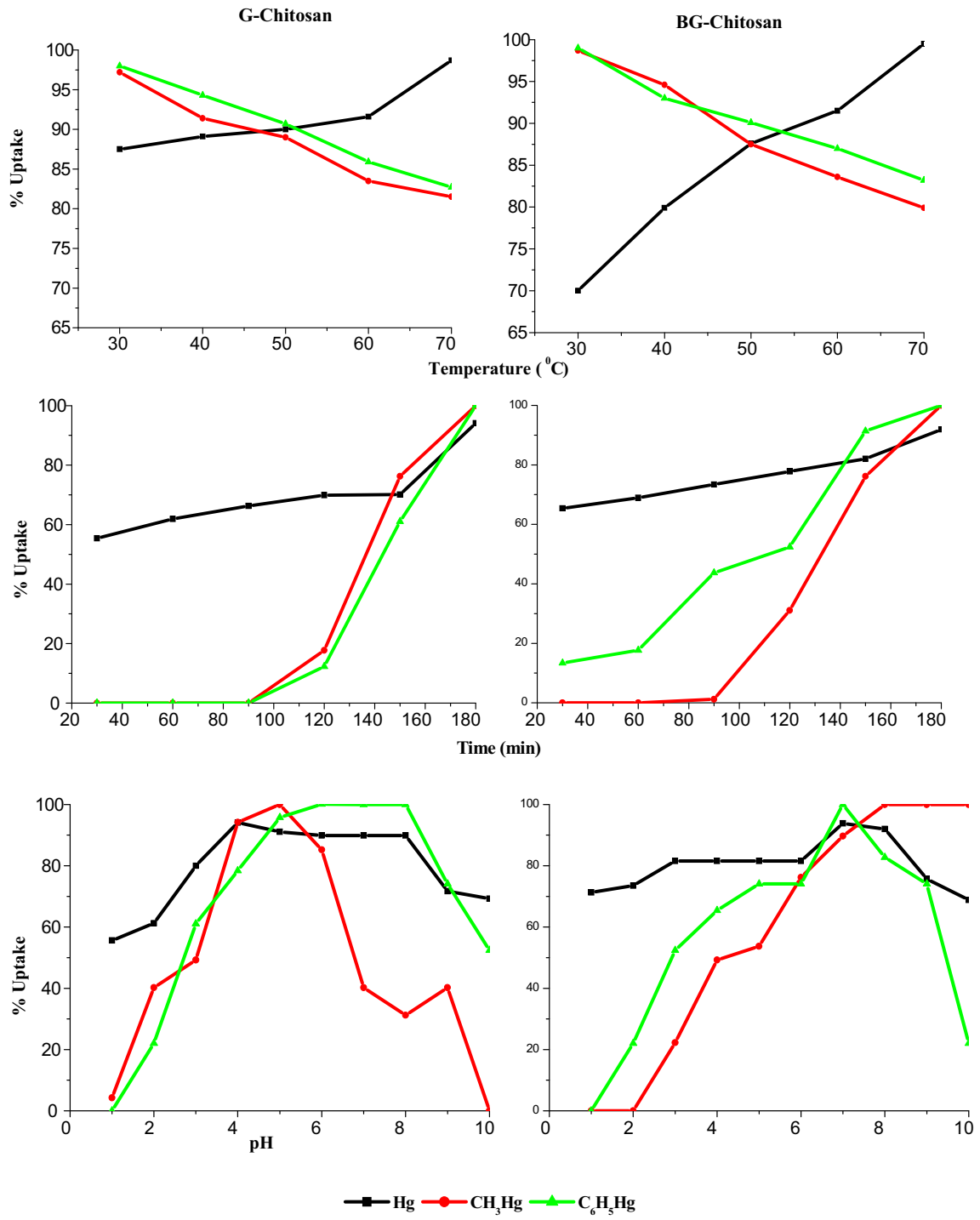

Fig. 2. Uptake studies with respect to the effect of temperature, time and pH.

Asem, & Heniesh, 2008). This could be due to the fact that all the mercury species which are likely to exist in the investigated pH range (0.5–8), might remain in soluble form due to the low concentrations of mercury studied (Baes & Mesmer, 1976). Furthermore, considerable uptake of Hg^{2+} is observed even under acidic pH conditions. Acid–base titrations of the adsorbents (Fig. 3) showed that pH_{Zpc} values are 7.5 and 7.9 for G-Chitosan and BG-Chitosan respectively. Thus the pH dependence of adsorption of mercury onto the adsorbents could be the result of both mercury speciation as well as changes in the ionisation of different groups on the adsorbents with pH.

4.3. Effect of temperature

The effect of temperature on the sorption of Hg^{2+}, CH_3Hg^{2+}, $C_6H_5Hg^{2+}$ was studied by carrying out a series of experiments at 30–70 °C at equilibrium times of the respective sorbates. Fig. 2 shows that effect of temperature is different for both the adsorbents. Uptake of inorganic mercury was found to increase with increase in temperature in the case of both G-Chitosan and BG-Chitosan as sorbents but sorption of organic mercury decreased with increase in temperature suggesting chemisorption mechanism in the latter case (Jonathan et al., 2009). The chemisorption

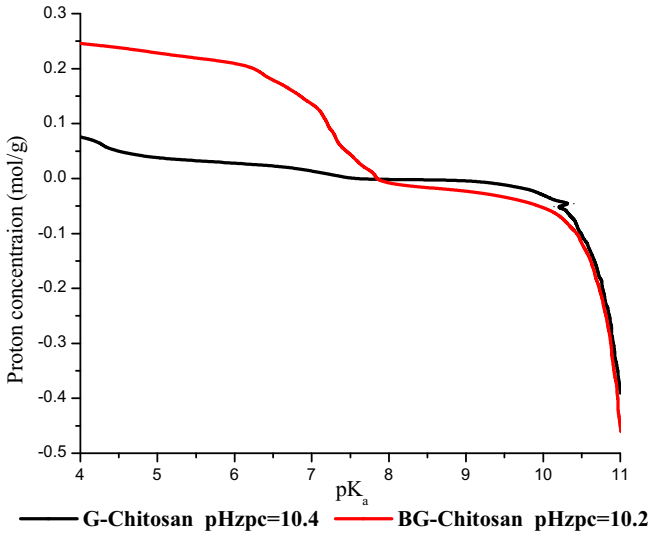

Fig. 3. Potentiometric titration of G-Chitosan and BG-Chitosan.

could be explained due to the greater softness of organomercury compounds.

4.4. Effect of agitation time

The effect of agitation time on the uptake of Hg^{2+}, CH_3Hg^{2+}, and $PhHg^{2+}$ on G-Chitosan and BG-Chitosan is shown in Fig. 2. It is seen that the rate of sorption is fast for the adsorbents in the case of Hg^{2+}, CH_3Hg^{2+}, and $C_6H_5Hg^{2+}$. However the time needed to attain equilibrium is longer when using G-Chitosan than BG-Chitosan. Also Hg^{2+} was found to adsorb at a faster rate followed by $C_6H_5Hg^{2+}$ and CH_3Hg^{2+}. More than 99% of total mercury was removed within a period of 160 min. This rapid initial binding rate suggests an instantaneous binding of mercury on surface binding sites followed by slower and non-specific binding to other components.

4.5. Sorption kinetics

In order to investigate the mechanism of sorption process three kinetic models were used including pseudo first order model, pseudo second order model and intraparticle diffusion model. Experiments were done for the sorption of Hg^{2+}, CH_3Hg^{2+}, and $PhHg^{2+}$ on both G-Chitosan and BG-Chitosan using series of measurements at time intervals extending from 30 min to 240 min (Table 1 and Fig. 4).

Pseudo first order model was fitted with a correlation coefficient of ~0.95 for all the three forms of mercury. Values of regression coefficients are shown in Table 1. This suggests that sorption was fast at the beginning of sorption and rate of removal using BG-Chitosan was faster. But in the case of all the four types of pseudo second order rate equation the correlation coefficients were found to be >0.90. Intraparticle diffusion mechanism was found to be followed by G-Chitosan for all the three species of mercury but in BG-Chitosan phenyl mercury did not follow intraparticle diffusion whereas others did with a correlation coefficient >0.92. This suggests that multiple mechanisms like fast ion exchange, inter and intra-molecular binding and diffusion are operating in the sorption of mercury on G-Chitosan and BG-Chitosan.

4.6. Sorption isotherms

The Langmuir and Freundlich models (Fig. 4) were used to determine the sorption capacity of mercury on chitosan derivatives. From the correlation coefficient values (r^2) obtained for the two models (Table 1), it can be seen that the sorption behavior on G-Chitosan is better described by the Langmuir model while the sorption data fit better for Freundlich model in the case of BG-Chitosan. The negative values obtained for Gibbs free energy suggests that the adsorption process is spontaneous in the case of both the sorbents G-Chitosan and BG-Chitosan.

4.7. X-ray diffraction analysis

The X-ray diffraction analysis is done and shown in Fig. 5. A sharp peak of 1436 (cps) and 8829 (cps) intensity at 20.14 and 19.34 theta for G-Chitosan and BG-Chitosan respectively has been observed. A shift in 2 theta value could be due to the difference in cross-linking agents. In G-Chitosan cross-linking is more patterned but in case of BG-Chitosan because of the presence of bulkier moiety, random cross-linking has occurred resulting in the shift of theta value. The peak is narrower in the case of G-Chitosan indicating atomic order in G-Chitosan as compared to BG-Chitosan. Size of the crystallite calculated from FWHM of XRD peak is 6.0577 nm for G-Chitosan and 1.19775 nm for BG-Chitosan. The interlayer distance calculated from 2 theta value was found to be 0.444 nm and 0.467 nm for G-Chitosan and BG-Chitosan respectively.

Table 1
Isothermal and kinetic parameters for sorption of inorganic and organic mercury.

Kinetics and Isotherms		G-Chitosan			BG-Chitosan		
		Hg^{2+}	CH_3Hg^{2+}	$C_6H_5Hg^{2+}$	Hg^{2+}	$CH_3 Hg^{2+}$	$C_6H_5Hg^{2+}$
Pseudo first order	q_e (mg/g)	0.0174	0.0151	0.0190	0.0355	0.0295	0.0478
	K (min^{-1})	0.0092	0.0081	0.0102	0.0195	0.0018	0.0213
	r^2	0.9170	0.9560	0.9290	0.9490	0.9590	0.9880
Pseudo second order	q_e (mg/g)	0.0212	0.2310	0.2030	0.0625	0.0591	0.0716
	K (g/mg min)	0.5600	0.6730	0.4950	0.0001	0.0003	0.0002
	r^2	0.9170	0.9210	0.9330	0.9100	0.9230	0.9190
Intraparticle	K_i (mg/g $min^{0.5}$)	0.0009	0.0008	0.0021	0.0018	0.0076	0.0082
	r^2	0.9780	0.9890	0.9880	0.9920	0.9230	0.8190
Langmuir	q_m (mg/g)	0.0077	0.0089	0.0098	0.0065	0.0072	0.0069
	K_a (L/mg)	228.10	234.50	257.80	240.50	189.57	314.00
	r^2	0.9940	0.9800	0.9960	0.9680	0.6670	0.8190
	ΔG (KJ/mol)	−13.68	−13.75	−13.99	−13.81	−13.21	−14.48
Freundlich	K_f (mg/g) (dm^3/mg)$^{1/n}$	0.0530	0.0817	0.0919	0.0008	0.0001	0.0006
	N	2.7800	3.1400	1.5670	1.815	2.321	1.513
	r^2	0.4760	0.5140	0.6780	0.9490	0.9590	0.8990

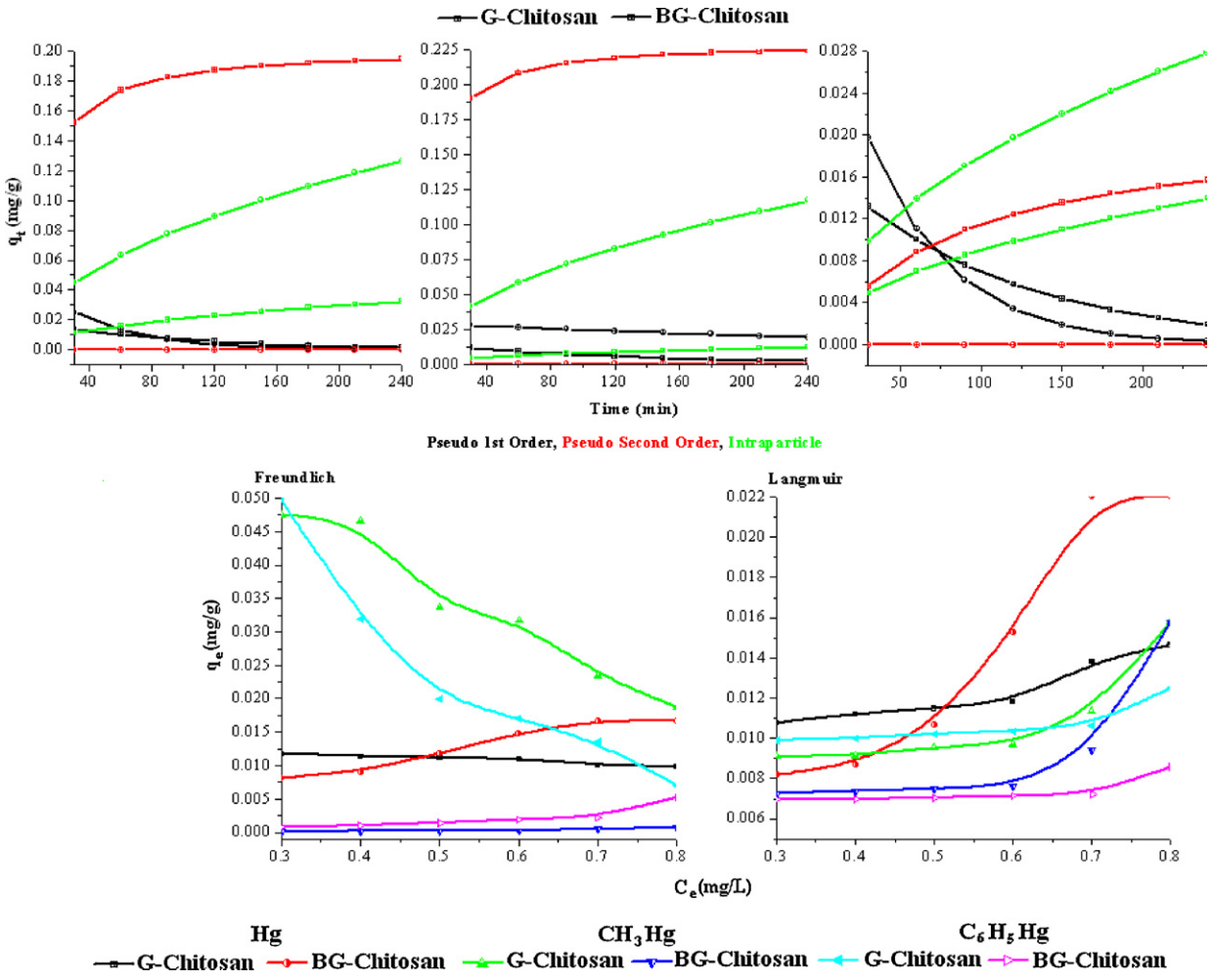

Fig. 4. Kinetics and isotherms for G-Chitosan and BG-Chitosan.

4.8. Fourier transform infrared spectroscopy

The strong broad band in the wave number region of 3300–3500 cm^{-1} is characteristic of the N—H stretching vibration in G-Chitosan and BG-Chitosan although there is the possibility of overlapping between the N—H and the O—H stretching vibrations corresponding to pyranose structure. The band corresponding to free amino groups is observed at 1629.95 cm^{-1} and 1599.31 cm^{-1} for G-Chitosan and BG-Chitosan respectively but the band is weaker in case of BG-Chitosan due to consumption of these groups during cross-linking of chitosan with 5-(2,4,6-trioxo-tetrahydro-pyrimidin-5-ylidene)-pentanal, the condensation product of glutaraldehyde and barbital. A band at 1725 cm^{-1} in G-Chitosan can be attributed to carbonyl groups of unreacted aldehyde functional groups of glutaraldehyde which are found to be absent in BG-Chitosan suggesting the condensation of these aldehydic groups of glutaraldehyde with barbiturate. A new band in BG-Chitosan at 1153 cm^{-1} appeared due to the formation of new C—N bonds after complexation of glutaraldehyde with barbital and cross-linking with chitosan. This 1153 cm^{-1} peak can be attributed to asymmetric stretching of C—O—C and C—N stretch. The band corresponding to free amino groups is observed at 1629.95 cm^{-1} and 1599.31 cm^{-1} for G-Chitosan and BG-Chitosan respectively but the band is weaker in case of BG-Chitosan due to the consumption of these groups during the cross-linking of chitosan with 5-(2,4,6-trioxo-tetrahydro-pyrimidin-5-ylidene)-pentanal.

The FTIR spectra after sorption of mercury on G-Chitosan shows a shift in 1725 cm^{-1} band to 1655 and 1700 cm^{-1} after mercury binding in case of Hg^{2+} and $CH3Hg^{2+}$ respectively suggesting the involvement of carbonyl arising from unbound sites of glu-

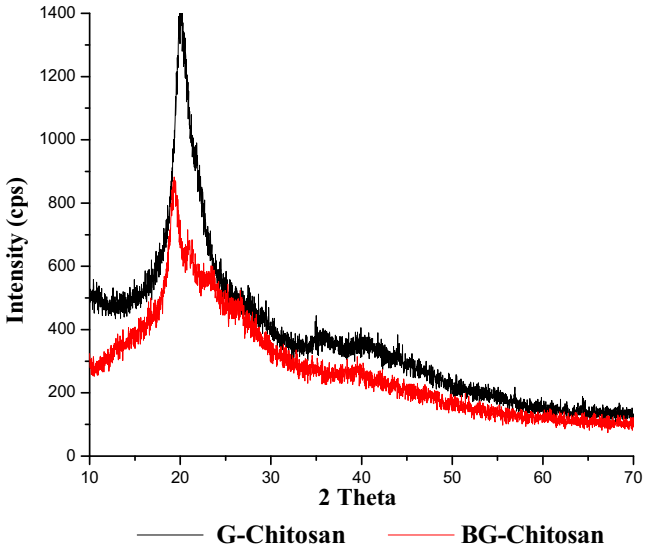

Fig. 5. X-ray diffraction pattern of G-Chitosan and BG-Chitosan.

taraldehyde in binding of mercury. This behavior is consistent with previous reported results on uranium removal by chitosan and molybdate removal by cross-linked chitosan beads (Muzzarelli, 2011; Guibal et al. (1999) and Piron, Accominotti, & Domard (1997)). A decrease in transmittance in the wave number region of 3434–3431 cm^{-1} after mercury sorption indicates that N—H vibration was affected due to sorption of mercury. In the case of BG-Chitosan the FTIR data showed that C—N stretching frequency at wave number of 1084 cm^{-1} shifted to 1070, 1028, 1062 cm^{-1} after mercury sorption suggesting the attachment of mercury to N and O bond of amide moiety A shift in the band at 1153 cm^{-1} to higher wavenumbers was also observed in BG-Chitosan suggesting that N and O of amide involved in the sorption process. After mercury sorption there is a large shift in N—H bending absorption frequency from 1599 cm^{-1} to 1635 cm^{-1}, 1618 cm^{-1} and 1637 cm^{-1} for Hg^{2+}, CH_3Hg^{2+} and $PhHg^{2+}$ respectively in BG-Chitosan. A shift in 1074 cm^{-1} band to 1066 cm^{-1}, 1068 cm^{-1} and 1062 cm^{-1} related to C—N stretching indicates that nitrogen atoms are main sorption sites in both. Thus all the bands are suggestive of involvement of bonds with N atoms and C=O of unreacted aldehyde in the case of G-Chitosan and C—N and C—O of amide in BG-Chitosan for sorption mercury.

Thus from FTIR and potentiometric studies we can conclude that for G-Chitosan sorption sites may be free aldehyde group of glutaraldehyde which has not been used in cross-linking of chitosan and amino groups in chitosan. In the case of BG-Chitosan the sorption sites could be amide groups of barbital where mercury can coordinate bidentately to both amide nitrogen and oxygen atoms (Hui-Chung & Carmay, 2006).

5. Conclusion

A new adsorbent BG-Chitosan was prepared which was less crystalline, more rigid and had more swelling capacity compared to G-Chitosan. Sorption studies of Hg^{2+}, CH_3Hg^{2+}, $C_6H_5Hg^{2+}$ on G-Chitosan and BG-Chitosan by batch experiments were done. Sorption of all the three forms of mercury showed similar behavior except for the fact that the process is endothermic for Hg^{2+} and exothermic for CH_3Hg^{2+}, $C_6H_5Hg^{2+}$. Equilibrium was found to be attained faster in the case of G-Chitosan as compared to BG-Chitosan. G-Chitosan showed higher adsorption capacity as compared to BG-Chitosan. Kinetic studies showed that the data could fit to pseudo first order, pseudo second order and intraparticle diffusion models suggesting multiple mechanisms operating in the sorption process. FTIR studies showed that free amino groups of chitosan and aldehyde groups of glutaraldehyde are used for binding of mercury in G-Chitosan while in the case of BG-Chitosan both the groups are absent and mercury is bound to amide groups of barbital present in BG-Chitosan.

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