# Bromine pretreated chitosan for adsorption of lead (II) from water

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**Abstract.** Pollution by heavy metals like lead (II) is responsible for health hazards and environmental degradation. Adsorption is a prevalent method applied for removal of heavy metal pollutants from water. This study explored adsorption performances of 30% bromine pretreated chitosan for lead (II) abatement from water. Bromine pretreatment alters porosity and specific surface area of chitosan by means of physicochemical interaction with cationic sites of chitosan skeleton, besides imparting anionic alteration at amino linkages of chitosan, to remove lead (II) by chemical interactions on superfluous active sites as characterized by FTIR, SEM, DTA and elemental analysis. Lead adsorptions were studied in batch mode by varying parameters viz. pH, bromine loading, sorbent dosage, initial lead concentration, contact time and temperature. The adsorption equilibrium data was well fitted to Freundlich isotherm and maximum sorption capacity of 30% bromine pretreated chitosan sorbent was 1·755 g/kg with 85–90% lead removal efficiency. Though cost and applicability of sorbent is unproven, yet contrast to raw chitosan derivatives, activated carbons and some resins, 30% bromine pretreated chitosan endow benign and efficient lead abatement technique.

**Keywords.** Lead; 30% bromine pretreated chitosan; water; adsorption; langmuir; Freundlich.

## 1. Introduction

Many toxic heavy metals like lead, copper, zinc, mercury, chromium, arsenic and cadmium etc are either contaminated as natural constituents in earth crust (sediments deposit as metal salts) or enter owing to urbanization and a high degree of industrialization such as metal plating factories, mining operations and tanneries which substantially enhance ecological degradation (Das *et al* 2008). Their intrusion in water also leads to severe detrimental effects on human life and environment. Therefore, to remove such pollutants from water with plausible choice of treatments becomes a challenge to cleaner, friendlier and safer environment.

Lead (*plumbum*) is a shiny chrome white luster heavy element with soft, malleable poor metallic character soon turning to grayish on exposure to air. Nevertheless, lead (II) materials are used in building construction, batteries, bullets shots, weights, as part of solders, pewter's, fusible alloys, radiation lead shields as well as utilized mainly in metal manufacturing, mining, extractive metallurgical, electroplating and pigment (Londrigan *et al* 1990). Aquatic pollution of lead (II) poses serious environmental problem, due to toxicity and accumulation tendency through food chains (ATSDR 2007). Amid metal pollution cycle being most heavy, this lead (II) is a highly cumulative poison seldom recovering from the environment, so must be priory detained from entering into ecology (Goyer 1993). Lead at certain exposure is poisonous to human and animals due to damaging nervous

system and causing brain disorders or showed neurological symptoms like pain, muscle weakness, paraesthesia, as well as rare encephalitis. Other common symptoms in lead poisoning includes gastrointestinal harms, like constipation, diarrhea, poor appetite, weight loss, abdominal pain, nausea and vomiting (Pearce 2007). More acute lead absorption may cause shocks because water loss from gastrointestinal tract governs fluid control in circulatory system. Further lead (II) damages kidney and causes decreased urine output (Brunton *et al* 2007). Lead intrusion in human daily needs is ubiquitous and many people have some measurable blood lead level (Hu *et al* 2007; Karri *et al* 2008). Since 1970, regulatory norms in developed countries control lead content in products which greatly reduced its exposure to habitants; still in many developing countries, lead utility in products is non-regulated (Pokras and Kneeland 2008).

Numerous methods employed to remove lead from water such as chemical precipitation, sludge separation, chemical oxidation or reduction, ion exchange, reverse osmosis, membrane separation, electrochemical treatment and evaporation (Rusten *et al* 1997; Bailey *et al* 1999; Gogate and Pandit 2004; Cochrane *et al* 2006; Igwe and Abia 2006). However, certain techniques are expensive or possess some disadvantages like fewer lead removals, poor selectivity, more load of toxic solid waste/sludge as well as high cost and energy consumption. Nevertheless, adsorption process is found to be effective and economic for a wide variety of water pollutant sorption (Gogate and Pandit 2004). The activated carbon is most extensively used for lead removal, which is quite expensive and less effective on large scale (Babel and Kurniavan

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2003; Nadeem *et al* 2006). Adsorption by using biosorbents has been an economically feasible bioremediation alternative for lead removal as it offers the advantages of low operating cost, minimizing secondary pollution and high efficiency in wastes. The non-living biomass in biosorption is more practically used and advantageous over living biomass cells as latter requires the addition of fermentation media which increase the biological oxygen demand or chemical oxygen demand of water. Besides, non-living biomass is unaffected by the toxicity of lead ions and they can be subjected to different chemical and physical treatment techniques to enhance their performance. In the recent past, considerable attention has been paid to natural biomaterials as alternative sorbent to reduce cost of adsorption systems (Quin *et al* 2008; Bulgariu *et al* 2009a). Hence, lead pollution from water was mitigated by assorted low-cost adsorbents like peat (Ho *et al* 1999; Bulgariu *et al* 2009b), lignin (Ucun *et al* 2003; Guo *et al* 2008) and fungi (Horsfall and Spiff 2005). Synthetic resins also showed high lead selectivity with excellent performance for lead removal; yet relatively very costly as compared to ion exchangers (Kuribayashi *et al* 1988; Abo-Farha *et al* 2009; Badawy *et al* 2009). Many such adsorbents either owe less adsorption capacity or technically non-feasible at field scale, besides the adsorption success hinges on developing environmentally benign, viably efficient and technically feasible sorbents. Consequently, selection of adsorbent critically focused on potential adsorption capacity, benign features and cost factors.

Chitosan is the most abundant polymer after cellulose and a hydrophilic natural polymer obtained by alkaline deacetylation of chitin as extracted from shrimp and crabshells (Arrascue *et al* 2003). Chitosan/chitin are excellent biosorbent due to unique structure, distinctive properties, safety and biodegradability, as a result frequently used for mitigation of toxic and strategic metals like mercury, cadmium, uranium, vanadium, platinum, gold, palladium and molybdenum (Milot *et al* 1998; Vieira and Beppu 2006; Fujiwara *et al* 2007; Sankararamakrishnan *et al* 2007; Wang 2008; Wang *et al* 2011). The surface modification of chitin/chitosan has become a popular method adopted to derive anticipated adsorbents characteristics for practical applications so far (Makkuni *et al* 2005; Nan *et al* 2005). N-atom/amino linkages of chitosan skeleton can be modified easily, so as to contribute towards chemical interactions with metal cations (Vieira and Beppu 2006). Chitosan derivatives are capable of adsorbing metal ions through many interactions like chemical/chelation, electrostatic and ion-exchange besides depending on metal chemistry and pH of medium (Dzul Erosa *et al* 2001; Ng *et al* 2003). Literature revealed chitosan's adsorption capacities for hydrochloric acid, sulfuric acid, nitric acid and iodine/bromine in aqueous conditions (Zhang *et al* 2009). Hence, chitosan was intentionally pretreated with 30% bromine (KBr) to investigate optimum conditions for lead (II) adsorption under operating parameters like temperature, pH and initial lead concentration. Although cost and applicability of bromine pretreated chitosan is unproven, yet compared to traditional activated granular carbons and some resins, it endows benign and efficient adsorption technique for mitigating lead pollution from water without affecting its quality.

## 2. Experimental

### 2.1 *Materials*

The coarse grains chitin was purchased from M/s B.R. Corporation, Mumbai. Chitosan were obtained by about 80% deacetylation of chitin by treatment with 10 N NaOH solution. Analytical grade potassium bromide (KBr), nitric acid and anhydrous ethanol were used. And all the solutions were made with deionized (DI) water.

### 2.2 *Synthesis of samples*

About 3 g of chitosan, 30 mL of deionized water and 10 mL of anhydrous ethanol were taken in a 50 mL bottle and vigorously stirred for 1 h, followed by addition of 1 g of potassium bromide slowly under constant stirring for 4 h. This bottle was stored for another 16 h at NTP. After soaking, the residual/bromine pretreated solid was vacuum filtered, dried at 75 °C in an air environment for two days. All pretreated chitosan sorbents were ground and sieved to 150 mesh size.

### 2.3 *Experimental apparatus and procedures*

The stock solution of lead (II) ions was prepared by dissolving an accurate quantity of Pb $(NO_3)_2$ in deionized water. And other lead (II) solutions (varying between 5 and 50 mg/L) were prepared from stock solution by dilution and pH was adjusted by 0·1 M $HNO_3$ and/or 0·1 M NaOH solutions. The fresh dilutions were made for each adsorption experiment.

### 2.4 *Batch adsorption studies*

All batch experiments were done in a beaker with 50 ml lead sample solution kept on a magnetic shaker at 250 rpm. The effect of pH on lead (II) adsorption was determined by equilibrating adsorption mixture with dried sorbents and 10 ppm of 50 ppm stock lead concentration at a range of pH 1–7. The effect of 20% iodine/bromine pretreated sorbent was studied by changing dose from 2·5–50 g/L. The optimum pH was then determined as 5–5·5, and adsorption studies were done at pH 5. At equilibrium, lead (II) adsorption attains its maximum removal from water, then resultant solutions were centrifuged at 4000 rpm for a while and supernatants were subjected to quantitative analysis by atomic absorption spectrophotometer. The adsorption studies were evaluated at a temperature range of 25–40 °C by applying Lagergren first order and pseudo-second-order kinetic models.

## 2.5 *Analytical methods*

Lead (II) ions concentrations were determined by using an atomic absorption spectrophotometer (Hitachi, Japan) with an air–acetylene flame. Deuterium background correction was used and the spectral slit width was 1·3 nm. About 50 ml of particular lead (II) containing solution was taken in shaking bottles and known weight of pretreated adsorbents were added to them followed by shaking on a rotary shaker with a stirring speed of 200 rpm for 24 h to attain its equilibrium. Subsequently, all solutions were filtered through Whatman filter paper No. 42 and corresponding filtrates were analysed for residual lead concentration by atomic absorption spectrophotometer (GBC, 932-AA., Australia).

## 3. Results and discussion

### 3.1 *BET surface area and pore structure parameters of bromine pretreated chitosan*

Textural characteristics of 30% bromine pretreated chitosan were determined by nitrogen ($N_2$) adsorption–desorption study at 77 K on adsorbent surface area and porosimeter (ASAP 2020, M.I). Adsorption isotherms studies were done to calculate average pore volume diameter of bromine pretreated chitosan which was found to be four times of average pore volume over BET surface area. BET surface areas and pore structure parameters of bromine pretreated chitosan sorbent are given in table 1. BET surface areas and pore volumes of both sorbents were found actually decreased by pretreatment with bromine that is due to blockage of internal porosity by bromine (in KBr form) insertion in chitosan inventive skeleton (figure 1). Further, blocked pores may become micropores and ultimately decrease specific surface area as well as total pore volume of pretreated chitosan sorbent (Gérente *et al* 2007). Average pore size was found to be increased after pretreatment of chitosan with bromine.

**Table 1.** BET surface area and pore structure parameters of bromine pretreated chitosan.

| Sl. no. | Adsorbents | BET surface area ($m^2/g$) | Total pore volume ($cm^3/g$) | Average pore diameter (nm) |
|---|---|---|---|---|
| 1. | Chitosan (pure) | 2·88 | 0·014 | 10 |
| 2. | Chitosan-Br-*A* | 0·72 | 0·002 | 14 |
| 3. | Chitosan-Br-*B* | 0·46 | 0·002 | 18 |
| 4. | Chitosan-Br-*C* | 0·41 | 0·002 | 19 |
| 5. | Chitosan-Br-*D* | 0·36 | 0·002 | 21 |

Chitosan was used as it is in the first case; while the bromine (Br) pre-treatment was done using different proportions (in weight by volume) indicated as $A = 5\%$, $B = 10\%$, $C = 20\%$ and $D = 30\%$. The surface properties of each material was measured in triplicates and the average values are presented in the table.

Generally, pure physisorption dominates sorbent's adsorptive capacity and runs parallel with its specific surface area (Atia *et al* 2003). In fact BET surface areas of bromine pretreated chitosan is rather smaller than normal activated carbon, hence, physisorption of lead is limited. Nevertheless, pretreatment of chitosan surface enhances chemisorptions over physisorption due to creation of new active sites which binds lead cations on linkages of 30% bromine pretreated sorbent.

### 3.2 *Elemental analysis of bromine pretreated chitosan*

Elemental analysis data estimates the density of active sites created in pretreated chitosan sorbent. Carbon, hydrogen and nitrogen absolute weight (wt %) were calculated by an elemental analyser (EL-2, Vario) and bromine relative weight (rwt %) were determined by X-ray fluorescence technique using fluorimeter. Pretreated chitosan were somewhat lower in composition C%, H% & N% elements than the pure chitosan and experimental values of iodine and bromine as provided in table 2.

### 3.3 *Differential thermal gravimetric analysis (DTA)*

Thermal stability of pure and bromine pretreated chitosan were done to establish upper temperature limit for adsorbents using thermal gravimetric analysis (DTA Mettler Toledo-851) as shown in figures 2 and 3. About 25 mg of pretreated adsorbent was taken for study of DTA under $N_2$ gas flow at 50 mL/min. The temperature involved in heating pretreated sorbent was at a rate of 10 °C/min from 25–100 °C (trapped for half an hour at this temperature), then heated further at the rate of 10 °C/min up to 500 °C for 24 h. The data showed two peaks/ differential thermogravimetry (DTA) curve for the weight loss rate corresponding to two desorption processes in different temperature ranges. The first DTG curve/peak is due to physically adsorbed water desorption which occurred in the temperature range of 50–100 °C. The second DTA curve exhibited a rapid weight loss at 200–225 °C reaching a maximum at 313·3 °C for chitosan, similarly at 317·4 °C and 460·3 °C for chitosan pretreated bromine. Pretreatment of bromine in chitosan alters its intrinsic inter as well as extra molecular hydrogen bonding besides provide some superfluous active sites in sorbent for lead (II) removal from water.

### 3.4 *FTIR analysis of bromine pretreated chitosan sorbent*

Fourier–transform infra red (Nicolet Magna IR 550-FTIR) technique of potassium bromide pressed pellet were used for chitosan before and after pretreatment to study structural changes besides surface chemistry as shown in figures 4 and 5. FTIR spectra were recorded in 400–4000 cm$^{-1}$ range at a resolution of 4 cm$^{-1}$ and 64 scans were accumulated which exhibits significant IR band changes
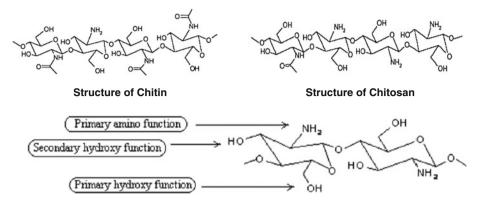
**Figure 1.** Molecular structures of chitin and chitosan indicating positions of functional groups.

**Table 2.** Element analysis of bromine pretreated chitosan sorbents.

| Sl. no. | Adsorbents | Element (wt/%) | | | Element (rwt %) |
|---|---|---|---|---|---|
| | | C | H | N | Br |
| 1. | Chitosan (pure) | 38·73 | 7·78 | 6·99 | 0 |
| 2. | Chitosan-Br-*A* | 36·20 | 7·12 | 6·59 | 4·81 |
| 3. | Chitosan-Br-*B* | 29·38 | 6·31 | 5·37 | 9·02 |
| 4. | Chitosan-Br-*C* | 23·95 | 5·99 | 4·39 | 18·37 |
| 5. | Chitosan-Br-*D* | 21·55 | 4·88 | 4·39 | 28·87 |

The chitosan purchased was used as it is in the first case; while bromine (Br) pre-treatment was done using different proportions (in weight by volume) indicated as $A = 5\%$, $B = 10\%$, $C = 20\%$ and $D = 30\%$. The surface properties of each material was measured in triplicates and the average values are presented in the table.

since each specific adsorbent's chemical bonding owes unique energy absorption pattern. Pure chitosan showed characteristics absorption band viz. at 3436 cm$^{-1}$ for O–H and/or N–H stretching, 2932 cm$^{-1}$ for C–H stretching, 1652 cm$^{-1}$ for C=O stretching in amide, 1580 cm$^{-1}$ for N–H bending in amide, 1149 cm$^{-1}$ for bridge-O-stretching and 1090 cm$^{-1}$ for C–O stretching (Cardenas and Patricia Miranda 2004).

Nonetheless, 30% bromine pretreated chitosan showed wide absorption band at 3395 cm$^{-1}$ (little shifted to lower wavenumber) due to stretched vibration of –NH$_2$ and –OH groups. Another smaller band at 1092 cm$^{-1}$ shifted to higher wavenumber which is due to C–O stretching indicates binding of iodine at linkages like –NH$_2$, –OH and C–O of chitosan skeleton. Further, significant decrease in absorption band of N–H stretching at 3100–3500 cm$^{-1}$ and N–H bending at 1400–1660 cm$^{-1}$ as pretreatment in chitosan surface modify all its skeletal bonds associated with amino linkages, indicated main adsorption site for bromine and subsequently lead too, after pretreatment. Accordingly new IR band at 2876 cm$^{-1}$ arises due to bromine in pretreated chitosan which closely relates to the phenomenon of N–H bending; C–N stretching and N–H rocking vibrations play signi-
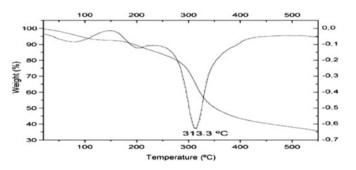


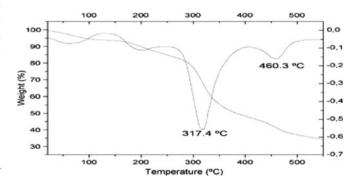**Figure 2.** DTA thermogram of pure chitosan.



**Figure 3.** DTA thermogram of 30% bromine pretreated chitosan.

ficant role in lead removal. Another major IR band changes in bromine pretreated chitosan observed at 3174 cm$^{-1}$ due to lead (II) adsorption which affects both C–H vibrations and O–H weak-broad stretching. Since lead is unlikely to be attached to a carbon of chitosan, results may, therefore, suggest that oxygen in hydroxyl group could also involve in lead adsorption which is less significant than amicable nitrogen of amino linkages.

### 3.5 *Performance of lead adsorption by bromine treated chitosan*

The key factor governing lead adsorption by 30% bromine pretreated chitosan sorbents includes pH, % bromine loading,
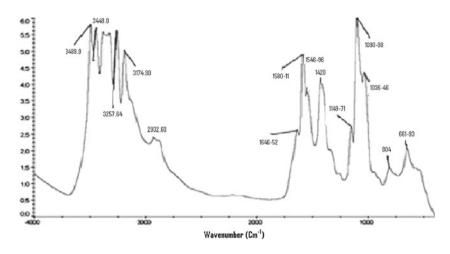
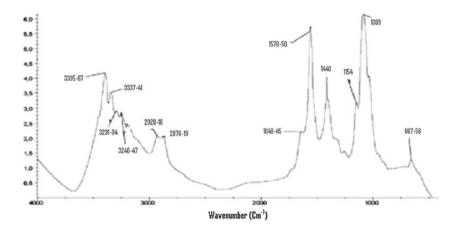**Figure 4.** FTIR spectrum of pure chitosan.



**Figure 5.** FTIR spectrum of 30% bromine pretreated chitosan.

sorbent dose, initial lead concentration, adsorption kinetics and temperature.

3.5a *Effect of pH*: The pH has a very significant effect in determining lead (II) sorption on 30% bromine pretreated chitosan from water. Since pH of adsorption solutions affects surface charges of pretreated chiotosan skeleton at specific functional groups such as hydroxyl and amino groups (Guibal 2004; Vilar *et al* 2005). Adsorption of lead (II) on 30% bromine pretreated chitosan as a function of pH is shown in figure 6 which indicated the maximum % lead removal achieved at a range of pH 5–5·5, with the efficiency of $Q_m = 0.8$ mg/g of sorbent as calculated according to following equation

$$Q_m = (C_i - C_{eq}) \, V/m, \tag{1}$$

where $V$ is volume of sample solution (ml), $m$ the mass of 30% bromine pretreated chitosan sorbent (g), $C_i$ and $C_{eq}$ are the initial and equilibrium/final concentration of lead in solution (mg/l), respectively.

3.5b *Effect of bromine load on sorbent dose*: The optimum breakthrough ratio of bromine loaded in pretreated chitosan sorbent was found to be 30% (w/v) of chitosan. Amongst pretreated sorbents used for lead removal, 30% bromine (w/v) pretreated chitosan exhibited excellent lead adsorption capacity with an optimized sorbent dose of 20 g/L as shown in figure 7.

3.5c *Effect of 30% (w/v) bromine pretreated chitosan dose*: The effect of 30% bromine pretreated chitosan on adsorption capacity of lead (II) was studied by varying 30% bromine pretreated adsorbent dose from 0·5 to 50 g/L as shown in figure 8. The maximum adsorption capacity of 0·81 mg/g were reached in sorbent's dose range of 15–20 g/L that further decreases with increasing sorbent dose as may be due to specific surface adsorption phenomenon. At low sorbent dose all the active sites of sorbent get utilized completely and effectively resulting in high lead adsorption capacity, on the contrary increasing sorbent dose while maintaining lead concentration steady escorts to surplus of adsorbent sites (Hirayama *et al* 1998; Meghat Hanafiah *et al* 2007).
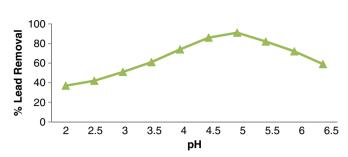
**Figure 6.** Effect of pH on lead adsorption (40 ppm lead concentration, 20 g/L sorbent and contact time, 6 h).

3.5d *Effect of initial lead concentration*: The amount of lead (II) distribution amongst sorbent and solution at equilibrium is vital in determining maximum lead adsorption capacity of adsorbent. Hence, the effect of initial lead (II) concentration on sorption capacity of 30% bromine pretreated chitosan was investigated at an optimized pH at 5·0 as shown in figure 9. The lead (II) adsorption increased much quickly with increasing initial metal concentration from 10–50 mg/L. A higher initial lead concentration provides driving force to overcome all mass transfer resistances between solution and sorbent surface, consequently lead (II) adsorption capacity increased. Besides, the number of collisions between lead (II)
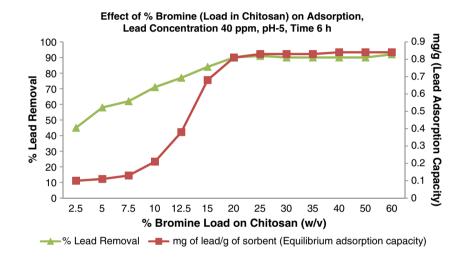


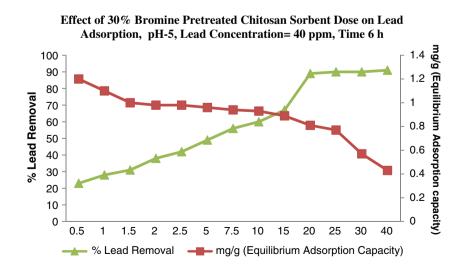**Figure 7.** Effect of % bromine (loaded in chitosan) on adsorption.



**Figure 8.** Effect of 30% (w/v) bromine pretreated chitosan dose.

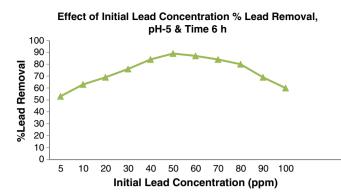**Effect of Initial Lead Concentration % Lead Removal, pH-5 & Time 6 h**



**Figure 9.** Effect of initial lead concentration on adsorption of lead.

ions and bromine pretreated sorbent increases parallelly with initial lead concentration (Jin and Bai 2002; Aksu and Tezer 2005; Trimukhe and Varma 2008). Moreover, lead (II) sorption rate decreases with increasing initial concentration from 50–100 mg/L which is due to the saturation of active sorption sites available for lead cations on bromine pretreated chitosan's surface.

3.5e  *Effect of temperature*: The temperature effect studies for lead removal were done at varied ranges from 20–50 °C with bromine pretreated chitosan. Adsorption experimental data exhibited obviously reduced capacity i.e. % lead adsorption decreases as temperature increases. At 20 °C initial value $\eta$ of lead breakthrough reached 0·35, but it increased rapidly with time and there is a slow increase of $\eta$ at 50 °C. The increase in lead removal efficiency is observed at elevated temperature, since lead adsorption is a chemical/chemisorption phenomenon and requires activation energy, so it proceeds in limiting rate which further enhances with rise in temperature (Schmuhl *et al* 2001).

### 3.6  *Possible lead removal mechanism*

The results of analysis data support chemical interaction of KBr with chitosan to produce $Br_2$ and some unreacted bromides exist in adsorption media. Amine group of chitosan via N-atom reacts with $Br_2$ as well as with some unreacted bromides and subsequently lead cations react with these active sites (such as $Br_2$ and some un-reacted bromides) yielding lead adsorption (Zhang *et al* 2009). The relatively higher lead removal efficiency by addition of sulfuric acid in pretreatment process of adsorbents was also observed. Generally, bromine pretreated chitosan demonstrated higher lead capture efficiency than that of sulfuric acid pretreated chitosan. Among all the sorbents used, 30% bromine loads on chitosan shows the best lead removal capacity of 85–90% in 6 h. The synthetic optimization of 30% bromine loading on pretreated chitosan and desorption/regeneration of sorbent is to be further evaluated for getting a type of promising and

low-cost adsorption technique. The following chemical interactions are proposed to account for chemisorptions of lead (II) on 30% bromine pretreated chitosan surface as:

$$R\text{-}NH_2 + H^+ \leftrightarrow R\text{-}NH_3^+, \tag{2}$$

$$R\text{-}NH_3^+ + Br^- \rightarrow R\text{-}NH_3^+ \cdot Br^-, $$

$$R\text{-}NH_3^+ \cdot Br^- + Pb^{2+} \rightarrow R\text{-}NH_2^+ Br^- (Pb^{2+})_{1/2}, \tag{3}$$

$$R\text{-}NH_3^+ Br^- + Pb^{2+} \rightarrow R\text{-}NH_2 Pb^{2+} + H^+ Br^-, \tag{4}$$

where $R$ represents organic components except -$NH_2$ in chitosan. At lower/acidic pH, more amino groups of chitosan are protonated besides bind bromide resulting in higher capture of lead cations (Dai *et al* 2010). However, at basic pH, $OH^-$ ions may be adsorbed on active surface of chitosan through inter-hydrogen bonding and contributes to less capture of lead cations as

$$R\text{-}NH_2 + OH^- \rightarrow R\text{-}NH_2 \cdots\cdots OH^-. \tag{5}$$

Further, the sorption dynamic followed pseudo-second order equation, as well adsorption performance cannot be simply explained through an electrostatic interaction, but complexation, ion exchange factors are also significant (Jin and Bai 2002). Rather lead adsorption process was complex, both boundary of liquid film (surface adsorption phenomen) and intra-particle diffusion contributed to rate-determining step. Thermodynamic study and kinetic analysis reveals spontaneous and rapid chemisorptions process with an increased randomness of lead (II) sorption onto 30% bromide pretreated chitosan, which showed possibility of a practicable operation in packed columns with pretreated sorbent.

### 3.7  *Lead (II) adsorption efficiency and capacity of 30% bromine pretreated chitosan*

The adsorption kinetic study is a vital physiochemical parameter to evaluate the potential and efficiency of sorbent. Hence, adsorption kinetic study was performed with different lead concentrations for sorption onto modified chitosan sorbent at an optimum pH of 5 and stirring speed of 200 rpm. At initial lead concentrations of 10, 20, 30, 40, 50 and 60 mg/L (ppm), amount of metal adsorbed were 8·5 mg/L, 17·1 mg/L, 26·1 mg/L, 35·4 mg/L, 45·1 mg/L and 54·1 mg/L, respectively. The lead (II) adsorption onto bromine pretreated chitosan is plotted as a function of time at various initial lead concentrations. Figure 10 showed increased lead (II) concentration so does the time taken before equilibrium is attained. At lower lead concentrations, lesser adsorption is found than at higher concentrations. The adsorption kinetic results showed that sorption is a rapid process, and the equilibrium is
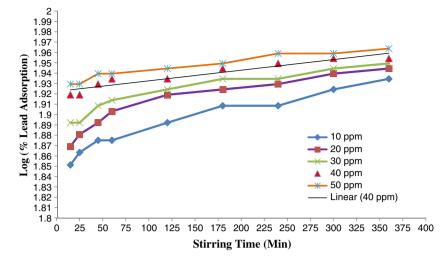
**Figure 10.** Adsorption kinetics of lead (II) on 30% bromine pretreated chitosan at different initial concentrations [$Pb^+$] of 10, 20, 30, 40 and 50 mg/L (ppm), sorbent dose, 20 g/L, pH 5, stirring speed = 200 rpm and temperature = 27 °C.
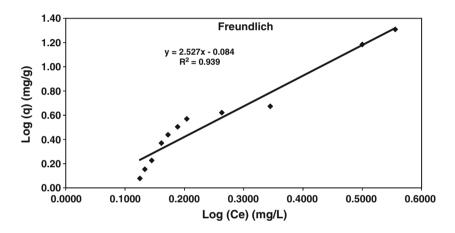


**Figure 11.** Freundlich isotherm for lead adsorption by 30% bromine iodine pretreated chitosan.

reached at 15 to 20 min for all lead (II) concentrations. These results clearly indicate that 30% bromine pretreated chitosan can potentially remove lead cations from aqueous solution. The amount of lead (II) adsorbed on sorbent is explained on the basis of ionic radii lead cation 1·21 Å and its less hydration energy. The distribution coefficient is the ratio of lead between 30% bromine pretreated chitosan and aqueous phase which is observed to be more than 1·0 indicated high sorption efficiency. Further this distribution coefficient is dependent on the initial metal ion concentrations and enhances parallely.

### 3.8 *Adsorption isotherms study*

The lead adsorption onto 30% bromine pretreated chitosan at room temperature has been studied with lead sample concentration which varied from 5–50 ppm at pH = 5 for 6 h of contact time. The adsorption experimental data matched in accordance with Langmuir and Freundlich models which are widely used to describe the equilibrium of lead adsorption (Asandei *et al* 2009). Freundlich adsorption model is appropriate to describe lead adsorption onto 30% bromine pretreated chitosan and linear Freundlich isotherm is presented in figure 11.

### 3.9 *Desorption/regeneration study*

Chemisorptions of lead onto 30% bromine pretreated chitosan were confirmed by FTIR and isothermal study and found to be low in acidic medium, due to protonation of all amino linkages of chitosan. Low acidic pH of adsorption medium induces an electrostatic repulsion to lead cations by competent $H^+$ for sorption onto active sites of chitosan (Wong *et al* 2003; Asandei *et al* 2009). However, this protonation of amino groups diminished as pH of sorption medium increased due to less competition with $H^+$ and consequently

uptake of lead were increased at pH range 5–5·5. Further, adsorbate surface is sufficiently negatively charged at pH 5 which strongly attracts lead by electrostatic force which is in accordance with lead speciation diagram (Lead Speciation Diagram 2009). Over this pH domain, lead occurs predominantly as divalent free cation, which gets involved in chemical processes during sorption onto sorbent.

Besides, desorption study was performed over whole pH range and maximum desorption of lead by bromine pretreated sorbent were observed at pH 3 due to main electrostatic binding of lead to amino groups of chitosan (Qin *et al* 2006). Further, lead removal efficiency was lower at pH 3 than at pH 5 presumably due to instability of chitosan at such extremely low pH. However, at basic conditions (pH > 7) chemisorptions of lead decreases, since chitosan surface undergoes deprotonation results in less sorption. The lead desorption efficiency experiments were done with 0·1 M $HNO_3$ solutions. About 1 g of bromine pretreated adsorbent were shaken with 50 ml of 40 ppm lead sample concentration into 100 mL of a $HNO_3$ solution on thermostatic shaking machine and the desorption was allowed for a time period up to 24 h. The desorption efficiency (DE) was determined by following equation:

$$DE = (C/q \times V/m) \times 100\%, \qquad (6)$$

where, $C$ (mg/L) is lead (II) sample concentration taken for desorption study, $V$ (litre) the volume of desorption solution, $q$ (mg/g) the amount of lead (II) ions adsorbed on the bromine pretreated chitosan before desorption experiment and $m$ ($g$) is the mass of the bromine pretreated chitosan used in the desorption experiments. Regeneration of 30% bromine pretreated chiotsan was done after lead adsorption at different initial pH values. The regenerated/desorbed sorbent were reused and comparative lead adsorption study of reused 30% bromine pretreated chitosan were done in four cycles and found overall 10–15% decrease in lead (II) removal efficiency as mentioned in table 3.

## 4. Conclusions

Bromine pretreated chitosan was found to be promising adsorbent for lead (II) removal from water. The major experimental observations are summarized below:

(I) 30% Bromine pretreated chitosan showed 85–90% lead (II) removal capacity at ambient conditions.

(II) The regeneration ability of 30% bromine pretreated chitosan was tested in four sequential cycles which exhibited an overall 10–15% loss of lead adsorption capacity.

(III) Lead adsorption capacity of 30% bromine pretreated chitosan increases from acid to neutral medium and maximum at pH = 5 to 5·5 in contact time of 6 h.

(IV) Maximum lead (II) removal efficiency of 85–90% was achieved at an optimum dose of 20 g/L of 30% bromine pretreated chitosan, indicating benign and cost-effective adsorption technique.

(V) FTIR showed binding of lead (II) onto nitrogen of amine and -OH groups of 30% bromine pretreated chitosan also contributes through a nonspecific electrostatic interaction although less significant compared to other active sites of sorbent.

(VI) Langmuir and Freundlich isotherm models applied for mathematical adsorption data were found to be very well fitted to Freundlich with a maximum adsorption capacity of 1·755 g lead per kg of 30% bromine pretreated chitosan.

**Table 3.** Comparative lead adsorption by reused 30% bromine pretreated chitosan.

| I Adsorption cycle | | II Adsorption cycle | | III Adsorption cycle | | IV Adsorption cycle | |
|---|---|---|---|---|---|---|---|
| pH | % Lead (II) removal | pH | % Lead (II) removal | pH | % Lead (II) removal | pH | % Lead (II) removal |
| 2·0 | 28 | 2·0 | 23 | 2·0 | 19 | 2·0 | 16 |
| 2·5 | 34 | 2·5 | 29 | 2·5 | 26 | 2·5 | 23 |
| 3·0 | 51 | 3·0 | 46 | 3·0 | 44 | 3·0 | 43 |
| 3·5 | 61 | 3·5 | 53 | 3·5 | 49 | 3·5 | 48 |
| 4·0 | 74 | 4·0 | 65 | 4·0 | 52 | 4·0 | 54 |
| 4·5 | 86 | 4·5 | 74 | 4·5 | 69 | 4·5 | 59 |
| 5·0 | 91 | 5·0 | 83 | 5·0 | 76 | 5·0 | 68 |
| 5·5 | 82 | 5·5 | 75 | 5·5 | 71 | 5·5 | 62 |
| 6·0 | 72 | 6·0 | 70 | 6·0 | 66 | 6·0 | 60 |
| 6·5 | 59 | 6·5 | 56 | 6·5 | 51 | 6·5 | 48 |
| 7·0 | 46 | 7·0 | 41 | 7·0 | 38 | 7·0 | 34 |
| 7·5 | 38 | 7·5 | 33 | 7·5 | 30 | 7·5 | 28 |
| 8·0 | 33 | 8·0 | 30 | 8·0 | 27 | 8·0 | 24 |
| 8·5 | 29 | 8·5 | 24 | 8·5 | 22 | 8·5 | 19 |
| 9·0 | 23 | 9·0 | 21 | 9·0 | 18 | 9·0 | 16 |

## Acknowledgements

## References

Abo-Farha S, Abdela-A A Y, Ashour A and Garamon S 2009 *J. Hazard. Mater.* **169** 190

Aksu Z and Tezer S 2005 *Process Biochem.* **40** 1347

Agency for Toxic Substances and Disease Registry (ATSDR) 2007 *Toxicological profile for Lead* (Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service)

Arrascue M L, Garcia H M, Horna O and Guibal E 2003 *Hydrometallurgy* **71** 191

Asandei D, Bulgariu L and Bobu E 2009 *Cellulose Chem. Technol.* **43** 211

Atia A A, Donia A M, Abou-El-Enein S A and Yousif A M 2003 *Sep. Purif. Technol.* **33** 295

Babel S and Kurniavan T A 2003 *J. Hazard. Mater.* **B97** 219

Badawy N A, El-Bayaa A A, Abdel-Aal A Y and Garamon S E 2009 *J. Hazard. Mater.* **166** 1266

Bailey S E, Olin T J, Bricka M R and Adrian D D 1999 *Water Res.* **33** 2469

Brunton L L, Goodman L S, Blumenthal D, Buxton I and Parker K L 2007 *Principles of toxicology*, in *Goodman and Gilman's manual of pharmacology and therapeutics*, 1st ed. (Nagpur, McGraw-Hill Professional) ISBN 0071443436, pp 1131

Bulgariu L, Bulgariu D, Malutan T and Macoveanu M 2009a *Adsorption Sci. Technol.* **27** 435

Bulgariu L, Robu B and Macoveanu M 2009b *Rev. Chim.* **60** 1025

Cardenas G and Patricia Miranda S 2004 *J. Chilean Chem. Soci.* **49** 291

Cochrane E L, Lu S, Gibb S W and Villaescusa I 2006 *J. Hazard. Mater.* **B137** 198

Dai J, Yan H, Yang H and Cheng R 2010 *Chem. Eng. J.* **165** 240

Das Nilanjana, Karthika P, Vimala R and Vinodini V 2008 *Nat. Prod. Radiance* **7** 133

Dzul Erosa M S, Saucedo Medina T I, Navarro Mendoza R, Avila Rodriguez M and Guibal E 2001 *Hydrometallurgy* **61** 157

Fujiwara K, Ramesh A, Maki T, Hasegawa H and Ueda K 2007 *J. Hazad. Mater.* **146** 39

Gérente C, Lee V K C, Le Cloirec P and McKay G 2007 *Crit. Rev. Environ. Sci. Technol.* **37** 41

Gogate P R and Pandit A B 2004 *Adv. Environ. Res.* **8** 553

Goyer R A 1993 *Environ. Health Perspect.* **100** 177

Guibal E 2004 *Sep. Purif. Technol.* **38** 43

Guo X, Zhang S and Shan X 2008 *J. Hazard. Mater.* **151** 134

Hirayama M, Caseri W R and Super U W 1998 *J. Colloid Interface Sci.* **20** 167

Ho Y S, Wase D A J and Forster C F 1999 *Water SA* **22** 219

Horsfall M and Spiff A L 2005 *Afr. J. Biotechnol.* **4** 191

Hu H, Shih R, Rothenberg S and Schwartz B S 2007 *Environ. Health Perspect.* **115** 455

Igwe J C and Abia A A 2006 *Afr. J. Biotechnol.* **5** 1167

Jin L and Bai R B 2002 *Langmuir* **18** 9765

Karri S K, Saper R B and Kales S N 2008 *Current Drug Safety* **3** 54

Kuribayashi H, Watanabe M, Sbibuya M and Suzuki K 1988 *Selective separation process of radionuclide in liquid waste* (Oak Ridge, USA: Pmt. DOE Model) **1** 169

Lead speciation diagram calculated using EpH-web http://www.crct.pbymtl.ca/ephweb.php, accessed at 15.01.2009

Londrigan P J, Silbergeld E K and Froisnes J R 1990 *Am. J. Public Health* **80** 907

Makkuni A, Bachas L G and Varma R S 2005 *Clean Technol. Environ. Policy* **7** 87

Meghat Hanafiah M A K, Yahya M Z A, Zakaria H and Ibrahim S C 2007 *J. Appl. Sci.* **7** 489

Milot C, Guibal E, Roussy J and Clorec P L 1998 *Miner. Process. Extract. Metall. Rev.* **19** 293

Nadeem M, Mahmood A, Shahid S A, Shah S S, Khalid A M and McKay G 2006 *J. Hazard. Mater.* **138** 604

Nan Li, Bai R B and Liu C K 2005 *Langmuir* **21** 11780

Ng J C Y, Cheung W H and McKay G 2003 *Chemosphere* **52** 1021

Pearce J M 2007 *Eur. Neurol.* **57** 118

Pokras M A and Kneeland M R 2008 *Eco-Health* **5** 379

Quin Y, Shi B and Liu G 2008 *Indian J. Chem. Technol.* **3** 464

Qin F, Wen B, Shan Y, Xie N, Liu T, Zhang S Z and Khan S U 2006 *Environ. Pollution* **144** 669

Rusten B, Kolkinn O and Ødegaard H 1997 *Water Sci. Technol.* **35** 71

Sankararamakrishnan N, Sharma A K and Sanghi R 2007 *J. Hazard. Mater.* **148** 353

Schmuhl R, Krieg H M and Keizer K 2001 *Water SA* **27** 1

Trimukhe K D and Varma A J 2008 *Carbohydr. Polym.* **71** 698

Ucun H, Bayhan Y K, Kaya Y, Cakici A and Algur O F 2003 *Desalination* **154** 233

Vieira R S and Beppu M M 2006 *Colloids Surf.* **A279** 196

Vilar V J P, Botelho C M S and Boaventura R A R 2005 *Process Biochem.* **40** 3267

Wang A Q 2008 *Chitin chemistry*, 1st ed. (Beijing, Science Press) pp 169–200 & 557

Wang Jing-Song, Bao Zheng-Lei, Chen Si-Guang and Yang Jin-Hui 2011 *J. Eng. Gas Turbines Power* **133** 3

Wong Y C, Szeto Y S, Cheung W H and Mckay G 2003 *Langmuir* **19** 7888

Zhang A, Xiang J, Sun L, Hu S, Li P, Shi J, Fu P and Su S 2009 *Ind. Eng. Chem. Res.* **48** 4980