

Synthesis and characterization of graphite doped chitosan composite for batch adsorption of lead (II) ions from aqueous solution

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ABSTRACT

The adsorption of poisonous lead (II) from aqueous solution using graphite doped chitosan composite as an adsorbent has been carried out. The characterizations of graphite doped chitosan composite were studied by using instrumental techniques like X-ray diffraction, Fourier Transform Infrared Spectroscopy and Scanning Electron Microscopy. The XRD study showed the crystalline nature of synthesized graphite doped chitosan composite with sharp and symmetric peaks. SEM morphology showed wide range of porosity that could achieve high lead (II) sorption. FTIR investigation evidenced that the presence of C=O and –OH functionalities participated in lead (II) adsorption from aqueous solution. The influence of pH, contact time, dose of adsorbent and initial metal ion concentration on removal of lead (II) was investigated. The adsorption efficiency was found to be pH dependent and the maximum 98% lead (II) removal observed at optimum pH 6. Results showed that the maximum adsorbent capacity was at dosage of 1g/L and equilibrium time achieved at 120 min. Equilibrium adsorption experiments were studied at room temperature and data obtained fitted to Langmuir and Freundlich adsorption isotherm. Langmuir model had higher R² values of 0.943 with sorption capacity of 6.711 mg of adsorbate/g of adsorbent which fitted the equilibrium adsorption process more than the Freundlich model. The adsorption kinetics was analyzed using pseudo first order, pseudo second order and intraparticle diffusion models. Experimental data better fitted with pseudo second order kinetics model. The results illustrated that graphite doped chitosan composite has the potential to remove lead (II) ions from aqueous solution. Copyright © 2015 VBRI Press.

Keywords: Graphite doped chitosan composite; lead (II); adsorption; isotherm; kinetics.



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Introduction

The presence and high concentration of heavy metal ions in various water resources can be adverse to the environment and public health. Among all the heavy metal ions, special attention has been given to Pb (II) ions contamination in water. Lead metal is listed second on the ATSDR (Agency of Toxic Substances and Disease Registry) list of top 20 hazardous substances. Pb (II) ions can be found in effluents from battery recycling plants, lead mining and electronic assembly plants. Lead elucidates destructive effects on human nervous system, blood circulation system, kidneys, reproductive system [1] and highly toxic and carcinogenic even at low concentration [2]. According to WHO, the maximum permissible limit (MPL) of lead in drinking water is 50 ppb in 1995, which is decreased to 10 ppb in 2010. The wide usage of Pb (II) in various industries has triggered the necessities of developing an efficient method to remove this heavy metal ion from wastewaters. Many conventional methods are known for lead removal from water namely chemical precipitation [3] membrane separation, ion exchange [4, 5] coagulation, reverse osmosis, evaporation [6] and adsorption. The adsorption process is found to be effective and economic for wide variety of water pollutant sorption [7]. Recently, adsorptions using biomaterials has been considered as one of the most favorable option in treating wastewater as they are adequate, biodegradable, ecofriendly, non-toxic and have the capability to physically or chemically interact with a variety of molecules [8]. A very fruitful natural material that can be obtained in large amounts and cheap is chitosan, a nitrogenous polysaccharide. Chitosan is produced by the N-deacetylation of chitin using an alkaline solution. It is a heterogeneous polymer of cationic nature, which is composed of 2-amino-2-deoxy-D-glucopyranose and residual 2-acetamido-2-deoxy-D-glucopyranose [9]. Chitin and chitosan are of commercial importance because of their high nitrogen content (6.89%) and their excellent properties such as biocompatibility, biodegradability, non-toxicity and adsorptive abilities [10, 11]. Chitosan shows high affinity for metal ions due to the amine ($-NH_2$) and hydroxyl ($-OH$) groups. These groups function as the adsorption sites for heavy metal ions [11, 12].

However, chitosan shows lower stability due to its hydrophilic nature and sensitivity to pH. It is soluble in most organic acids (acetic acid, formic acid, lactic acid) and mineral acids (dilute hydrochloric acid) but is moderately stable in sulfuric acid solution [13, 14]. In addition, it is non-porous and has a low specific surface area [15]. Several attempts of physical and chemical modification of chitosan structure were carried out in order to improve its chemical and mechanical stability. Chemical modification is the application of chemical treatment on chitosan, which improves the mechanical strength and enhances the adsorption capacities. A variety of processes for chemical modification such as crosslinking and grafting of functional groups can be used. However, chemical modifications are relatively complex and expensive procedure. On the other hand, physical modification refers to the process of coating or spreading chitosan on physical supports [16-20]. This results in the expansion of the polymer network and consequently enables large size

molecules to diffuse into the polymer network openings where binding sites become more accessible [21].

Various chitosan based adsorbents such as magnetic chitosan/graphene oxide material [22], chitosan clay composite [23], Chitosan/sisal/banana fibre hybrid [24] chitosan-tripolyphosphate [25] for lead (II) ion removal has been reported. Chitosan nylon 6 composite for Cu(II) and Cd(II) removal [26], chitosan immobilized on silica for removal of Zn(II), Cu(II), Cd(II), Pb(II), Fe(III) V(V), Mo(VI) has been investigated [27]. Support materials for chitosan that have been previously studied are sand for Cu(II) and Pb(II) removal [28], Chitosan-magnetite composite beads for Pb(II) and Ni(II) removal [29] Chitosan-bentonite for Cu(II), Ni(II) and Pb(II) removal [30-32]. Modified magnetic chitosan adsorbent for Hg (II) removal [33], Novel polyaluminium chloride-chitosan composite coagulant for natural organic matter (NOM) removal from synthetic and natural water has been studied [34].

To the best of our knowledge, there is no literature reported on the removal of lead (II) ions from water using graphite doped chitosan composite (GDCC). In fact, the ability of GDCC to adsorb other heavy metal ions was also not reported. This gave way for more adsorption studies to be conducted using GDCC. The present study aims to explore the adsorption of Pb (II) ions onto GDCC in aqueous solution. The influence of initial pH of the heavy metal ions solution, agitation period, adsorbent dosage and initial concentration of heavy metal ions solution on the adsorption of Pb (II) ions were studied. The Langmuir and Freundlich isotherms were used to evaluate the equilibrium adsorption data. The adsorption rates were also determined based on the pseudo first order, Pseudo second order kinetic and intraparticle diffusion models.

Experimental

Materials

All chemicals used were of analytical reagent grade; Lead (II) nitrate of (99.9% Merck, India) was used for preparation of lead (II) ion solution. Stock solution of 1000 mg/L of lead (II) was prepared by dissolving lead nitrate and working standards of required mg/L were prepared from stock lead nitrate solution by successive dilution with double distilled water. Chitosan used as an adsorbent was purchased from Sisco Research Laboratories, Mumbai (India) and powdered graphite of particle size 50 mm, bulk density of 20-30 g/100 ml was obtained from Loba Chemie, Mumbai (India). Acetic acid (99.5% Merck, India) and ammonium hydroxide (30% NH_3 ; Merck, India) used without further purification. The pH of the medium was adjusted using nitric acid (70% Fisher scientific, India) and sodium hydroxide (97% Merck, India).

Instrumentations

Fourier Transform Infrared (FTIR) study was performed using Perkin Elmer spectrometer one FTIR model. The samples were diluted in 5 % KBr and cast in disks for analysis. FTIR spectra were recorded in the range of 450-4000 cm^{-1} . X-ray diffraction (XRD) measurements were taken with Rigaku MiniFlex2 Goniometer using Cu $K\alpha$ (30 kV, 15

mA) radiation. The surface morphology of the composite was studied by using scanning electron microscope (SEM) at an accelerating voltage of 15kV. A sample was mounted on carbon tapes and supported on metallic disc. SEM photographs were taken at different magnification in the range of 20X to 5000X using JSM 6380 A. The Brunauer-Emmett-Teller (BET) surface area was measured using Micromeritics ASAP 2020 V3.04 H analyser. Carbon/hydrogen/oxygen/nitrogen/sulphur (C/H/O/N/S) contents were used as a means of investigating the residues left behind in the preparation of GDCC. The elemental analysis of the sample (3 mg) was carried out using an elemental analyzer model Vario El Cube at 230 V. For each analysis, the standard sample sulfanilic acid was first analyzed for checking the experimental error within $\pm 1\%$.

Analysis of lead (II) ions

The concentration of residual lead (II) ions was determined by using Atomic absorption spectrophotometer (SensAA GBC scientific equipment) with lead hollow cathode lamps and air acetylene mixture as an oxidant at wavelength of 283.3 nm. Deuterium background correction was used and spectral slit width was 1.3 nm. A digital pH meter (Hanna instrument) was used for pH measurement. pH meter was standardized using buffer solution of pH 4 and pH 9 (Fisher Scientific, India). Rotary Shaker (Remi Make, India) at 200 rpm was used for agitating the samples during batch adsorption experiments.

Synthesis of graphite doped chitosan composite (GDCC)

GDCC has been synthesized by impregnation methodology. Chitosan dissolved in 3% acetic acid and heated at 40-50°C to obtain gel. Powdered graphite was added to chitosan gel in (1:1 w/w) and mixture was stirred magnetically at room temperature for 5-6 hours. This mixture was dropped in 50% aqueous ammonia to obtain beads. Finally it was filtered, washed several times with distilled water and dried in oven at 70-80 °C. The adsorbent was grounded and stored into the sorbent bottle for further adsorption study.

Batch adsorption studies

Batch adsorption experiments were carried out to examine time dependent sorption behavior, pH of solution, dose of adsorbent and initial concentration of adsorbate on the adsorption performance. All adsorption experiments were carried out at room temperature (27°C) in 250 ml Erlenmeyer flasks containing 100 ml of test solution agitated on rotary shaker at 200 rpm.

Adsorption isotherm studies were carried out by mixing 0.1 g of GDCC with 100 ml solution of varying initial concentration of lead (II) from 35 to 95 mg/L in 250 ml conical flasks at optimum pH 6. pH adjustments were done using 0.1 N HNO₃ or 0.1 N NaOH. After shaking the flasks at 200 rpm at 27 °C for 120 minutes to reach adsorption equilibrium, the mixture was filtered through Whatman filter paper-41 and analyzed for residual lead (II) ions concentration by atomic absorption spectrophotometer (AAS).

Adsorption kinetic experiments were carried out by batch adsorption method at 27 °C on rotary shaker at 200 rpm using 250 ml Erlenmeyer flask containing 100 ml of

solution with 35 mg/L lead (II) and 0.1 g of adsorbent. Samples were agitated and withdrawn at interval of 10 to 150 min to determine metal ion concentration by AAS. All batch adsorption experiments were carried out in duplicate and average values are reported.

The percentage removal of lead (II) was calculated using equation (1)

$$\% \text{ removal} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

Adsorption capacities were calculated using equation (2) and (3) respectively.

$$q_e = \frac{C_i - C_f}{m} \times V \quad (2)$$

$$q_t = \frac{C_i - C_t}{m} \times V \quad (3)$$

where, q_e and q_t were the amount of metal ion adsorbed at equilibrium and at time t respectively in (mg/g); C_i and C_f were the initial and final lead (II) ion concentration in (mg/L). C_t was the residual metal ion concentration at time t in (mg/L); V denoted volume of solution (L) and m for mass of adsorbent (g).

Results and discussion

Physical and chemical characterization of adsorbent

The scanning electron micrographic examination of GDCC (**Fig. 1**) shows a porous morphology with pores of different sizes and shapes. The image also reveals flaky, smooth, shiny appearance with some voids or cavities, suggested that GDCC exhibits a good surface area required for adsorption of metal ions.

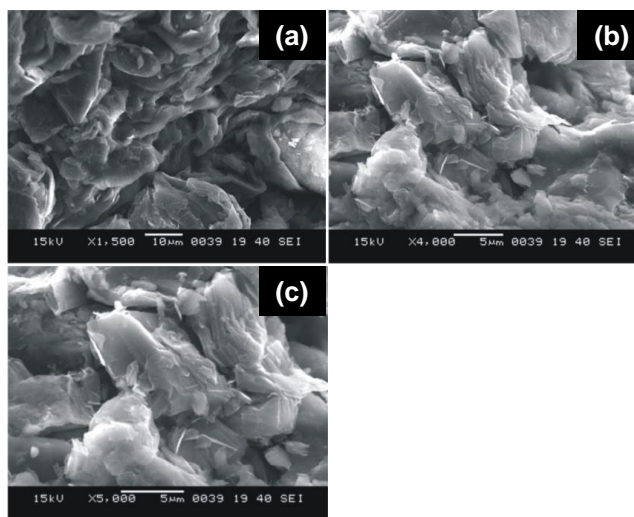


Fig. 1. SEM images of GDCC at (a) 1500 X (b) 4000 X (c) 5000 X.

XRD analysis

XRD pattern of pure chitosan, pure graphite and GDCC is illustrated in (**Fig. 2a, b, c**) respectively. X ray diffraction pattern of chitosan exhibited broad diffraction peak at $2\theta = 20^\circ$ with d - spacing of 4.2 Å is characteristics of semi

crystalline chitosan [35]. A very small peak appeared at $2\theta = 20.74^\circ$ is also reported in chitosan. The peak appeared at 2θ value 20.2° which matches well with the literature value [36]. The peaks are broadened due to the amorphous nature of chitosan polymer. There is no impurity peaks observed in the XRD of pure chitosan. The diffraction peak appeared at $2\theta = 26.5^\circ$ which indicated d-spacing of about 3.35 \AA is a characteristic of graphite peak [37]. The XRD pattern of the graphite doped chitosan indicated the formation of single phase composite and the peaks were obtained at 2θ value 26.5 . The broad peak at around $2\theta = 20^\circ$ which was due to the chitosan decreased in intensity after doping with graphite which confirms that graphite is doped on the surface of chitosan. A predominant peak of graphite along with small peak of chitosan appeared in GDCC showed that the incorporation of graphite in matrix was successful and effectively provided a support to the chitosan.

Table 1. Characteristics of graphite doped chitosan composite.

Properties	GDCC
Particle size	175 μm – 245 μm
BET surface area	3.890 m^2/g
Proximate analysis (wt% dry basis)	
Moisture	7.20%
Volatile matter	55%
Ash	4%
Fixed Carbon	33.80%
Ultimate analysis (wt%, ash and moisture free)	
Carbon	57.69%
Hydrogen	3.78%
Nitrogen	4.03%
Sulphur	0.23%
Oxygen	34.27%

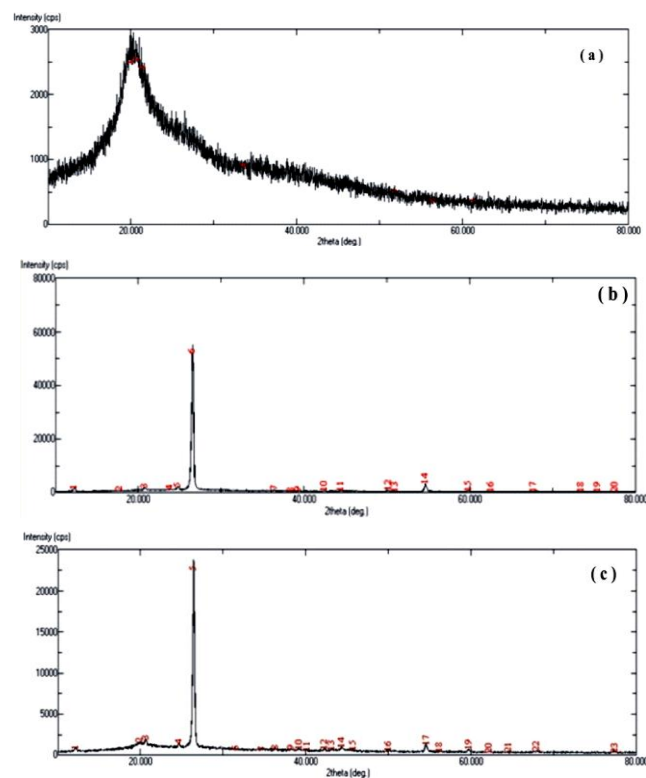


Fig. 2. Powder XRD pattern of (a) chitosan (b) graphite (c) graphite doped chitosan composite.

FTIR analysis

FTIR spectra of chitosan powder, graphite powder and chitosan/graphite blend before and after adsorptions of lead (II) are presented in (Fig. 3). Pure chitosan showed characteristic absorption band namely 3695 cm^{-1} and 3073 cm^{-1} for stretching vibration of $-\text{OH}$ group. Absorption band at 2876 cm^{-1} in range of $2800\text{--}2950 \text{ cm}^{-1}$ are assigned to the hydroxyl groups present in chitosan [38]. 1667 cm^{-1} for carbonyl $\text{C}=\text{O}$ stretch in amide and 1152 cm^{-1} for bridge-O-stretching [39]. Bending vibrations of methylene and methyl groups were visible at 1375 cm^{-1} and 1434 cm^{-1} respectively. The absorption peak at 1262 cm^{-1} attributed for C-O-H stretching. The broad peak at 1077 cm^{-1} ascribed to C-O stretching vibration of the ring C-O-H, C-O-C and CH_2OH [40, 41].

The absorption peak of chitosan at 1667 cm^{-1} for $\text{C}=\text{O}$ stretch in amide was disappeared when doped with graphite. Similarly absorption band of chitosan at 1375 cm^{-1} for C-H stretch was remarkably shifted to lower wave number of 1367 cm^{-1} . This is due to the fact that when two or more polymers are mixed, changes in characteristic spectra peaks occur due to the reflection of the physical blends and chemical interactions [42]. These observations indicate the existence of good miscibility and doping between chitosan and graphite. The spectral analysis of GDCC before and after adsorption of lead (II) showed that the peaks either decrease in intensity or disappear might involve in metals adsorption [43]. The FTIR spectrum of lead-loaded GDCC shows some shift in wavenumbers. For instance, the wavenumber at 2872 cm^{-1} little shifted to 2875 cm^{-1} after lead adsorption, suggesting the participation of $-\text{OH}$ in forming complexes with lead (II) ions [44]. The weak broad band at 2681 cm^{-1} shifted to 2662 cm^{-1} . Another absorption band change was observed at wavenumber of 1081 cm^{-1} to 1077 cm^{-1} due to C-O stretching vibrations suggested the involvement of the C-O group in binding of lead (II) on GDCC [45-47]. The shift in absorption bands showed that there was an adsorption of lead (II) on GDCC and $-\text{OH}$ and $\text{C}=\text{O}$ groups were concerned with adsorption performance.

Effects of contact time on adsorption

The impact of contact time on lead (II) removal by GDCC was illustrated in (Fig. 4). Experimental studies were carried out at optimum condition of pH, dose of adsorbent at 200 rpm with initial metal ion concentration of 35 mg/L at 27°C . It was observed that metal ion removal increased with contact time and was maximum at 120 minutes with 91% removal efficiency of lead (II). After 120 minutes, lead (II) removal was not substantial as equilibrium adsorption established. It is clearly stated that rate of adsorption is higher at the beginning due to availability of large amount of active binding sites on the adsorbent. As these sites are worn-out, uptake rate of metal is controlled as the adsorbate is transported from the exterior to the interior sites of the adsorbent surface [48]. The lead adsorption on GDCC was due to the presence of functional groups providing active binding sites for the metal ion. According to these results in this study equilibrium time was set to be 120 min.



Fig. 3. FTIR spectrum of the (a) graphite, (b) chitosan, (c) graphite doped chitosan composite before lead (II) adsorption and (d) graphite doped chitosan composite after lead (II) adsorption.

Effect of adsorbent doses on adsorption

Effects of dose of adsorbent on lead (II) sorption were shown in (Fig. 5). Experimental studies were carried out by varying the dose of adsorbent from 0.2 to 1.2g using 35 mg/L of lead (II) ion concentration at optimum pH 6 using contact time 120 min. Results shown that the adsorption of

lead (II) ions increased with increased dose of adsorbent and reached the maximum at dosage of 1 g of adsorbent. After this dose no further adsorption efficiency was remarkable. It can be concluded that as the adsorbent dosage increases, the surface area and consequently more active binding sites for the metal ion to get adsorb, increases [49, 50]. With further addition of dose of adsorbent the adsorption efficiency remains constant due to attainment of equilibrium.

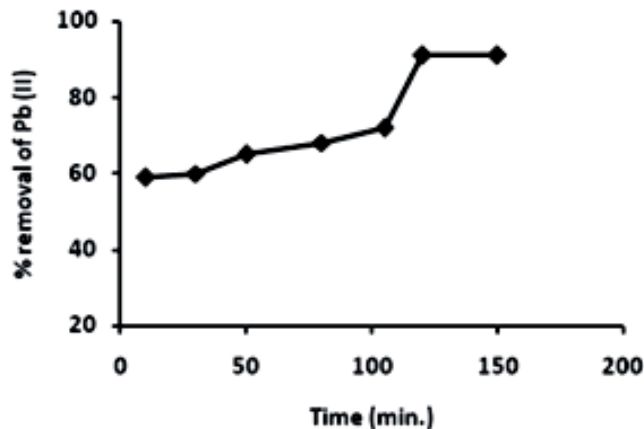


Fig. 4. Effect of contact time of GDCC on removal of lead (II) ions. Initial Pb^{2+} concentration: 35 mg/L; pH: 6; temperature: 27 °C; agitation speed: 200 rpm.; dose of adsorbent: 1 g/L; contact time: 10 to 150 min.

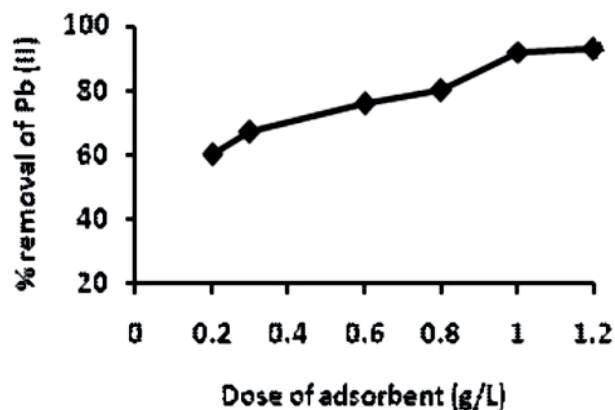


Fig. 5. Effect of dose of adsorbent GDCC on removal of lead (II) ions. Initial Pb^{2+} concentration: 35 mg/L; pH: 6; temperature: 27 °C; agitation speed: 200 rpm.; contact time: 120 min.; dose of adsorbent: 0.2 g to 1.2 g.

Effects of pH on adsorption

The pH of solution is the most vital and controlling parameter in the adsorption process. Effects of pH on adsorption performance of lead (II) ions were studied in range of 2 to 8 with GDCC. pH affects the solution chemistry, speciation and adsorption efficiency of metal ions [51]. Fig. 6 demonstrates that lead uptake increased with increasing pH and maximum removal appeared at pH 6 with 98% removal. This can be justified on the bases that at lower pH values, the concentration of hydronium ions (H_3O^+) increases that competes with metal cation for adsorption onto the available active binding sites of the adsorbent. However as pH of solution increased further, the negative charge on adsorbent surface increases that weakens the competition between hydronium ion and metal cation. This facilitates the attraction between metal cation

and adsorbent results in better metal removal. In alkaline medium lead tend to hydrolyze and undergoes precipitation (PbOH^+), $\text{Pb}(\text{OH})_2$ rather than adsorption. pH of solution should be lower than the critical pH of hydroxide precipitation (6.69 for Pb^{2+}) when considering the adsorption efficiency [52]. In above study pH 6 found to be optimum for lead (II) removal from water.

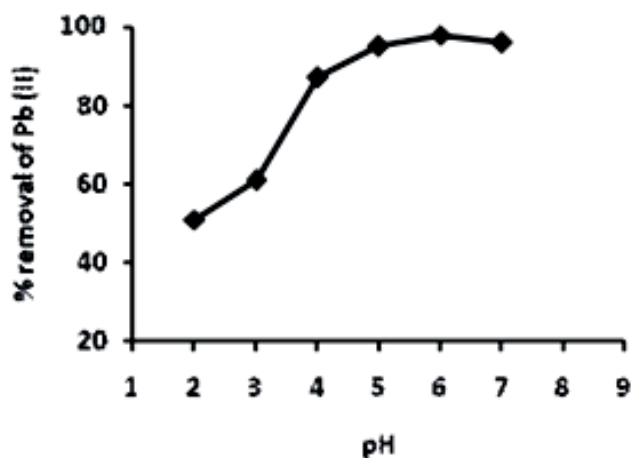


Fig. 6. Effect of pH on removal of lead (II) ions. Initial Pb^{2+} concentration: 35 mg/L; temperature: 27 °C; agitation speed: 200 rpm; contact time: 120 min.; dose of adsorbent: 1g/L; pH: 2-8.

Effects of initial concentration of adsorbate

Effects of initial concentration in the range of 35 mg/L to 95 mg/L on adsorption of lead (II) were studied by keeping other parameters like pH, dose of adsorbent, agitation speed and contact time as constant and shown in (Fig. 7). The initial metal ion concentration provides an important driving force to overcome all mass transfer resistance of the metal between aqueous and solid phase [53]. From the results it can be revealed that as the initial metal ion concentration increases, the percentage removal of lead (II) decreases. At low concentration of metal ion the active binding sites of adsorbent remains unsaturated offering large surface area for metal ion adsorption while at higher concentration accumulation of adsorbent particles leads to decrease in total surface area of the adsorbent.

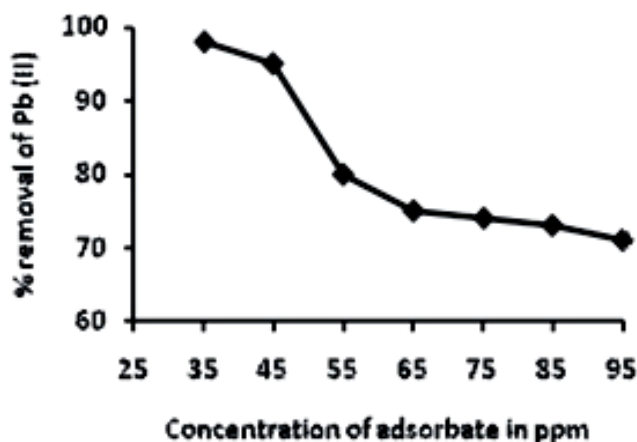


Fig. 7. Effect of initial metal ion concentration on removal of lead (II) ions; temperature: 27 °C; agitation speed: 200 rpm; contact time: 120 min.; dose of adsorbent: 1g/L; pH: 6; initial sorbate concentration: 35-95 mg/L.

Adsorption isotherm

The relationship between the amount of substance adsorbed per unit mass of adsorbent at constant temperature and its concentration in the equilibrium solution is called as adsorption isotherm. The equilibrium adsorption isotherms are important in determining the adsorption capacity of lead (II) ions onto GDCC. The experimental data were fitted into the Langmuir and Freundlich isotherm models.

Langmuir adsorption isotherm

The Langmuir model assumes monolayer adsorption and the maximum adsorption capacity was obtained from the expression (4)

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad \text{----- (4)}$$

where, C_e (mg/L) is equilibrium concentration of lead (II) in solution, q_e (mg/g) is the amount of lead (II) adsorbed per unit weight of adsorbent at equilibrium. Q_0 (mg/g) is the maximum adsorption amount. b (L/mg) is the Langmuir constant representing energy of adsorption. Q_0 and b are obtained from slope and intercept of the plot of C_e/q_e against C_e . (Fig. 8a) were found to be 6.711 mg/g and 0.367 L/mg respectively. The Langmuir isotherm model also provides R_L , a dimensionless constant expressed as $1/(1 + b.C_0)$ [54]. The value of R_L in many adsorption systems in the range 0 to 1 indicates favorable adsorption [55]. The correlation coefficient and the other parameters for sorption of lead (II) ions are shown in (Table 2). In this study the value of R_L for the adsorption on the GDCC material was in the range of 0.027-0.072 for 35 mg/L to 95 mg/L lead (II) concentration and this specifies effective adsorption under the optimized experimental conditions.

Freundlich adsorption isotherm

Freundlich adsorption isotherm is an empirical equation employed to describe heterogeneous system. Freundlich adsorption isotherm from aqueous solution is represented in linear form as follows

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \text{-----(5)}$$

where, K_F and n are the constants of Freundlich isotherm indicating adsorption capacity and adsorption intensity respectively. The Freundlich constants i.e. $1/n$ and K_F were calculated from the slope and intercept of Freundlich plots of $\ln q_e$ versus $\ln C_e$. The correlation coefficient and other parameters obtained for the adsorbent are shown in (Table 2). Constants K_F and n were found to be 3.564 mg/g and 6.62 respectively obtained from the intercept and slope of the plot of $\log q_e$ against $\log C_e$ (Fig. 8b). The correlation coefficients obtained from the Langmuir and Freundlich plots were 0.943 and 0.807 respectively. The higher correlation coefficient R^2 value and R_L value between 0-1, indicates the better fit and applicability of Langmuir isotherm model to the adsorption experimental data.

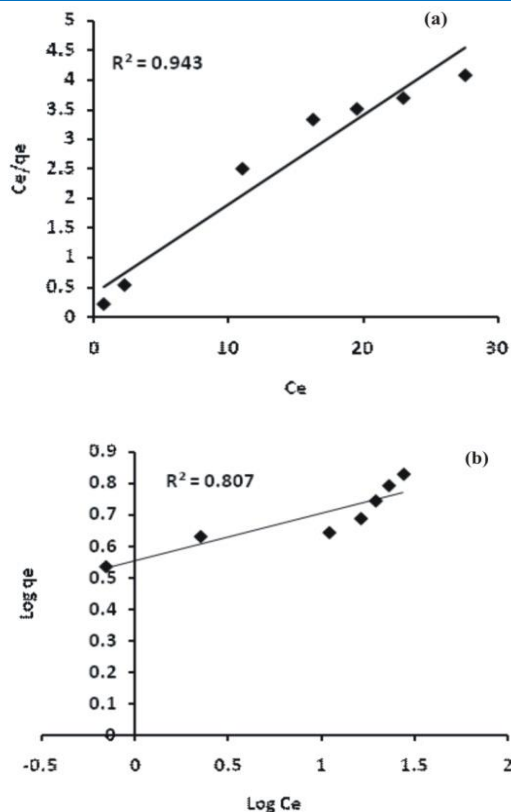


Fig. 8. (a) Langmuir adsorption isotherm, (b) Freundlich adsorption isotherm.

Table 2. Langmuir and Freundlich parameters for the adsorption of lead (II) ions on GDCC.

Equilibrium model	Langmuir constants			Freundlich constants			
	Qmax (mg/g)	b (L/mg)	R ²	R _L	K _F	1/n	R ²
Value	6.711	0.367	0.943	0.027 - 0.072	3.564	0.151	0.807

Adsorption kinetics

Adsorption kinetics was modeled by the pseudo first order equation, the pseudo-second-order equation and the intraparticle diffusion models (Fig. 8c, d and e). Rate equations for the pseudo first order, pseudo second order and intra particle diffusion models are shown below as Eqs. (6) and (8), respectively. The maximum amount of lead ions was adsorbed within 120 min with 91 % removal. After 120 min. equilibrium reached for the initial lead (II) concentration range studied. This might be attributed to extremely slow diffusion of the metal ions from the surface film into the pores which were least accessible sites for adsorption [56]. Pseudo first order Langergren equation is given by [57].

$$\text{Log}(q_e - q_t) = \frac{-K_1 t}{2.303} + \text{log } q_e \quad \text{-----(6)}$$

where, K₁ (min⁻¹) is the Langergren rate constant of adsorption; q_e (mg/g) and q_t (mg/g) are the quantities of metal ions adsorbed at equilibrium and at time t, respectively.

Pseudo second order model given by Ho and McKay [58].

$$\frac{t}{qt} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e t} \quad \text{-----(7)}$$

$$H = k_2 q_e^2$$

Where H is the initial sorption rate (mgg⁻¹min⁻¹); K₂ (mgg⁻¹min⁻¹) is the second order rate constant, K₂ and q_e can be obtained from the intercept and slope of plotting t/q_t versus t.

The intraparticle diffusion model is expressed as [59].

$$qt = K_{id} t^{1/2} + C \quad \text{-----(8)}$$

where, qt is the amount of solute adsorbed (mg g⁻¹) at time t, t is the time of adsorption (min), k_{id} is the intraparticle diffusion rate constant (mg g⁻¹min^{-1/2}) and C is the intercept which represents the value of the thickness of the boundary layer [60]. According to this model, the plot of uptake qt versus the square root of time (t^{1/2}) should be linear and if the line passes through the origin then intraparticle diffusion is the rate-controlling step.

The experimental data were fitted with these kinetic models where the kinetic parameters such as rate constant and equilibrium adsorption capacities of adsorption for lead (II) are summarized in (Table 3). Results presented in table clearly shows that the coefficient of determination for pseudo second order equation (R²= 0.99) is higher than pseudo first order (R²=0.964) and intraparticle diffusion model (R²=0.939). From the plot of intraparticle diffusion model, the straight lines did not pass through the origin suggesting that it was not the only rate-controlling step. Similarly high K₂ of pseudo second order suggested that the metal could be rapidly sequestered by carbon functional groups, resulting in the system quickly reaching equilibrium. These results suggest that experimental data for the adsorption kinetics of lead (II) ions on GDCC better fit the pseudo second order kinetic model. The confirmation of pseudo second order kinetics indicates that in the adsorption process, concentration of both adsorbent and adsorbate are involved in rate-determining step, which may be chemical adsorption or chemisorptions [61].

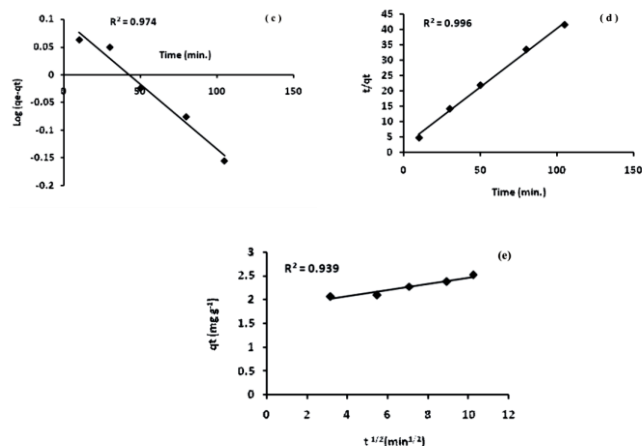


Fig. 8. (c) Pseudo first order kinetic plot, (d) Pseudo second order kinetic plot and (e) Intraparticle diffusion model.

Table 3. Pseudo first order, pseudo second order and intraparticle diffusion rate constants for lead (II) ions.

Metal	Pseudo first order			Pseudo second order			Intraparticle diffusion model		
	K_1	q_e (mg/g)	R^2	K_2	q_e (mg/g)	R^2	K_{id}	C (mg/g)	R^2
Lead (II)	-0.02	17.1	0.974	0.072	2.59	0.99	0.066	1.807	0.939

Conclusion

The present study shows that GDCC synthesized by impregnation methodology is an effective adsorbent for the removal of lead (II) ions from aqueous solution. The FTIR study revealed that the functional groups -OH and C=O was concerned with the adsorption performance by GDCC. XRD pattern displayed the amorphous nature of chitosan whereas crystalline structure of chitosan-graphite blend proved successful doping and formation of composite. SEM morphology shows some pores and cavities on the adsorbent surface facilitated adsorption of lead (II) ions. The batch adsorption of lead (II) by GDCC is a function of pH, dose of adsorbent, contact time and initial metal ion concentration. It was observed that lead (II) ions adsorption by GDCC had highest adsorption capacity at pH 6, while maximum adsorbent dosage was 1 g/L. The maximum adsorption capacity was 6.711 mg of adsorbate/g of adsorbent. The kinetic study shows that the metal removal approached equilibrium within 120 minutes of contact time. The adsorption isotherm studies revealed the higher correlation coefficient (R^2) values of 0.943 for Langmuir isotherm model proved better fit than the Freundlich model with R^2 of 0.807. Experimental data better fitted with pseudo second order kinetics model. Batch adsorption studies indicated that GDCC can be used for removal of lead (II) from moderately acidic aqueous solutions. It has been shown that the use of GDCC for lead (II) ion removal appears to be technically viable, ecofriendly and with high efficacy. The cost of removal of lead (II) is expected to be quite low as the adsorbent are cheap/economical and easily available in large amount. This adsorbent can be a good candidate for adsorption of not only lead (II) ions but also other heavy metal ions in wastewater.

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