PAPER • OPEN ACCESS

Enhanced Removal of Lead from Aqueous Solution Using Modified Chitosan

View the article online for updates and enhancements.

Enhanced Removal of Lead from Aqueous Solution Using Modified Chitosan

M Devasena[1*], D Pricilla[1] and K Mohamed Mydeen[2]

[1] Department of Civil Engineering, PSG Institute of Technology and Applied Research, India
[2] Department of Chemistry, PSG Institute of Technology and Applied Research, India
*e-mail: devasena@psgitech.ac.in

Abstract. This paper aims to investigate the enhanced removal of lead from aqueous solution using chitosan coated carbon (CNC) in comparison with the commercially purchased chitosan (CN) and activated carbon (AC) materials. Functional groups such as -OH and $-NH_2$ present in chitosan along with the functional groups of oxygen and aromatic compounds found in activated carbon makes CNC as the best adsorbent for lead removal for all concentrations of lead investigated. Batch adsorption experiments were performed as a function of adsorbent dosage, initial lead concentration, pH and contact time. At pH 6 and a contact time of 60 min, CNC showed enhanced adsorption capacity of 1.80 mg/g when compared to CN's adsorption capacity of 0.21 mg/g which is an order of magnitude higher. The equilibrium modelling was described better by Langmuir isotherm model and the Pseudo second order kinetic model was applicable to the kinetic data.
Keywords: Chitosan coated carbon, activated carbon, chitosan, lead.

1. Introduction

Heavy metals are dense compounds which are toxic and cause detrimental effects to the environment [1]. Anthropogenic activities lead to an astounding increase in heavy metal pollution which causes damage to the health and the environment. Among them, lead (Pb) acts as one of the predominant pollutants that finds its source from lead smelting industries, waste batteries, lead-based paints, mining and lead manufacturing industries [2]. Increase in lead concentration in water beyond 0.05 mg/L leads to neurological and cardiovascular problems and much higher concentration causes cancer in humans [3]. It is therefore indispensable to remove the lead present in water. Various techniques are available to eliminate lead including precipitation, coagulation, electro-dialysis, electro-coagulation, reverse osmosis, ion exchange and adsorption [4].

Adsorption is proven to be an effective and economical method for the removal of lead from the environment. To date, plethora of adsorbents have been examined for the removal of lead ions from water. Commercial activated carbon is most commonly used for the removal of soluble lead from water. A plenty of studies have been reported to prove successful adsorption of lead onto coal based activated carbon. However, usage of activated carbon might become uneconomical in future because of the huge demand of coal. It has been reported by Shi et al. (2018) [5] that while employing activated carbon for removal of lead, there exists adsorption between lead and calcium, lead and sulphate and lead and dihydrogen phosphate ions. This may lead to competitive adsorption, and to the formation of lead sulphate and lead phosphate complexes on activated carbon surfaces which brings down the efficiency of carbon in the longer run.

In recent times, sea-based adsorbent materials have been the focus of research as they improve the surface complexation of carbon-based materials. Also, they are in huge demand because of their easy accessibility, eco-friendly nature and cost-effectiveness. One such is chitosan, a biopolymer, that is produced from deacetylation of chitin which is biodegradable, non-toxic, easily available and inexpensive polymer [6]. Chitosan is a biocompatible polysaccharide and can chemically or physically entrap lead and various other metal ions with the aid of amine and hydroxyl groups present in chitosan. In publication [7], Saha et al. (2019) investigated the application of chitosan for the removal of heavy metals including lead. Carbon composites are reported to enhance adsorption due to the improved surface structure and resultant adsorption property. Past research work has stated the efficacy of chitosan on the removal of heavy metals [2–3, 6, 8–15]. Pratiwi and Prinajati [16] studied the optimum efficiency of lead removal using chitosan obtained from shrimp shells where they tested the adsorption potential of shrimp derived chitosan using different concentrations of lead at varying pH and varying time. High removal percentage of 99.88% was obtained at pH value of 4 in a time span of 90 min. The amine groups ($-NH_2$) which are nucleophiles have contributed to the removal of lead.

Chitosan is considered as a favorable bioadsorbent with high removal efficiency of lead and other heavy metals in spite of its limitations such as low porosity and low specific surface area that confines the diffusion of lead ions into the chitosan matrix [17]. The widely used chitosan combinations are manganese oxide nanoparticles, magnetic gelatin, sodium alginate beads, rice husk ash, nano alumina, oligosaccharide composites, biochar, graphene oxide, nanoclay and activated alumina. Sahebjamee et al. [18] examined the adsorbent behaviour of chitosan-polyvinyl alcohol membrane for the removal of Copper (Cu), Nickel (Ni) and Cadmium (Cd) ions and reported that the membrane exhibited good adsorption efficiency. Several studies were carried to assess the adsorption behaviour of chitosan and chitosan modified with activated carbon for the removal of Cu, Cd and Ni [19–23].

Hydari et al. [24] compared the adsorption capacities of activated carbon, chitosan and chitosan modified with activated carbon for removal of Cadmium. They found that the adsorption capacity was 52.63 mg/g for chitosan modified with activated carbon when compared to 10 mg/g for other independent adsorbents. Chitosan modified with activated carbon was evaluated for many applications including removal of phenols, dyes, heavy metal ions and organic compounds by a number of researchers [25]. The application of chitosan modified adsorbents is limited and considering the huge potential of chitosan-based products in environmental clean-up, this paper aims to investigate the adsorption of lead using activated carbon modified with chitosan termed as chitosan coated carbon (CNC) and compare the results with the adsorption of commercially purchased chitosan (CN) and activated carbon (AC).

2. Materials and methods

Stock solution of lead (1000 mg/L) was prepared by dissolving $Pb(NO_3)_2$ in distilled water. Standard lead concentrations of 1–5 mg/L were prepared by diluting the stock solution with distilled and deionized water. Laboratory grade chitosan and activated carbon were purchased from Sigma Aldrich (India). The method of modification of chitosan by using activated carbon was similar to the method used by [26]. Five grams of chitosan was added to 100 mL of 10% acetic acid and was kept in the hot plate at 50°C to which 50 g of activated carbon was added. To facilitate uniform dispersion and to obtain chitosan coated carbon, the entire mix was agitated using a magnetic stirrer for 24 h. The modified carbon was then washed thoroughly with distilled water and was oven-dried. Functional groups of both chitosan (CN) and chitosan coated carbon (CNC) were identified using FTIR analysis (Jasco, FT/IR 4100) and were used for adsorption of lead.

Batch adsorption experiments were carried out for investigating the operating parameters including dosages of the three adsorbents AC,CN and CNC , pH, initial lead concentration, and contact time. All experiments were carried out at room temperature. The dosage of the adsorbents was varied between 0.01 to 0.05 g per 250 mL of lead solution. The pH of the solution was adjusted to values between 1 to 10 by addition of 0.15 N hydrochloric acid or 1 N sodium hydroxide. Experiments were performed at three different contact times of 30, 60 and 120 min. Initial lead concentrations were varied between 1 to

5 mg/L. A known amount of each of the three adsorbents was added to a specific concentration of lead and stirred at 200 rpm. Samples were then collected at specific time intervals, filtered and analysed for lead using atomic adsorption spectroscopy (Systronics, 263) at a wavelength of 283 nm. All experiments were carried out in duplicates.

To study the effect of adsorbents and their dosage, 0.01 to 0.05 g of each of the adsorbents was added to 250 ml of 1, 2, 3, 4 and 5 mg/L of each solution and treated for 60 min at 200 rpm of mixing rate. To study the effect of pH on lead adsorption efficiency by AC, CN and CNC, experiments were run at pH range of 1-10 with 250 ml of 5 mg/L solutions on 0.05 g of the AC, CN and CNC at 300 rpm mixing rate for AC and CN and static mixing for CNC for a span of 60 min The amonut of lead uptake at equilibrium condition Q_e (mg/g), and the percentage of removal due to adsorption were calculated using equations 1 and 2 respectively.

$$Q_e = \frac{C_0 - C_e}{M} V \tag{1}$$

Percentage of removal due to adsorption $= \dfrac{C_0 - C_e}{C_0} \times 100 \tag{2}$

where C_0 and C_e are the initial and final concentrations of lead in mg/L respectively, M (g) is the mass of adsorbent used in grams, V (L) is the volume of the absorbate in L and Q_e is the adsorption capacity (mg/g).

3. Results and discussion

3.1. *Effect of adsorbent dosage on lead removal*

The removal effieciency of lead with initial concentraion of 5 mg/L is shown in figure 1. Removal of lead increased with the increasing dosage of the adsorbents and the maximum adsorption capacity was achieved for adsorbent dose of 0.05 g for all the three adsorbents. Further increase to 0.1 g of adsorbent dose resulted in decreased adsorption. In all cases, it is reasonable to suggest that, for high adsorbent dosage, there is a large possibility of the metal ions to interact. However, maintaining an optimum dosage of adsorbent as 0.05 g is vital. It is also apparent from the results that the removal efficiency of lead using CNC (96–97%) was similar to AC (94–97%) but greater than CN (86–89%) for the same adsorbent dosage and initial lead concentration. Similar results were obtained for all other concentrations of lead solutions.
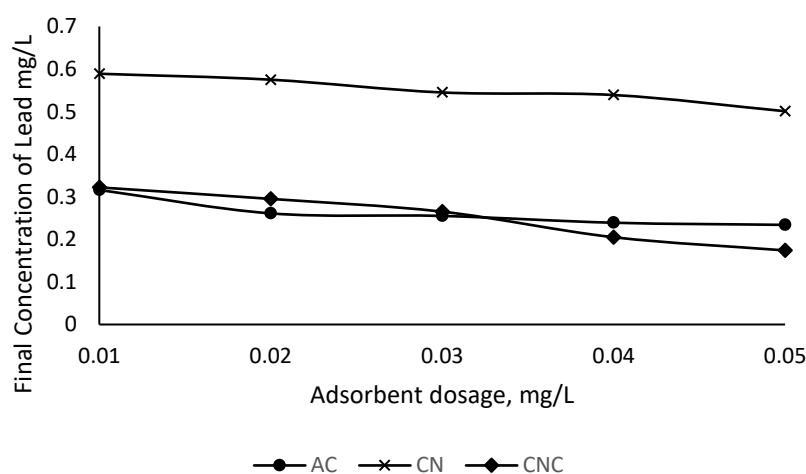

Figure 1. Effect of adsorbent dosage on the removal of lead against AC, CN and CNC

3.2. *Influence of pH on Adsorption Capacity*

To elucidate the optimum pH for lead removal, experiments were performed at different pH ranges between 1 to 10. Increasing the pH of the sample solution led to decrease in adsorption in all cases due to precipitation of lead as $Pb(OH)_2$ which turned the solution milky. For initial lead concentration of 5 mg/L, removal of lead byCN was found to vary between 86 to 88 % at pH 5 and with CNC, the removal efficiency was between 97 to 98% at pH 6. Similarly, AC showed lead removal efficiency of 94 to 95% at pH 4, 5 and 6. This indicates that the lead uptake had taken place at pH greater than 4 and less than 7 for all adsorbents. Adsorption declined at pH greater than 5 with CN and at pH greater than 6 with CNC and AC.

It could be inferred that the functional groups of the adsorbents get protonated at low pH and result in decreased adsorption. At lower pH values, lead uptake is less due to the competition between H^+ and lead ions. Similar observations were made by Shi et al. (2018) [5] during metal adsorption with activated carbon and chitosan. The types of bonds formed between CNC surface and the lead ion is different from AC. Hence the removal efficiency of lead was high for CNC at the same pH. The active groups present in AC obtained by coating with chitosan increased the pH value to 6 where maximum removal efficiency of 97-98% was exhibited

3.3. *Effect of contact time on lead removal*

Batch studies were carried out for varying contact times of 30, 60 and 120 min with the initial lead concentration of 1, 2, 3, 4 and 5 mg/L. Optimum adsorbent dosage was taken as 0.05 g and optimum pH of 5 for CN and 6 for CNC was maintained. The amount of lead adsorbed generally increases with the increase in contact time showing a greater number of vacant sites for adsorption. In this study, the removal efficiency was found to decrease after 60 min with the material reaching the equilibrium state for all lead concentrations investigated.

3.4. *Removal Efficiency*

Table 1 shows the removal efficiency of CN and CNC for initial lead concentrations of 1 to 5 mg/L. Lead removal efficiency was between 82–89, 96–99 and 93–97% for CN, CNC and AC respectively where the adsorbent dose was fixed at 0.05 mg and pH maintained at 5 for CN and 6 for AC and CNC. When the lead concentration was increased to 10 mg/L, the efficiency dropped to 70 to 75% in the order of CNC>AC>CN. This may be due to the lesser number of sites on the surface of the adsorbent.

Table 1. Removal efficiency of lead

Adsorbents	pH	Contact time	Initial lead concentration, mg/L				
		min	1	2	3	4	5
Chitosan	5	60	83–89	82–89	86–89	87–88	86–88
Chitosan coated Carbon	6	60	98–99	98–99	96–97	97	97–98
Activated carbon	6	60	93–97	94–96	94–97	95–97	94–95

3.5. *Adsorption Isotherms*

To understand the nature of adsorption onto the sorbents, the experimental data was fitted to Langmuir and Freundlich isotherm models. Langmuir isotherm, as proposed first by [27], assumes a reversible adsorption with the formation of a homogeneous monolayer. The linearized form of Langmuir adsorption isotherm is expressed as given in equation 3.

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{Q_m b C_e}$$
(3)

where Q_e is the mass of adsorbed substance (mg/g), b is the Langmuir adsorption constant (L/mg), Q_m is the maximum adsorption capacity (mg/g) and C_e is the equilibrium concentration of the adsorbate in the solution (mg/L).

Freundlich isotherm was proposed by [28] which represents non-ideal adsorption widely used for heterogenous systems. The linearized form of Freundlich adsorption isotherm is expressed as shown in equation 4.

$$\log\left(Q_e\right) = \log\left(k_f\right) + \frac{1}{n}\log\left(C_e\right) \tag{4}$$

where k_f and n are Freundlich isotherm constants related to adsorption capacity and adsorption intensity respectively.

Adsorption isotherms were evaluated by keeping the optimum adsorbent dose as 0.05 g and varying the initial lead concentration. The values of other independent variables, contact time and pH remained constant as 60 min and 5 for CN and 6 for AC and CNC respectively. The experimental data were fitted to both isotherm models and isotherm constants are presented in Table 2. It was observed from the graphical plot of $1/Q_e$ versus $1/C_e$ that the experimental values fitted well with the Langmuir isotherm for the different lead concentrations investigated. Adsorption capacities Q_m (mg/g) were maximum for AC (4.77) followed by CNC (1.80) and CN (0.21) for lead concentration of 5 mg/L. Similar results were observed for all other concentrations and therefore, AC acts as the better adsorbent for lead removal as compared to CNC and CN. In this study, the separation factor R_L, defined as

$$R_L = \frac{1}{1 + bC_0} \tag{5}$$

were found to be 0.11 for CN, 0.09 for CNC and 0.06 in the case of AC respectively for initial Pb concentration of 5 mg/L showing that adsorption is favorable.

Table 2. Results of Isotherm Models

Adsorbent	C_0, mg/L	Langmuir				Freundlich		
		R^2	b, L/mg	Q_m, mg/g	R_L	R^2	k_f, mg/g	$1/n$
CN	1	0.91	2.28	0.64	0.30	0.87	8.66	1.69
	2	0.95	3.53	0.13	0.12	0.88	6727.7	6.29
	3	0.99	2.43	0.21	0.12	0.98	937.29	6.25
	4	0.98	1.89	0.20	0.12	0.91	832.97	8.12
	5	0.94	1.59	0.21	0.11	0.85	431.38	9.22
CNC	1	0.73	2.79	2.42	0.26	0.64	36.89	1.48
	2	0.93	2.88	3.55	0.15	0.88	6.91	0.93
	3	0.96	2.37	2.00	0.12	0.93	30.63	1.72
	4	0.97	3.12	0.91	0.07	0.95	155.40	2.82
	5	0.93	1.97	1.80	0.09	0.84	40.93	2.22
AC	1	0.88	6.07	7.77	0.14	0.78	65.19	1.73
	2	0.97	7	3.15	0.07	0.97	2825.4	3.53
	3	0.99	3.99	8.68	0.08	0.95	105.8	2.45
	4	0.82	3.12	9.07	0.07	0.73	119.33	2.52
	5	0.86	2.97	4.77	0.06	0.95	1915	5.15

Figure 2 shows the relationship between $1/C_e$ versus $1/Q_e$ for AC, CN and CNC for initial lead concentration of 5 mg/L. The adsorption isotherms are found be linear with all three adsorbents. Similar results were obtained for other concentrations of lead and adsorbent dosages.
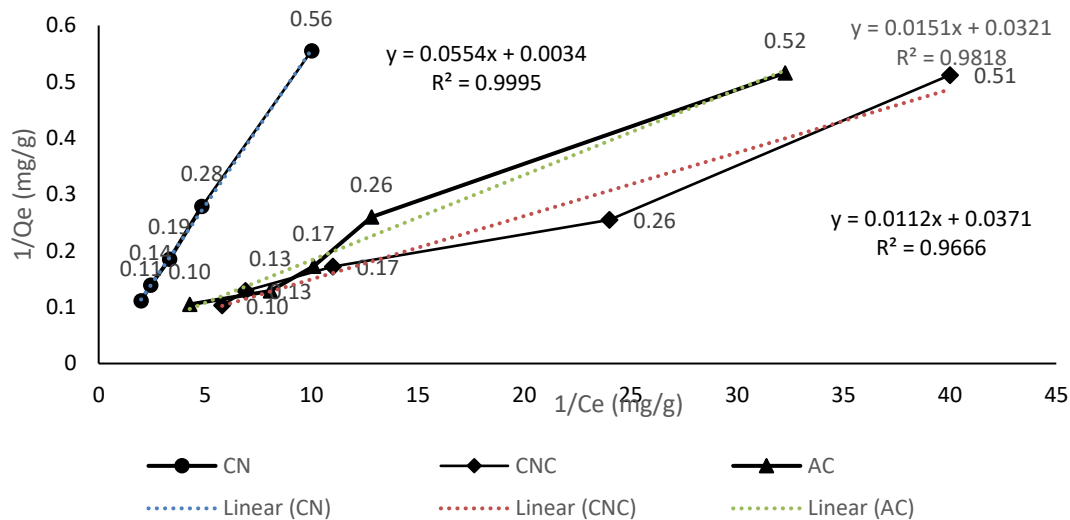

Figure 2. Relationship between $1/C_e$ and $1/Q_e$ of Langmuir equation for AC, CN and CNC

The Freundlich isotherm was also representative for lead adsorption by the three adsorbents. The correlation coefficient R^2, k_f and $1/n$ were calculated from the slopes of the Freundlich plots and $1/n$ values were found to be 9.22; 2.22 and 5.15 for CN, CNC and AC respectively. The magnitude of k_f and $1/n$ shows good removal of lead and moderate adsorption capacity. As compared to literature sources [29], the average values of $1/n$ signifying the forces that are exerted on the surface of the chitosan during lead adsorption are moderate. The intensity of adsorption was minimal in CNC as observed with the $1/n$ values of CN, CNC and AC. Hence desorption of lead is possible when CN and AC are used as adsorbents.

With both CN and CNC, lead adsorption occurs onto the surface of the amino groups. The $-NH_2$ group present in the chitosan undergoes protonation to $-NH_3$ at pH equal to or less than 7. When pH rises, protonation is reduced and adsorption becomes weak. Figure 3 shows the plot of t/Q_t versus t representing pseudo second order kinetic model. It was found that the q_e experimental and the q_e calculated values from the pseudo second-order kinetic model are very close to each other as the correlation coefficients are close to $R^2 = 0.99$ for all three adsorbents.
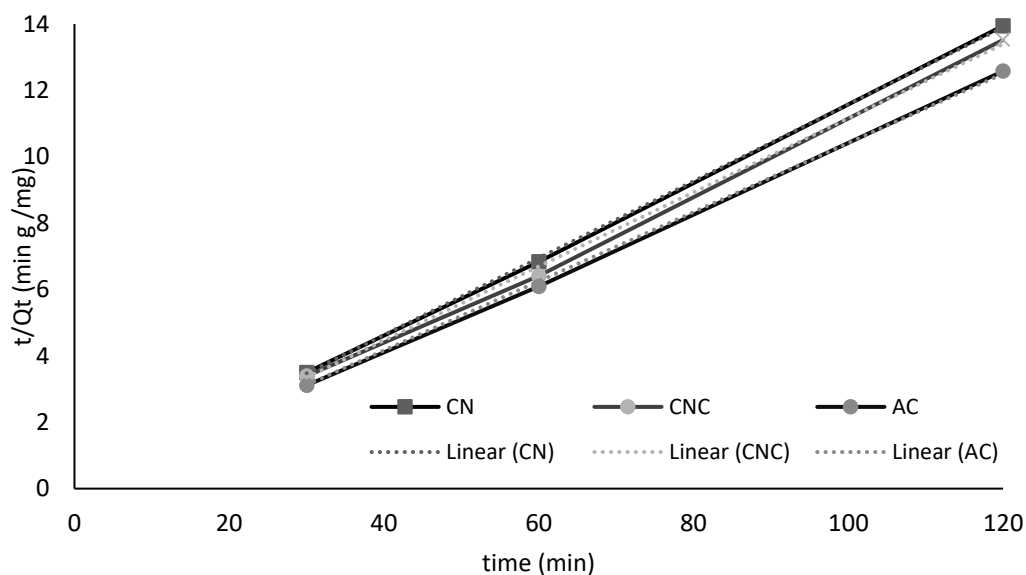
Figure 3. Pseudo-second order kinetic plots for the removal of lead on CN, CNC and A (Co = 5 mg/L, adsorbent dosage = 0.05 g/L).

3.6. FTIR Analysis

Figure 4 shows the FTIR analysis of chitosan and chitosan coated carbon. The FTIR spectra of chitosan shows the characteristic peak appeared around 1650-1590 cm^{-1} corresponding to the amide band, primarily associated with the stretching vibrations of the C=O bond in the amide group. The amide band appears around 1560-1530 cm^{-1} and is associated with the bending vibrations of the N-H bond in the amide group. The existence of hydroxyl (-OH) group in the chitosan exhibits as a broad peak around 3500-3200 cm^{-1}. The presence of the glycosidic linkage (C-O-C) in chitosan was noticed at 1150 cm^{-1}. On comparing with chitosan, the FTIR spectrum of chitosan coated carbon after adsorption of Pb^{2+} ions the following characteristic peaks are shifted at 1606.56 cm^{-1}, 1417 cm^{-1} and 1041.03 cm^{-1} related to the N-H and C-O stretching bands respectively. Further O-H stretching and C-H bending also found to be shifted at 3394.25 and 2598.08 cm^{-1}. All these changes may due to the coordination of metal ions (Pb^{2+}) to the amino group of the chitosan. It was noteworthy that these results rely with the earlier study [31] reported that the presence of amino groups (-NH$_2$) in the chitosan effectively serve as binding sites for metal ions.
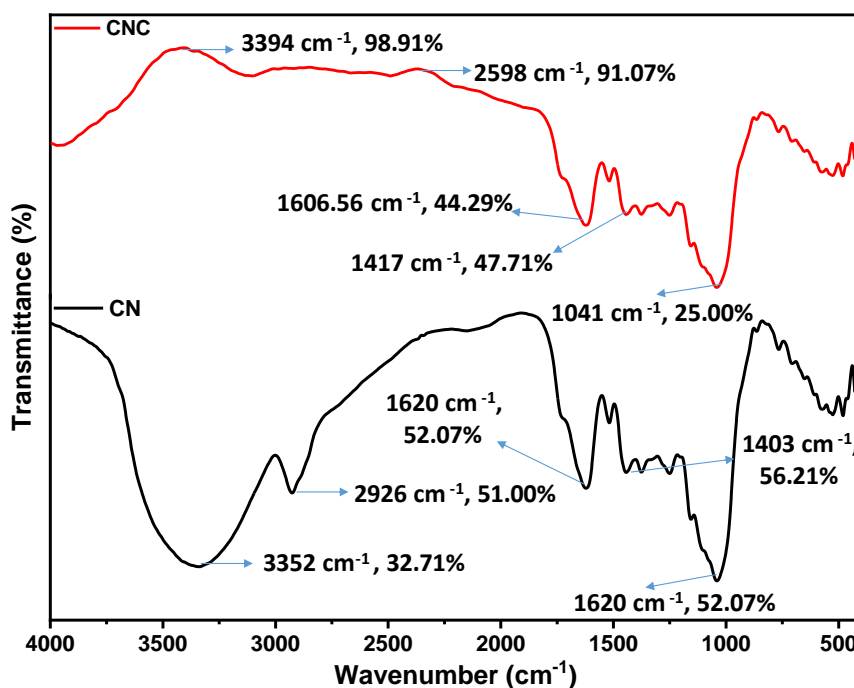
Figure 4. FTIR analysis for chitosan and chitosan coated carbon

The protonated functional groups such as amine ($-NH_2$), hydroxyl (O-H), alcohol (CH_2-OH) groups are responsible for metal uptake. In this case, Pb^{2+} ions are present in an aqueous solution containing chitosan, they can interact with the amine groups through coordination bonds. The lone pair of electrons on the nitrogen atom of the amine group in chitosan and CNC forms a coordination bond with the Pb^{2+} ion. The coordination bonds between the amine groups and Pb^{2+} ions stabilize the interaction, leading to the adsorption of Pb^{2+} from water or aqueous solutions onto the chitosan surface. Moreover, the coordination bonds contribute to the strong binding between chitosan and Pb^{2+} ions, enabling the removal of toxic metal ions from the environment.

4. Conclusions

The present study compared the removal efficiency of lead by chitosan coated activated carbon with commercially available chitosan and activated carbon. Operating parameters such as pH of solution, contact time, initial lead concentration and adsorbent dose were investigated. Langmuir and Freundlich isotherm models were used to fit the experimental data. Results indicated that the adsorption equilibrium data correlated well with the Langmuir isotherm model indicating homogenous monolayer adsorption. While comparing the percentage removal of lead and adsorption capacities of the three adsorbents, CNC was found to be superior. AC, though characterized by its high adsorbing capacity, suffers from the fact that desorption might occur. CN is an inexpensive and naturally available abundant material which shows greater metal uptake due to the presence of amino groups compared to AC. For practical usage, direct chitosan may not be advisable as it possesses low mechanical suitability and solubility at lower pH. Hence if the already successful AC is coated with chitosan, enhanced removal of lead occurs. Due to the –OH and NH_2 functional groups of the chitosan, the modified adsorbent showed high removal efficiency of lead at all concentrations tested. CNC has more active functional groups present and works at a higher pH; all this leads to the conclusion that CNC is the best adsorbent for lead removal.

Consent to participate
All authors agreed with the content.

Consent to publish

All authors agreed with the content and gave explicit consent to submit the work.

Competing interests

The authors declare no competing interests

Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

References

[1]   Briffa J, Sinagra E and Blundell R 2020 *Heliyon.* **6** e04691

[2]   Dinh V P, Le N C, Tuyen L A, Hung N Q, Nguyen V D and Nguyen N T 2018 *Mater.Chem. Phys.* **207** 294

[3]   Dewage B N, Fowler R E, Pittman C U, Mohan D and Mlsna T 2018 *RSC Advances.* **8** 25368

[4]   Arbabi M, Hemati S and Amiri M 2015 *Int. J. Epidemiol.* **2** 105

[5]   Shi Q, Sterbinsky G E, Prigiobbe V and Meng X 2018 *Langmuir.* **34** 13565

[6]   Fooladgar S, Teimouri A and Ghanavati Nasab S 2019 *J. Polym. Environ.* **27** 1025

[7]   Saha S, Zubair M, Khosa M A, Song S and Ullah 2019 *J. Polym. Environ.* **27** 1389

[8]   Ablouh E H, Hanani Z, Eladlani N, Rhazi M and Taourirte M 2019 *Sustain. Environ. Res.* **29** 1

[9]   Atangana E 2019 *J. Polym. Environ.* **27** 2281

[10]   Lavanya R, Gomathi T, Vijayalakshmi K, Saranya M, Sudha P N and Anil S 2017 *Int. J. Biol. Macromol.* **104** 1495

[11]   Li B, Zhou F, Huang K, Wang Y, Mei S, Zhou Y and Jing T 2017 *Sci. Rep.* 43082

[12]   Okoya A, Akinyele A, Amuda O and Ofoezie I 2016 *ACSj.* **11** 1

[13]   Pal P and Pal A 2017 *J. Mol. Liq.* **248** 713

[14]   Sadeghizadeh A, Ebrahimi F, Heydari M, Tahmasebikohyani M, Ebrahimi F and Sadeghizadeh A 2019 *J. Environ. Manage.* **232** 342

[15]   Samuel M S, Shah S S, Bhattacharya J, Subramaniam K and Pradeep Singh N D 2018   *Int. J. Biol. Macromol.* **115** 1142

[16]   Pratiwi R and Prinajati P D 2018 *Indones. J. Urban. Environ. Technol.* **2**

[17]   Hao C, Wang W, Wang S, Zhang L and Guo Y 2017 *Mar. Drugs.* **15** 1

[18]   Sahebjamee N, Soltanieh M, Mousavi S M and Heydarinasab A 2019 *Carbohydr. Polym.* **210** 264

[19]   Kuczajowska-Zadrożna M, Filipkowska U and Jóźwiak T 2020 *J. Environ. Chem. Eng.* **8** 103878

[20]   Malayoglu U 2018 *Sep. Sci. Technol.* **53** 2741

[21]   Mei J, Zhang H, Li Z and Ou H 2019 *Carbohydr. Polym.* **224** 115154

[22] Mone M, Lambropoulou D A, Bikiaris D N and Kyzas G 2020 *Polymers*. **12**

[23] Xiao F, Cheng J, Cao W, Yang C, Chen J and Luo Z 2019 *J. Colloid Interface Sci.* **540** 579

[24] Hydari S, Sharififard H, Nabavinia M and Parvizi M R 2012 *Chem. Eng. J.* **193** 276

[25] da Silva Alves D C, Healy B, de Almeida Pinto L A, Anna Cadaval T R S and Breslin C B 2021 *Molecules.* **26** 594

[26] Amuda O S, Giwa A A and Bello I A 2007 *Biochem. Eng. J.* **36** 174

[27] Langmuir I 1917 *J. Am. Chem. Soc.* **39** 1848

[28] Freundlich H 1907 Zeitschrift für Physikalische Chemie – Stöchiometrie und Verwandschaftslehre. **57** 385

[29] Dima J B, Sequeiros C and Zaritsky N E 2015 *Chemosphere.* **141** 100

[30] Ayawei N, Ebelegi A N and Wankasi D 2017 *J. Chem.* 3039817

[31] Dewage N B, Fowler R E, Pittman C U, Mohan D and Mlsna T 2018 *RSC Adv*. **8** 25368