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Kinetic and Isotherm Studies for Removal of Lead Using Bentonite and Bentonite Activated Charcoal Mixture

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Abstract The present study is aimed at devising a low cost and eco- friendly method of lead removal from aqueous medium. A comparative study of removal of Pb(II) by bentonite and bentonite activated charcoal mixture (I:I) was done. Batch experiments were done to find optimum condition as a function of variables such as pH, agitating time, initial concentration of Pb2+ adsorbent doses. The results showed that experimental results were the best fit for Langmuir isotherm. The kinetic studies confirmed the pseudo-first order reaction. The bentonite was characterised by TGA, DTA, XRD, and FITR. The maximum adsorption maximum adsorption capacity was evaluated to be 99.97percentage .Further uptake capacity by bentonite activated charcoal mixture was almost same as the bentonite. Bentonite activated charcoal mixture has emerged as a potential adsorbent of lead (II) ions from aqueous medium.

Keywords: *Bentonite, activated charcoal, adsorbent, lead, removal*

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1. Introduction

Lead is one of the most hazardous heavy metals which pollute biotic and ecosystems [1,2]. The entry- pathway of lead into the groundwater is both geochemical and anthropogenic. Owing to extraction of lead from its ore galena, association with other sulphide ores add to the contamination of groundwater. Anthropogenic activities such as paints, explosive and industries are a significant source of lead contamination in water. Lead enters the body through food chain and binds to proteins in the bloodstream causing kidney, brain and nerve damage [3]. Lead pollutants have caused concern among the researchers all over the world to maintain environmental health [4]. Amongst traditional methods of adsorption by biomass agriculture solid waste, bentonite has emerged as an eco- friendly low cost adsorbent for removal of lead (II) from aqueous medium [5,6,7]. The increased adsorption potential of bentonite may be attributed to high surface area, cation exchange capacity and presence of mesophores as well as micropores. Bentonite mineral contains essentially a unit of montmorillonite unit confirmed by the blue colour test from benzidine, blue colour with paraphenylenediamine, red colour with orthophenylenediamine.

The surface area of bentonite may be increased by intercalation with cetyletrimethyl ammonium bromide (CTAB) hexadeciletrimethyl ammonium bromide surfactant (HDTMA), amine functionalised groups and natural surfactants for greater adsorption potential [8]. Cellulose has also the potential to adsorb toxic heavy metal so clay minerals modified with cellulose have also gained importance because of a number of groups on the surface.

2. Experimental

2.1 Bentonite mineral has been procured from Barmer Rajasthan. Activated charcoal has been purchased from suppliers of Merck. Bentonite and activated charcoal mixed in the ratio of (I:1) by weight and stirred on mechanical shaker for homogeneous mixture. FTIR analysis was done by Perkins Elmer version 10.4 1 us. The XRD characterization was done by Brucker D8 advance.

TGA ,DTA was done using Perkin Elmer version (STA-6000) thermal analyser at a heating rate 10 degree per minute in N_2 atmosphere .The surface morphology was done by SEM Analysis using ZEISS EVO-MA10,Germany .Calorimetric determination of SiO2 2 and Al 2O3 and the alizarin red –S complex has been done from UV Visible spectrophotometer Systronic 2203. The residual concentration of Pb(II) were known by induced couple plasma- atomic emission spectroscopy.

2.2.2 Batch adsorption studies of Pb2+ solution at different concentration was agitated at 200 RPM using magnetic shaker optics technology Delhi at various values 3-7 up to 15, 30, 60, 90 minutes.

The PH level was adjusted to the required level by addition of N / 2 HCl and (N/2) NaOH. After certain time intervals the used filter paper is dried and the powder mask was analysed for SEM and EDAX. The supernatant was analysed by UV double beam spectrophotometer model 2203 and the result were compared with the ICP-AES. Both the results are in good agreement with each other. Similar experiments were repeated with 2 gm and 3 gm of bentonite and bentonite charcoal mixture up to 15 minutes. The lead percent removal and uptake was evaluated by the formula given below $qt = \frac{ci - ct}{m} \times V$

$$\% \text{ removal} = \frac{Ci - Ct}{Ci} \times 100$$

Where C_i= initial concentration

C_t = concentration at any time

V = volume in litres

M = mass in gram

Activated charcoal has OH groups on the surface [Gabriel, et al. 2020; O'Connell, et al.] Clay minerals have also OH^- groups on its surface which makes it easier to be made tied with amino functional group [9]. Bentonite minerals can also be modified with EDTA to remove Cu^{2+} and Pb^{2+} [10]. Thus EDTA modified bentonite can also be used as an effective adsorbent of heavy metals such as Pb and organic dyes. The activated charcoal has also been utilised for removal of toxic heavy metals [11]. A mixture of bentonite and charcoal 1: 1 has been utilised in the present study for remediation of Pb^{2+} ·The cation exchange capacity of bentonite ranges from 89 to 110 milli equivalent 100^{g-14}.The exchangeable cations are K^+ Na^+ and ca^{+2} [12,13]. High cation exchange capacity along with presence of major mesopores and micropores have made it useful for industrial purposes [13]. Bentonite minerals are characterised by PXRD, FTIR, TGA, DTA, and SEM [13,14,15]. A weight loss of 16.384% in TGA confirms the presence of montmorillonite unit .The major oxides of bentonite minerals are Si and Al along with trace metals [16,17]. In view of abundance of bentonite minerals, low cost and sustainability, bentonite minerals as well as modified bentonite have emerged as the most useful method of reducing heavy metal pollution in general and Pb(II) in particular [18]

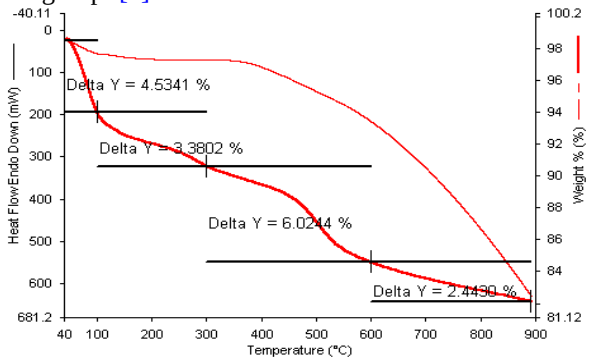

Figure 1a. TGA of BB_2

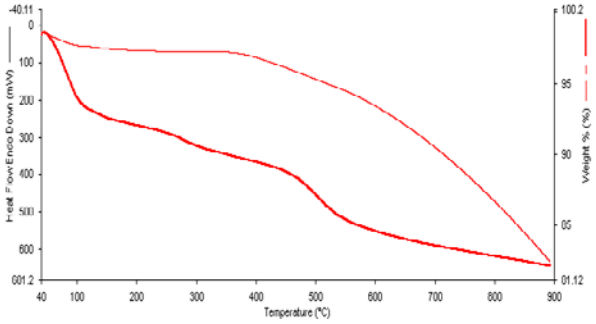

Figure 1b. DTA of BB_2

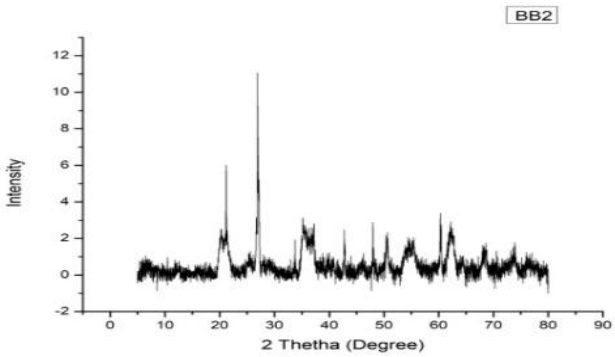

Figure 2. XRD of BB_2

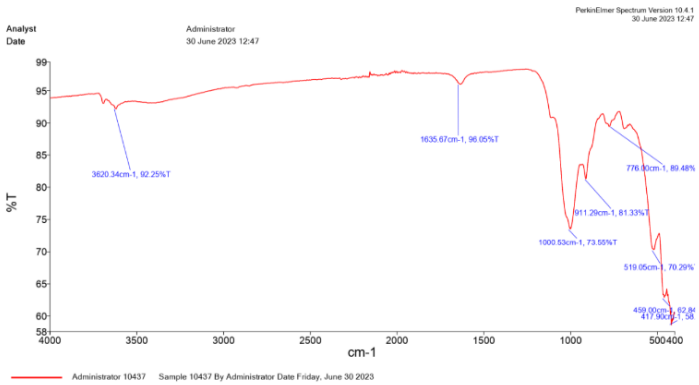

Figure 3. FTIR of Bentonite (BB2)

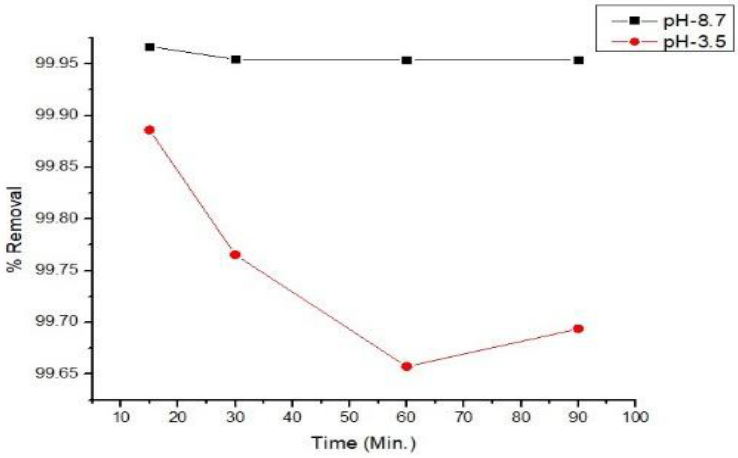

Figure 4. Percentage Removal Vs Time (Min)

3. Result and Discussion

3.1. Effect of Contact Time

A batch experiment has been done at different contact times such as 15 minutes, 30 minutes, 60 minutes and 90 minutes (shown in Table 1). With increasing time, number of active sites of the absorbent come in contact with lead ions which contributed to the rapid uptake of $Pb^{2+}$by bentonite and bentonite charcoal mixture. Several kinetic models including pseudo first order kinetics, pseudo 2^{nd} order kinetics and intraparticle diffusion have been studied to see the best fit of experimental data. The adsorbed amount of lead ions has been measured. Amongst all the models, Langmuir model was the best fit for experimental data .The removal of lead by bentonite and bentonite charcoal mixture may be attributed to adsorption by bentonite as well as exchange.

3.2. Effect of Adsorbent Doses

The adsorbent doses have also been varied for determination of optimum condition. 2g and 3gof bentonite as well as bentonite charcoal mixture 1:1 have been treated with different initial concentrations and pH values with increased dose of adsorbent, availability of vacant sites increases leading to increased percent removal.

3.3. Effect of pH

pH of solution is an important factor which affects the presence of ions on the binding surface leading to adsorption. The optimal pH has been determined by conducting the batch experiment at PH 3 and 8 with different initial concentrations of 50 ppm. The adsorbent used are pure bentonite and bentonite charcoal mixture (1:1).The increase in uptake of Pb^{2+} takes place with increasing pH .At low pH the repulsion between H^+ ion in aqueous solution and Pb^{2+} in aqueous medium becomes prominent leading to reduced uptake of Pb^{2+} ions. At higher pH the amount of H^+ in aqueous solution decreases leading to low Pb^{2+} uptake.

3.4. Adsorption Isotherms Model

Freundlich and Langmuir adsorption isotherms are frequently used to analyse the experimental data. Freundlich adsorption isotherm refers to multilayer adsorption whereas Langmuir refers to monolayer [19,20]. Elovich model of adsorption has also been analysed both for bentonite and bentonite charcoal mixture Thus linear fitting plots of Freundlich, Langmuir and Elovich isotherm models can be utilised to see the best fit of experimental data of adsorption [21,22,23]. A comparison of the adsorption capacities of bentonite and bentonite activated charcoal mixture can be done for Pb^{2+} removal

from aqueous medium. Despite the Freundlich isotherm is not the best fit, the adsorption process is favourable due to strong interaction between Pb2+ Ion and bentonite [24,25,26].

Figure 1a and 1b show TGA and DTA of bentonite mineral whereas Figure 2 and Figure 3 show XRD and FTIR respectively. Figure 4 represents percentage removal. Figure 5 and Figure 6 stand for Freundlich isotherm whereas Figure 7 and Figure 8 stand for pseudo first order reaction. Figure 9 and Figure 10 show linearity indicating that Langmuir adsorption isotherm is the best fit for experimental data. Intraparticle diffusion does not take place which becomes clear from Figure 11 and Figure 12. Figure 13 and Figure 14 clearly show that Elovich isotherm is not obeyed.

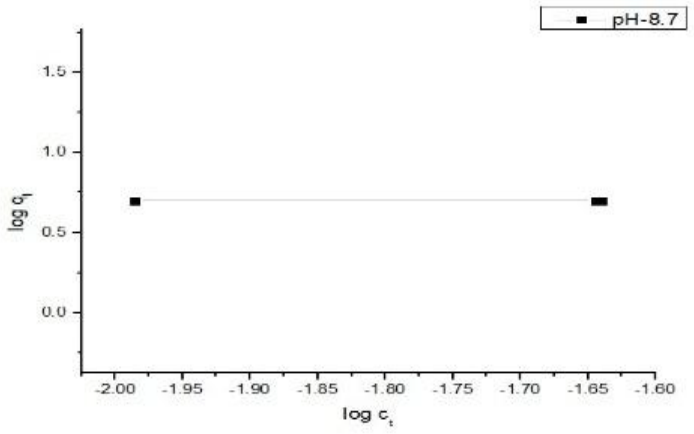

Figure 5. log q_t Vs log C_t

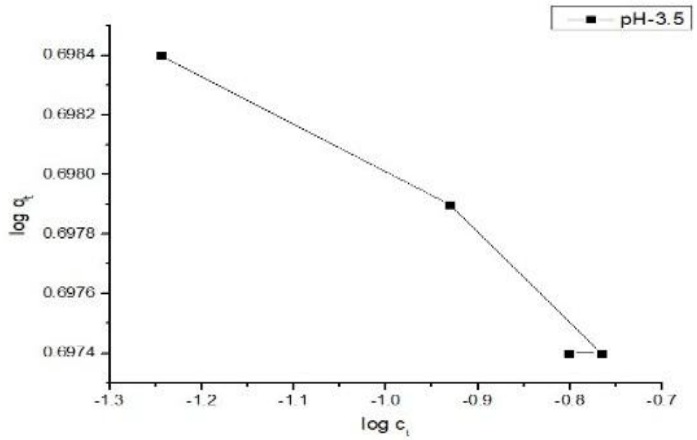

Figure 6. log q_t Vs log C_t

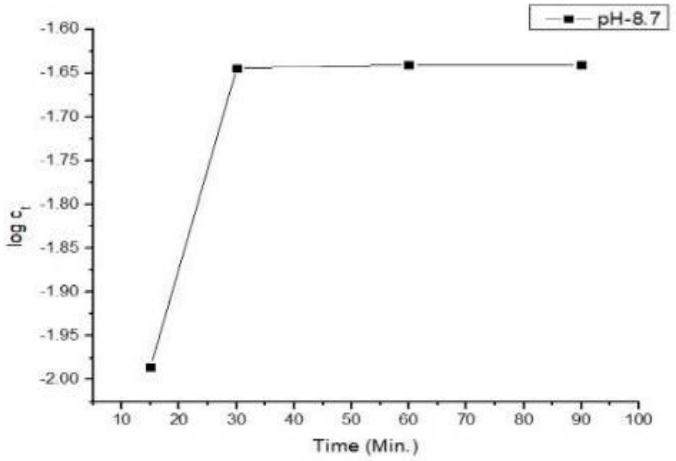

Figure 7. log C_t Vs Time (Min)

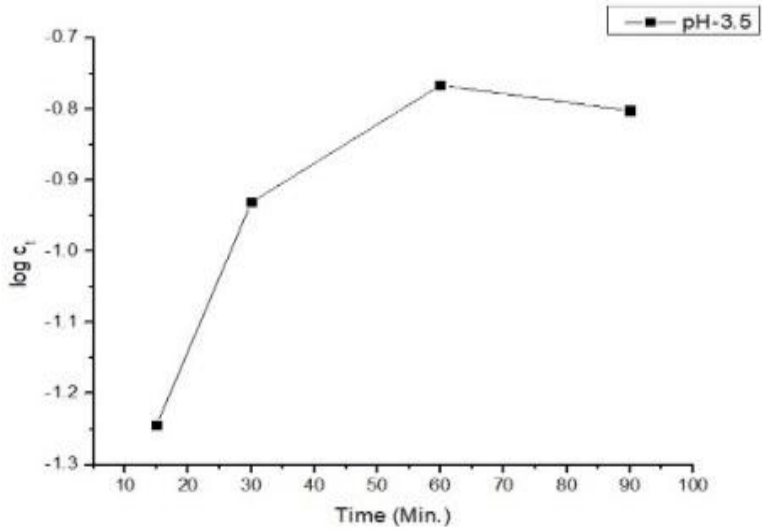

Figure 8. log C_t Vs Time (Min)

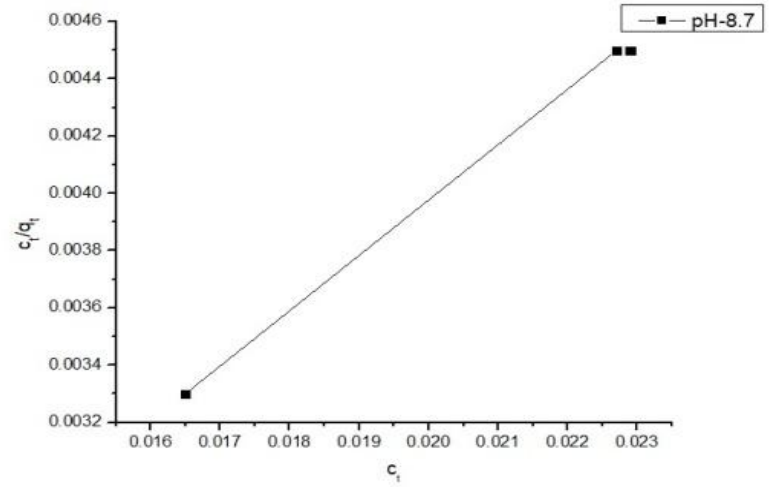

Figure 9. C_t/q_t Vs C_t

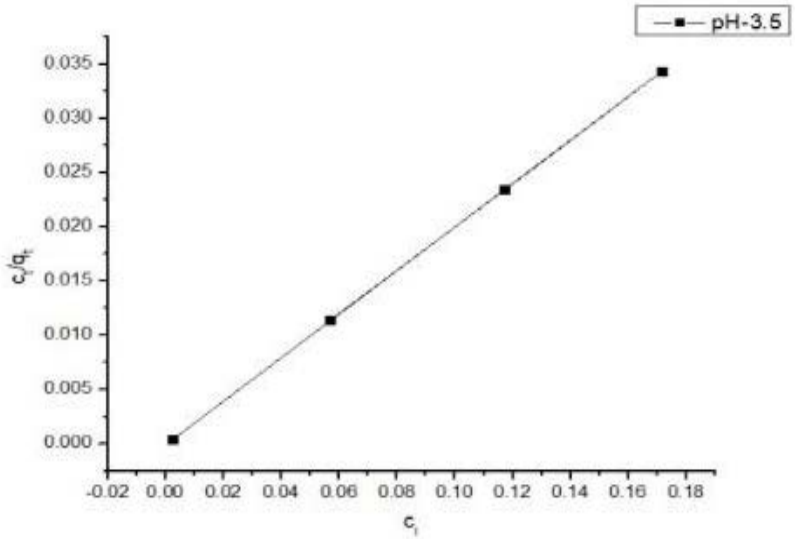

Figure 10. C_t/q_t Vs C_t

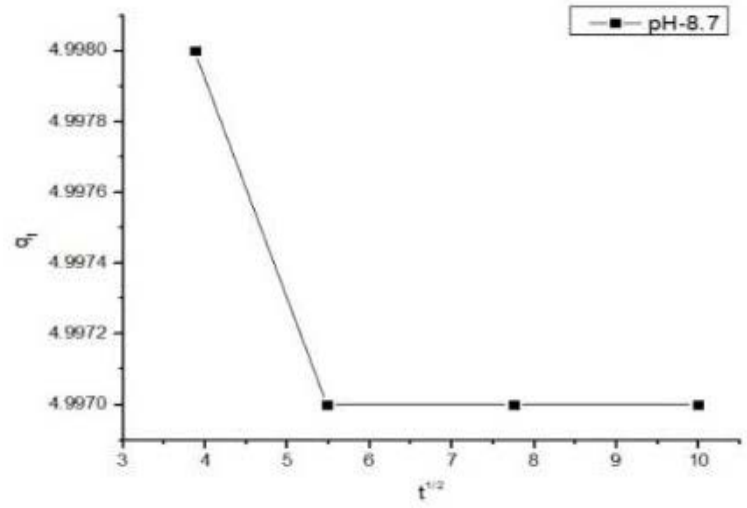

Figure 11. q_t Vs $t^{1/2}$

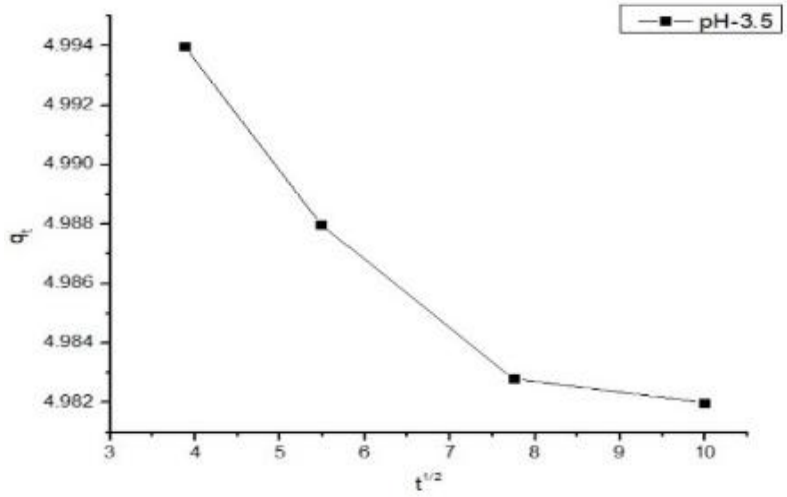

Figure 12. q_t Vs $t^{1/2}$

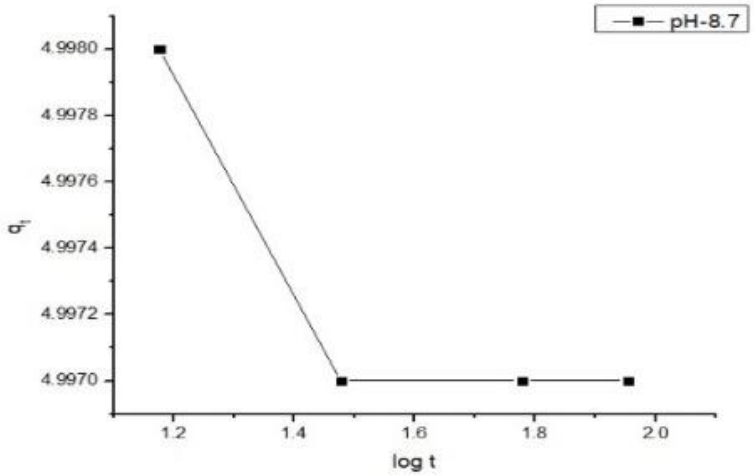

Figure 13. q_t Vs log t

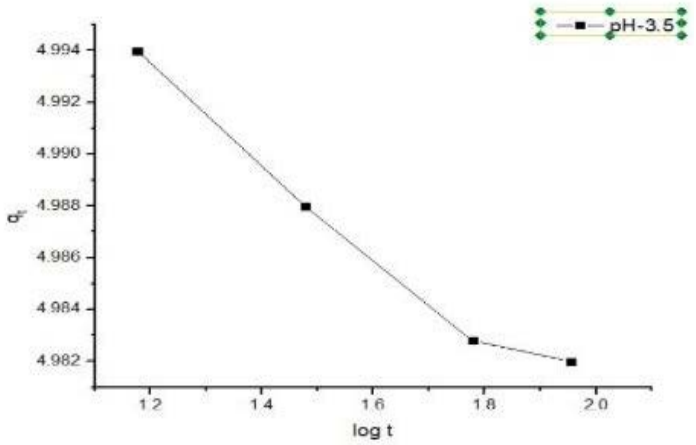

Figure 14. q_t Vs log t

Table 1. Residual concentration of Pb(II) after treatment with Bentonite and Charcoal

Sample No	Initial concentration in ppm	pH	Mass of bentonite	RPM	Time(minutes)	Residual concentration in ppm
B11	50	8.7	1g	221	15	0.01653
B12	50	8.7	1g	221	30	0.02276
B14	50	8.7	1g	221	60	0.02291
B15	50	8.7	1g	221	90	0.02293
B16	50	8.7	2g	221	15	0.02785
B17	50	8.7	3g	221	15	0.02531
B18	50	3.5	1g	221	15	0.05694
B19	50	3.5	1g	221	30	0.1173
B21	50	3.5	1g	221	60	0.1714
B22	50	3.5	1g	221	90	0.1581
B23	50	3.5	2g	221	15	0.05574
B24	50	3.5	3g	221	15	0.09014
B25	50	8	Bentonite+ charcoal (I:I)	221	15	0.0172
B26	50	8		221	30	0.011
B27	50	8		221	45	0.0136
B28	50	8		221	60	0.0139
B29	50	8		221	90	0.0021
B30	50	8	2g	221	15	0.01705
B31	50	8	3g	221	15	0.0192
B32	50	3.3	1g	221	15	0.0085
B33	50	3.3	Bentonite+ charcoal (I:I)	221	30	0.0127
B34	50	3.3		221	45	0.0096
B35	50	3.5		221	60	0.0128
B36	50	3.5		221	90	0.0156
B37	50	3.5	2g	221	15	0.00588
B38	50	3.5	3g	221	15	0.0044

Conclusion: The studies concluded that bentonite was a potential adsorbent of Pb^{2+} from water. The removal percentage is 99.7 for an initial concentration of 50 ppm. The results showed that Langmuir adsorption isotherm was followed and first order kinetics fitted the experimental values.

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Funding Declaration: No fund had been provided by anybody for conducting the research.

Data availability declaration: We declare that all the concerned data have been incorporated and given below the Reference section. Thus all the data have been made available and the data is original and based on laboratory work.

Author Contribution declaration: All the three authors have contributed significantly.

Pallavi Kumari has done the laboratory work in the department. Dr. Ashok Kumar Jha prepared and supervised the manuscript. Dr. Usha Sharma helped in conducting analytical tests outside the laboratory.

Data Availability Statement

All the data used in the manuscript are available with the author and will be provided when needed.

Additional Information

The authors do not have any conflict of interest

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