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REMOVAL OF LEAD (II) FROM AQUEOUS WASTE USING (CD-PCL-TiO₂) BIO-NANOCOMPOSITES

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Abstract:

Lead (Pb) pollution in our water system is a major concern, as this metal is toxic even at low concentration. This study aims to fabricate a bio-nanocomposite (cyclodextrin-polycaprolactone titanium dioxide) that will be used as an adsorbent for the removal of lead in aqueous waste. In this study, titanium dioxide was synthesized via sol-gel technique then incorporated in a polymer blend (CD-PCL) via solution blending method. The resulting bio-nanocomposites were characterized using Scanning Electron Microscopy (SEM), transmission electron microscope (TEM) and Brunauer Emmett and Teller (BET). The effect of how factors such as pH, concentration and adsorbent dose affect the removal efficiency of the bio-nanocomposites were studied. Maximum adsorption of lead obtained was 98% at pH 9.7, 10 ppm with 0.005 g dosage. Kinetic studies and adsorption isotherms were also investigated. The adsorption data fit Langmuir isotherm. Pb (II) obeyed pseudo-second order kinetics.

Keywords: Nanocomposite; Adsorption; Aqueous waste; Isotherm; Kinetics.

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1. INTRODUCTION

Water is the most vital substance and valuable resource for human civilization; therefore it is crucial to keep it clean and toxin free. Access to fresh and potable drinking water is regarded as one of the most essential humanitarian goals, and still is a foremost global challenge even to date¹. Various water resources are contaminated by heavy metals and these contaminants are known to have several harmful health effects on living organisms due to their toxicity. Cadmium (Cd), arsenic (As), chromium (Cr) and lead (Pb) are some of the heavy metals that cause toxicity in our water systems². This study focuses on the removal of lead from wastewater. Lead is released in water streams as a result of industrial processes such as electroplating, battery manufacturing, metallurgical industry, acid mine drainage and lead smelting, to name a few. Our water streams have high concentrations of Pb which exceed the limit set by the World Health Organization. The World Health Organization (WHO) reported the maximum acceptable limit for lead in drinking water to be 0.05 mg/L³. Concentration levels above this limit may cause ill-health effects such as reduced growth and development, cancer, organ damage, kidney disease, nervous disorders and in extreme cases may even result in death⁴⁻⁶. Therefore, elimination of these metals before they are discharged into the water systems is essential.

Techniques such as ion-exchange, precipitation, solvent extraction, adsorption, chemical precipitation and reverse osmosis have been employed for the removal of toxic metals from wastewater⁷. However, adsorption is considered to be one of the most promising techniques due to the advantages it has over conventional methods, such as removal of metals even at low concentrations, ease of operation, high selectivity, low cost, adsorbent of choice, least sludge production and regeneration of adsorbent⁸, amongst others. However, these adsorbents alone cannot efficiently remove heavy metals from wastewater and some of them are labeled as being expensive. As an alternative, recent studies have shown great interest on the technology of bionanocomposite for the removal of toxic metals. In this study we fabricated bionanocomposites (CD-PCL-TiO₂) for the removal of Pb. Cyclodextrins (CDs) are natural group of macro cyclic oligosaccharides composed of glucose units connected by α -1,4-glycosidic linkages in a torus shaped structure with numerous available hydroxyl groups that are active sites for forming different types of derivatives and linkages^{9,10}.

Because of their nontoxicity, biodegradability, and low affinity of sorption to the solid phase at a wide range of pH values, cyclodextrins are considered advantageous over regular surfactants¹¹. Polycaprolactone is aliphatic polyester composed of hexanoate repeat units. PCL is prepared by the ring-opening polymerization of the cyclic monomer ϵ -caprolactone using stannous octoate as catalyst¹². PCL is a semi-crystalline polymer having a glass transition temperature (T_g) of -60 °C and melting point ranging between 59 °C and 64 °C. PCL is a hydrophobic, biodegradable, nontoxic biopolymer which displays a rare property of being miscible with many other polymers¹³. Titanium dioxide is incorporated into the polymer blend (CD-PL) to enhance properties such as thermal stability and surface area.

2. MATERIALS AND METHODS

2.1 Materials

All chemicals (AR grade) were purchased from Sigma Aldrich, South Africa. Titanium (IV) isopropoxide (TTIP), (97% purity) and 2-propanol (C_3H_8O), anhydrous, 99.5% were used for the synthesis of titanium dioxide. Deionized water was used as a hydrolyzer. For preparation of the polymer blends and the bio-nanocomposites, crystalline β -cyclodextrin (CD) and polycaprolactone (PCL), average mn 80,000 and toluene, for HPLC, 99.9% were used. For preparation of lead (Pb) stock solutions (100 ppm), Lead (II) chloride, powder, 98% and deionised water were employed.

2.2 Synthesis of titanium dioxide.

Titanium dioxide (TiO_2) was synthesised via sol-gel method¹⁴ using titanium isopropoxide (TTIP) as a precursor. Figure 2.1 depict a step by step sol-gel synthesis of titanium dioxide. TTIP and isopropyl alcohol were used as the starting materials where, 100 ml isopropyl alcohol was added to 15 ml of TTIP in a 200 ml beaker. The mixed solution was then stirred for 10 minutes using a magnetic stirrer. For the hydrolysis reaction, 10 ml of de-ionised water was added to the solution drop wise. The solution was continuously stirred for 2 hours. The mixed solution was transformed into a gel and aged for 24 hours. After aging, it was dried overnight. The dried material was then calcined at different temperatures.

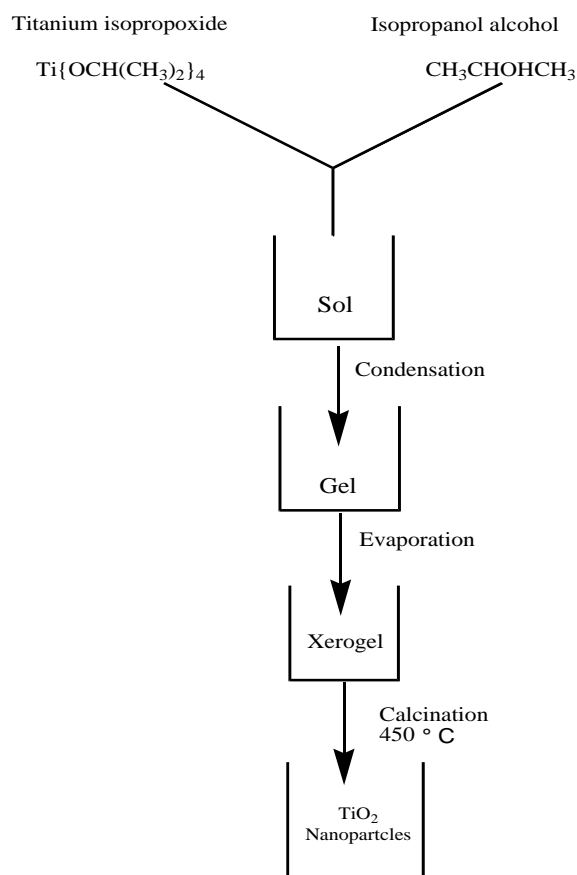


Figure 2.1 Titanium dioxide (TiO₂) synthesis via sol-gel method.

2.3 Synthesis of the polymer blends and bio-nanocomposites

2.3.1 Polymer blends preparation

The polymer blends were synthesized using a solution blending technique. The polymer blends were prepared using the ratios presented in Table 2.1. The mass percentage of each biopolymer was calculated using equation (1). The weighed masses of each polymer were dissolved separately in different beakers using toluene as a common solvent. Both mixtures were stirred until the polymers were dissolved using a magnetic stirrer. After dissolving, the two solutions were mixed together to form a polymer blend under constant stirring. The solution was then dried at 100 °C for 24 hours to allow the solvent to dry out. All the ratios of the polymer blends were synthesised using the same method. The polymer blends were then used in application of the removal of heavy metals in synthesised aqueous waste to get a best ratio with high removal efficiency to be incorporated with the nanoparticle.

$$\%M = \frac{W_i}{W_t} \times 100 \quad (1)$$

Where: %*M* is the mass percentage

W_i and W_t are the initial and total mass

Table 2.1 Mass percentages of polymer blends.

Cyclodextrin %	Polycaprolactone%
95	5
90	10
85	15
80	20
75	25

2.3.2 Bionanocomposite preparation

Bio-nanocomposite represent a new generation of nanostructured materials. These groups of materials are made up from combining natural polymers (biopolymers) and an inorganic material with at least one dimension on the nanometer scale. Polymer blend differ from bio-nanocomposite in such a way that they do not comprises of a nanoparticles. Polymer blend is defined physical mixture between two or more polymers with or without chemical interaction. The bio-nanocomposite (cyclodextrin-polycaprolactone-TiO₂) was fabricated using a solution blending technique. Firstly the weight percentage masses of each component (cyclodextrin, polycaprolactone and TiO₂) were calculated using equation 1. Cyclodextrin and polycaprolactone were separately dissolved in toluene under constant stirring for 2 hours. Polycaprolactone was then added into the dissolved cyclodextrin solution and stirred for two hours to allow the biopolymer to blend. TiO₂ was then added into the mixture under continuous stirring. The sonicator was then used to further disperse the TiO₂ nanoparticle into the polymer blend. The solution was then dried at 100 °C overnight.

2.4 PREPARATION OF STOCK SOLUTION (100 PPM OF LEAD)

To prepare 100 ppm stock solution of lead, 0.68 g of lead chloride was weighed. The weighed mass was transferred to a 500 ml volumetric flask and filled it to the mark with distilled water. The solution was then stirred using a magnetic stirrer until the lead chloride dissolved.

2.5 CHARACTERIZATION OF BIO-NANOCOMPOSITES.

2.5.1 Scanning electron microscopy (SEM)

A JOEL (JSM 840) Scanning Electron Microscope instrument was used to examine the surface morphology of the materials synthesized. The instrument was run under the following conditions: 15 kV acceleration voltage, working distance of 20 and a spot size of 35. Doubled-sided carbon conductive scotch tape was used to deposit specimens. The samples were coated with gold since they are non-conductive. SEM for analysis and imaging of micro- and nano-structures was coupled with energy dispersive X-ray diffraction (EDX) for elemental analysis.

2.5.2 Fourier Transformed Infrared Spectroscopy

In this study a fourier transform infrared (FTIR) spectroscopy measurements were performed on a Perkin Elmer FTIR spectrometer 100 over the range of 4000–500 cm^{-1} . KBr powder-pressed pellets were used for the identification of the functional groups of the synthesized samples.

2.5.3 BET

Bet was conducted for measurement of specific surface area and porosity was carried out using Tristar II 3020, Germany. The analysis was carried out using the standard N_2 gas absorption method. Samples were degassed at 400 °C for 3 hours before running.

3. RESULTS AND DISCUSSION

3.1 FTIR - Fourier transform infrared spectroscopy

The FTIR spectra of CD-PCL and CD-PCL-TiO₂ are shown in Figure 3.1 In the FTIR spectrum of CD-PCL, all the major peaks for the individual biopolymers were present in

the polymer blend which suggest that the biopolymers were successfully blended. The peaks located at $3\ 339\ \text{cm}^{-1}$, $2\ 944\ \text{cm}^{-1}$, $1\ 732\ \text{cm}^{-1}$, $1\ 157\ \text{cm}^{-1}$ and $1\ 025\ \text{cm}^{-1}$ are assigned to the stretching vibration of O-H stretching, $-\text{CH}_2$ stretching, $-\text{C}=\text{O}$ stretching, C-O-O stretching and $-\text{O}$ stretching, respectively¹⁵. In the FTIR spectra of CD-PCL-TiO₂ similar peaks are depicted but with reduced peak intensity. This is because of the physical interaction of the presence of TiO₂. There is a slight shift in the peaks and this could be attributed to formation of bonds between the blend and the nanoparticle. Since the nanoparticle was added in a small quantity, its peak is hindered but should appear between 400 to $500\ \text{cm}^{-1}$ ¹⁶.

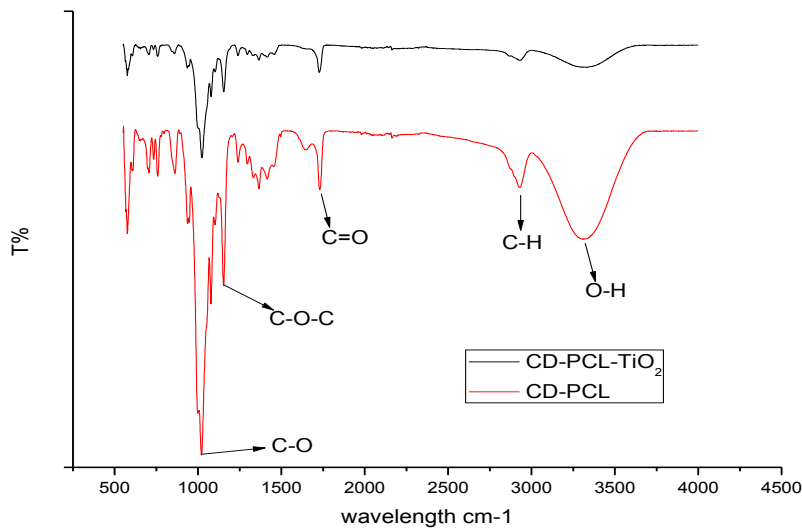


Figure 3.1: The Fourier transform-infrared (FTIR) spectra of CD-PCL and CD-PCL-TiO₂

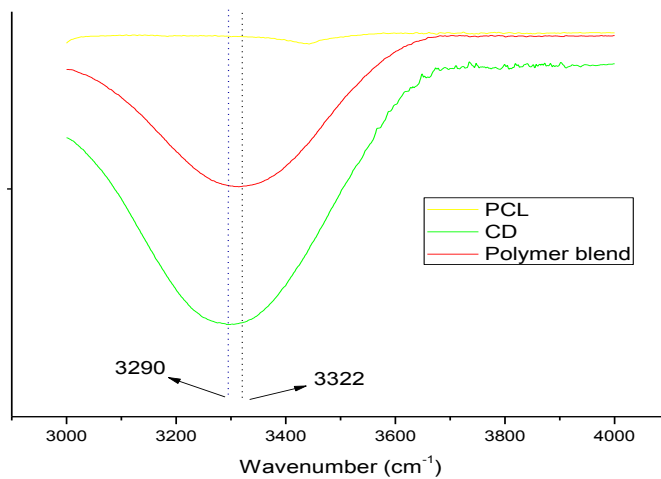


Figure 3.2: Infrared spectra of CD, PCL and polymer blend.in the $3\ 000$ to $4\ 000\ \text{cm}^{-1}$ region

The presence of different types of functional groups in a polymer blends leads to several types of interactions, be it repulsive or attractive. These interactions can be detected by FTIR. When CD is blended with PCL, the hydroxyl stretching band of pure CD shifts from $3\ 290\ \text{cm}^{-1}$ to $3\ 322\ \text{cm}^{-1}$ indicating the formation of hydrogen bonding between the hydroxyl group of CD and the carbonyl group of PCL. The two biopolymers can form two types of hydrogen bonding namely, hydroxyl-hydroxyl hydrogen bonding or hydroxyl-carbonyl hydrogen bonding.

3.2 TEM - Transmission electron microscope

TEM was used to evaluate the size, shape and aggregation of the CD-PCL-TiO₂ nanocomposite. As it can be seen (Fig. 3.3) CD-PCL-TiO₂ showed multi-morphological; these include rod-like structure with an average diameter of 395 nm, and few rectangular shapes. In addition agglomeration of CD-PCL-TiO₂ is observed. The particles are attached to each other, as the result forming an irregular crystal structure. However, TiO₂ nanoparticles are not visible, this is attributed to that TiO₂ was well distributed within the bionanocomposite matrix.

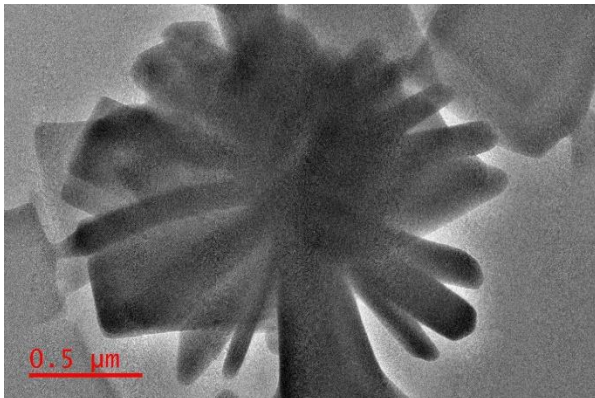


Figure 3.3: TEM image of CD/PCL/TiO₂.

3.3 SEM- scanning electron microscope and EDS- energy dispersive X-ray spectrometry

Figure 3.4 shows SEM images for surface morphology of TiO_2 , CD/PCL and CD/PCL/ TiO_2 . The SEM image of TiO_2 NPs reveals a spherical shape and the high agglomeration of particles. The TiO_2 NPs were observed to be present in the bionanocomposite. For the CD/PCL, it is shown that both polymers have a strong interaction and compatibility with each other. They have a homogeneous surface and this is because both the biopolymers are miscible with each other. In the CD/PCL/ TiO_2 bionanocomposites, the TiO_2 particles are randomly distributed in the composite matrix. There is a decrease in compatibility between the TiO_2 NPs and polymer matrix, which is caused by the reduction in the interfacial interaction between the NPs and the polymer matrix.

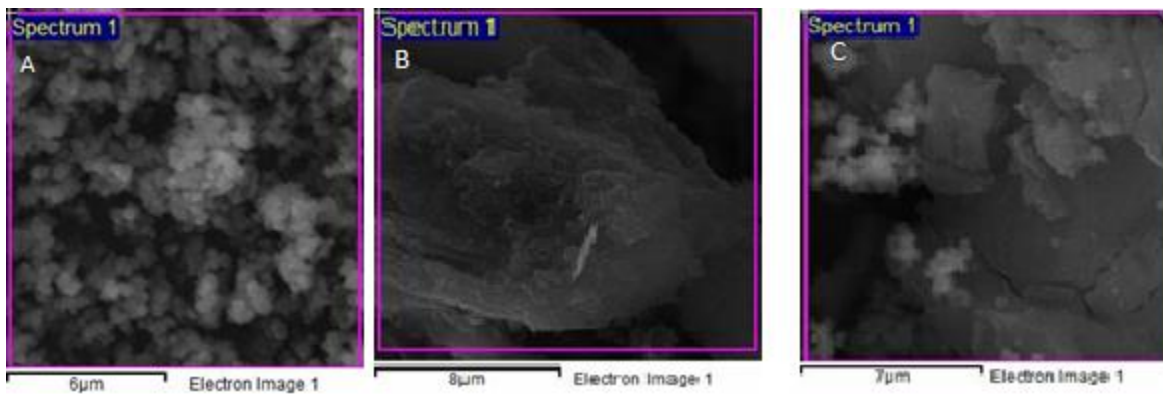


Figure 3.4: SEM micrographs of (A) TiO_2 , (B) CD/PCL and (C) CD/PCL/ TiO_2 .

3.4 Zeta potential

The change in zeta potential of CD-PCL- TiO_2 as affected by pH is shown in Figure 3.5. The zeta potential of CD-PCL- TiO_2 was measured at different pH values from 5 to 11. The isoelectric point of the bio-nanocomposite was reached at pH 8.8. Isoelectric point/ point of zero charge is a point where the surface of a material exhibits a net zero charge at a certain pH^{17} . From pH 5 to pH 8.8 the surface of the CD-PCL- TiO_2 showed a positive surface charge and below the point of zero charge, the surface charge of the CD-PCL- TiO_2 exhibited a negative charge. In this case, a negative charge at the surface point out that the molecular aligning of the CD-PCL- TiO_2 is such that the unsubstituted $-\text{OH}$ groups are facing the aqueous environment. This study is focused on the removal of Pb^{2+} from aqueous solution. Since Pb^{2+} is positively charged, a material that is negatively charged will be efficient in the removal of Pb^{2+} . Based on the results of the adsorption studies, the maximum removal of

Pb^{2+} by CD-PCL-TiO₂ was achieved at pH 9.7 (Figure 3.6). This findings is corroborated by the fact that CD-PCL-TiO₂ exhibited a negative surface from pH 8.8 and beyond.

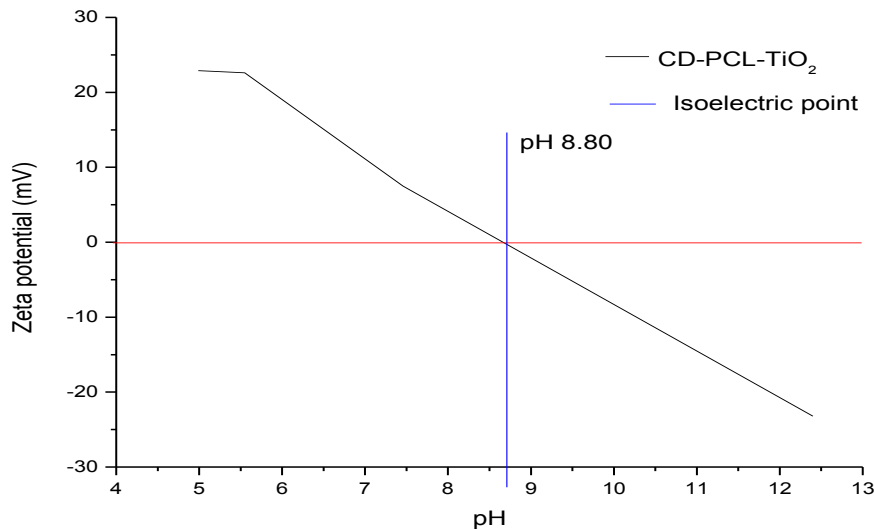


Figure 3.5: Zeta potential analyses of CD-PCL-TiO₂ as affected by different solution pH values

3.5 BET - Brunauer–Emmett–Teller

The BET technique was used to determine the pore size, pore volume and the specific surface area on CP-PCL-TiO₂, CD-PCL and TiO₂. Titanium dioxide proved to have a high surface area amongst all the samples. The high surface area of TiO₂ (61.7749 m²/g) correspond with the value found in literature¹⁸. The specific area of the polymer blend (CD-PCL 34.0458 m²/g) is low compared to TiO₂ this is due to the fact that TiO₂ have small particles compared to the polymer blend. Materials with small particles produce a large specific surface area. The surface area of the polymer blend CD-PCL increased from 34.0458 m²/g to 43.5196 m²/g upon incorporation of TiO₂. The TiO₂ particles penetrate the chains of the polymers and increase their surface area. The high surface area of the bio-nanocomposite (CP-PCL-TiO₂) is good for adsorption studies since adsorption strongly depends on the surface area of a material. The higher the surface area, the higher the adsorption capacity.

Table 3.1: BET surface area, pore size and pore volume

Sample	Pore volume	Pore size	Surface area
TiO ₂	0.107375 cm ³ /g	97.1268 nm	61.7749 m ² /g
CD-PCL	0.078195 cm ³ /g	176,2332 nm	34.0458 m ² /g
CD-PCL-TiO ₂	0.170875 cm ³ /g	137.8688 nm	43.5196 m ² /g

3.6 Adsorption studies

In adsorption studies, CD (85 %) - PCL (10 %) - TiO₂ (5 %) was used as an adsorbent. Adsorption studies of the bio-nanocomposites and the metal ion were done to determine the maximum Pb²⁺ removal efficiency in aqueous waste. The effect of concentration, dosage, pH and time was evaluated. The maximum Pb²⁺ removal percentage was found to be at a concentration of 10 mg/L. For the effect of pH, 0.0125 M HCl or 0.0125 M NaOH were used to find the desired pH. The solutions with a mixture of adsorbent and metal ions were agitated at a speed of 200 r/min at room temperature. After adsorption, the solutions were filtered to remove the suspended solids and the amount of metal ions remaining was analysed using ICP-OES

3.6.1 Effect of pH

The adsorption of heavy metals from wastewater is strongly affected by the pH of the solution. Hydrogen ion concentration in the adsorption process is considered as one of the most important parameters that influence the adsorption behaviour of metal ions in aqueous

solution¹⁹. Figure 3.6 shows the removal percentages of Pb^{2+} as a function of pH. The maximum adsorption of Pb^{2+} was found to be at pH 9.7. The amount of adsorption is a minimum at a pH of less than 4 and increases as the pH increases. The adsorption efficiency is a maximum at pH 9.7, and the amount of adsorption decreases with an increase above this limit. At a higher pH the surface charge of the bio-nanocomposite is more negative; this is in accordance with the pH titration graph (Figure 3.5). When the pH value of the solution is higher than the point of zero charge, the surface charge of the adsorbent will be negatively charged.

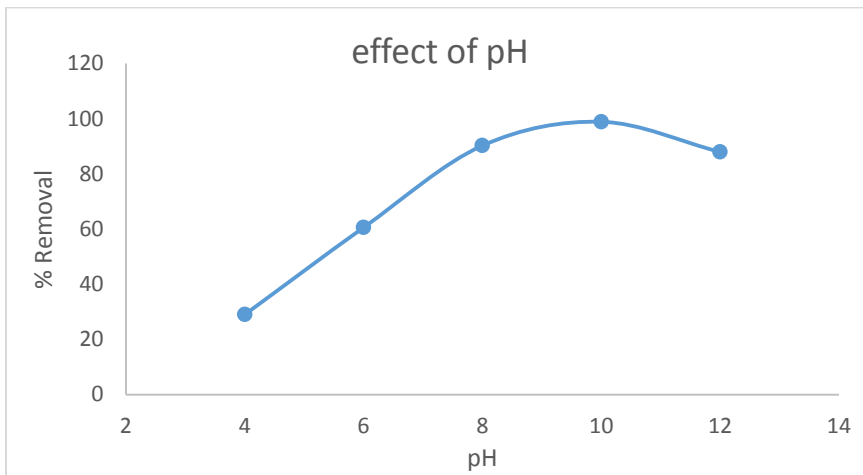


Figure 3.6: Effect of pH on Pb^{2+} adsorbed

3.6.2 Effect of metal concentration

The initial metal concentration is another factor that influences the adsorption process. Figure 3.7 shows the percentage removal of Pb^{2+} as a function of concentration. The maximum amount adsorbed is at 10 mg/L. As the concentration increases the percentage removal of the metal starts to decrease. This can be explained on the basis that the increase in the number of ions competing for the available binding sites and also because of the lack of active sites on the adsorbent at higher concentrations. Therefore, more metal ions were left un-adsorbed in solution at higher concentration levels²⁰.

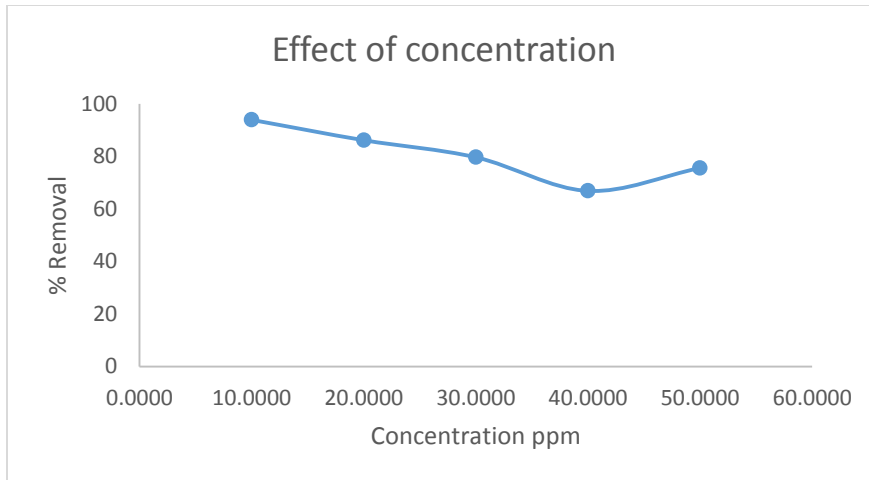


Figure 3.7: Effect of initial concentration on Pb^{2+} adsorbed

3.6.3 Effect of adsorbent dose

The adsorbent dose is another factor which influences the adsorption process. It is based on the assumption that when the adsorbent doses increase, the adsorption rate also increases²¹. However, the adsorption rate can decrease if the adsorbent dose further increases, due to the presence of more occupied active sites when the concentration gradient of the adsorbate is kept constant²². Figure 3.8 depicts a graph of percentage removal of Pb^{2+} as a function of dosage. The maximum percentage removal of Pb^{2+} is observed to be at 0.05 g. as the adsorbent dosage is increased the removal efficiency decreases. This is due to the aggregation of adsorbent and consequently the decrease in the available sites.

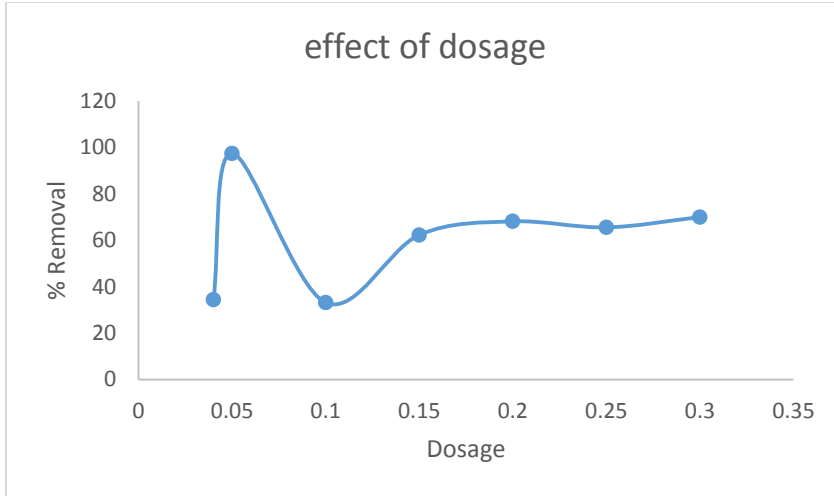


Figure 3.8: Removal percentages of Pb^{2+} as a function of dosage

3.7 Equilibrium isotherms

3.7.1 Langmuir adsorption isotherm

The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The isotherm equation further assumes that adsorption takes place at specific homogeneous sites within the adsorbent. The Langmuir equation is given by Equation (1).

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

In this study a plot of $\frac{C_e}{q_e}$ vs. q_e produced straight line which indicates that the adsorption of the contaminants on the bio-nanocomposite fits the Langmuir isotherm with a correlation coefficient (R^2) of 0.999.

To verify whether adsorption takes place at a specific homogeneous site within the adsorbent, R_L is calculated from the Equation (2). R_L is the separation factor which is calculated to check if the sorption system is favourable or not. Studies have shown that an R_L value

between 0 and 1 indicates favourable adsorption^{23,24}. In this study the R_L value was found out to be 0.20 which indicates favourable adsorption

$$R_L = \frac{1}{1 + bC_0} \quad (2)$$

R^2 , b and Q_0 values were calculated from this isotherm and they are given in Table 3.2.

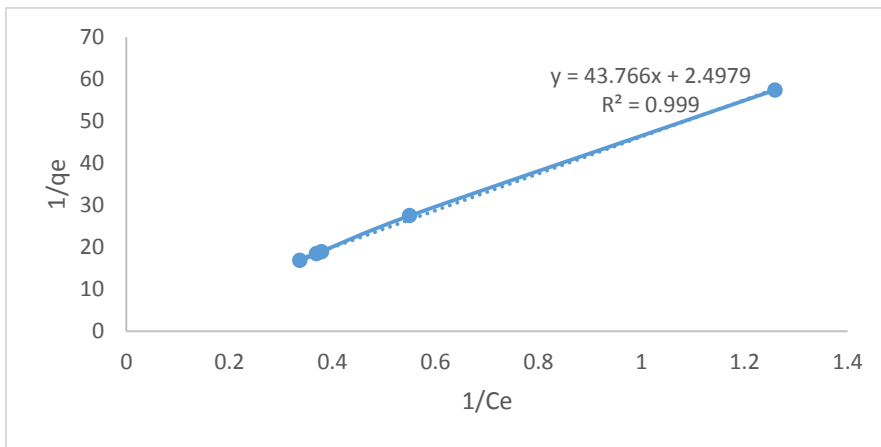


Figure 3.9: Langmuir isotherm

3.7.2 Freundlich adsorption isotherm

The Freundlich isotherm model is commonly used to describe the adsorption characteristics for the heterogeneous surfaces with interactions occurring between the adsorbed molecules and is not restricted to the formation of a monolayer. This isotherm is commonly used to describe the adsorption of organic and inorganic compounds on a wide variety of adsorbents. Freundlich suggested that the ratios of the amount of solute adsorbed onto a gained mass of adsorbent to the concentration of the solute in the solution are not constant at different concentration of solution^{25,26}. The Freundlich isotherm given in Equation (3) was used.

$$\log q_e = \log K_F \frac{1}{n} \log C_e \quad (3)$$

Figure 3.10 shows a plot of $\log q_e$ vs. $\log C_e$ which indicates that the adsorption fit the Freundlich isotherm model with a correlation coefficient of 0.997. As seen from Table 4.3, the n value was high enough for the separation of Pb(II) ions from aqueous solution and being above unity, indicative that the adsorption was physical.

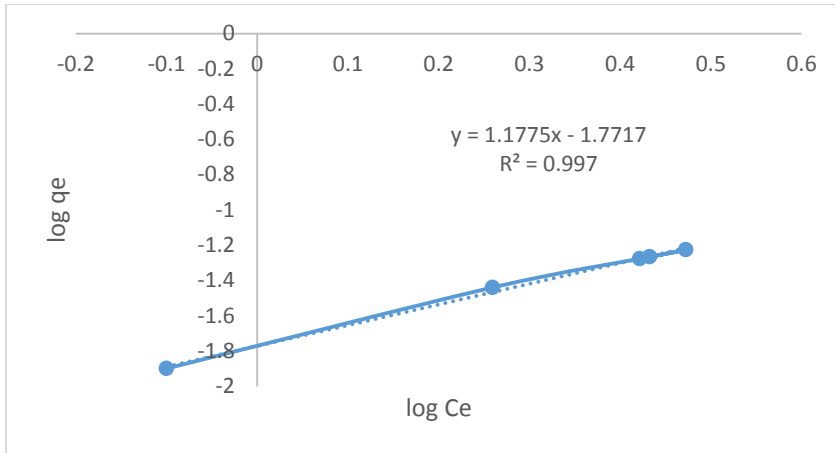


Figure 3.10: Freundlich isotherm

Table 3.2: Summary of adsorption isotherms

Adsorbent	Langmuir isotherm				Freundlich isotherm		
	Q_0	b	R_L	R^2	K_F	n	R^2
CD 85% – PCL 10% – TiO ₂ 5%	0.06	0.40	0.20	0.999	0.017	0.84	0.997

3.8 Adsorption kinetics

Kinetic studies were employed in order to determine the controlling mechanism of adsorption. This studies were carried out to investigate the time required for the aqueous and solid phase to reach equilibrium and how the amount of adsorbed metal changes with time. To investigate whether the adsorption followed monomolecular or bimolecular reaction, pseudo-first-order and pseudo-second-order models were employed. The pseudo-first-order equation is given by Equation (4).

$$\log(q_e - q_t) = \log q_e - \frac{K_{ad}}{2.303} t \quad (4)$$

In this study, a plot of $\log(q_e - q_t)$ versus t was plotted. The correlation coefficient was calculated from the linear plot and it was found to be 0.8681. The poor correlation coefficients indicate that the sorption of Pb^{2+} ions onto bio-nanocomposite could not obey pseudo-first-order kinetics.

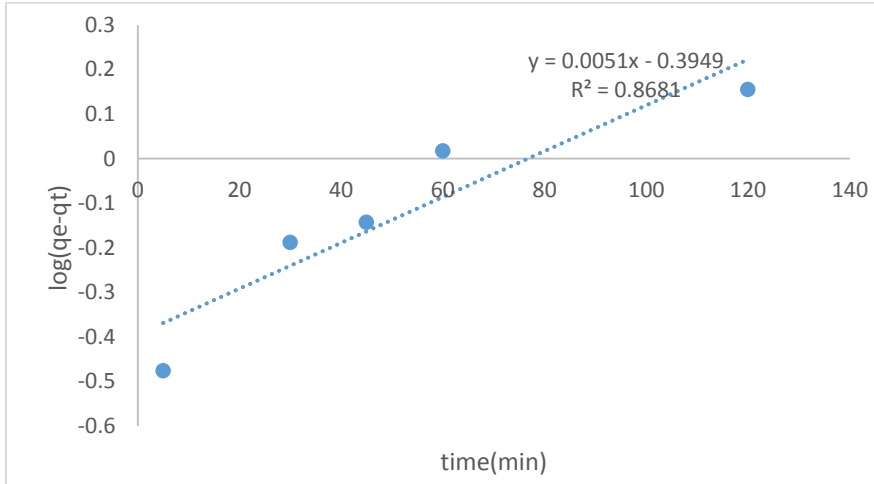


Figure 3.11: Pseudo-first-order kinetics

The pseudo-second-order equation is expressed in the following form:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \quad (5)$$

The plot of $\frac{t}{q_t}$ versus t should give a straight line if the second-order kinetics is applicable.

The gradient is given by $\frac{1}{k}$ and the y-intercept is given by $\frac{1}{kq_e^2}$. The correlation coefficient of

0.9735 obtained from the linear fit is an indication that the adsorption follows the pseudo-second-order model best, compared to the correlation coefficient obtained in the pseudo-first-order model.

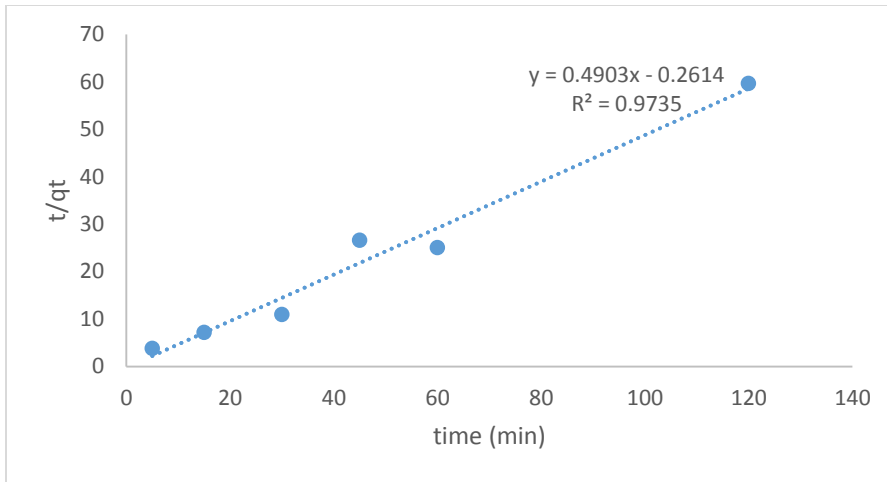


Figure 3.12: Pseudo second-order kinetics

4. CONCLUSIONS

This study proved that bio-nanocomposites could be used as adsorbent material for removal of Pb(II) ions from aqueous waste. Adsorption experiments proved that factors such as pH, contact time, initial concentration and adsorbent dose of the solution influenced adsorption of Pb(II) by CD-PCL-TiO₂. The maximum uptake of Pb(II) ions was 98% obtained at pH 9.7, concentration 10 ppm with 0.005 g dosage. The adsorption data of the adsorbent seems to be in good agreement with Langmuir isotherm than Freundlich. This suggest monolayer type of adsorption. The kinetic data best fit follow pseudo second-order rate equation. The synthesised adsorbent (CD-PCL-TiO₂) was shown to have distinct advantages and may be the preferred choice over other adsorbents as it removes heavy metals without introducing secondary pollutants into the water.

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