A Novel Approach for Adsorption of Lead (II) Ions from Wastewater Using Cane Papyrus

Mohammed Jaafar Ali Al-atabe

Al-Mustansaryah University, Baghdad- Iraq

Abstract

Lead (II) ions are a very toxic element known to cause detrimental effects to human health even at very low concentrations. An adsorbent prepared using Cane Papyrus was used for the adsorption of lead (II) ion from aqueous solution. Batch experiments were performed on simulated aqueous solutions under optimized conditions of adsorbent dosage, contact time, pH and initial lead (II) ion concentration at 25C^{o}. The Freundlich isotherm model more suitably described the adsorption process than the Langmuir model with linearized coefficients of 0.986 and 0.9733, respectively. Pseudo-second order kinetic equation best described the kinetics of the reaction. Fourier transform infra-red analysis confirmed the presence of amino (–NH), carbonyl (–C=O) and hydroxyl (–OH) functional groups. Furthermore, 0.2M HCl was a better desorbing agent than 0.2 M NaOH and de-ionized water. The experimental data obtained demonstrated that Cane Papyrus can be used as a suitable adsorbent for lead (II) ions removal from wastewater.

Keywords: Adsorption; Lead (II) ions; Kinetics; Cane Papyrus; Removal Efficiency.

Introduction

Heavy metal pollution has been one of the most challenging environmental problems due to their toxicity, persistence and bioaccumulation tendencies [1, 2]. Most industries produce and discharge metal-containing wastes mostly into water bodies, which affect the aesthetic quality of the water and also increase the concentrations of metals present [3, 4]. Activities such as mining and smelting operations, wastewater treatment facilities, various agricultural works and metal castings contribute significantly to the concentration of heavy metals in the environment [5,6]. Heavy metal contamination is not a recent problem, but its management and prevention is still of global concern [6]. Lead(II) ions has been implicated as being responsible for intellectual disabilities in children and causes about 143,000 deaths annually in developing countries [7,8]. Young children are more vulnerable to lead exposure because it affects the development of brain and nervous system [7,9]. It also causes kidney damage and high blood pressure in adults and can lead to miscarriage, low birth weight, stillbirth and premature birth in pregnant women [7–l0]. Ingestion of lead contaminated water has been implicated as a major route of lead toxicity [8–l0]. Several techniques have been designed for heavy metals removal from aqueous solutions and these include ion exchange, chemical precipitation/co-precipitation, filtration, coagulation, membrane technologies and commercial activated carbon [2,ll–l3]. The major disadvantages of these methods lie in the cost involved the efficiency of the processes and disposal of wastes generated [ll–l3]. These shortcomings have made researchers seek alternative techniques for heavy metal remediation. Adsorption using naturally available materials has been reported to be efficient in the removal of hazardous metals from industrial effluents. The materials employed in this technique often range from the use of microbes and naturally abundant plant materials to dead waste biomass [l2, l4]. The sorption capacity of some bio-sorbents is high due to the presence of adequate functional groups that sequester metals from aqueous solutions [ll]. The use of this technique is cheap, environmentally friendly and naturally available. These bio-based materials have shown the tendency to remove metals at trace levels, thus overcoming some of the major shortcomings of the conventional methods [l4]. Several adsorbents from plant origin have been used and modified for heavy metal removal from wastewater and aqueous solution which include: maize tassels , watermelon shell , coffee beans , coconut shell , peanut shell , Annona squamosa shell , rice husks , rice bran , orange peels , sunflower stem , groundnut shells , and avocado seed , This study presents the use of Cane Papyrus as a potential, novel, environmentally friendly and low cost adsorbent for the remediation of Pb^{+2} ions from aqueous solution and wastewater samples.

The objective of the present study is to investigate the adsorption potential of Cane Papyrus in the removal of Pb^{+2} ions from aqueous solution. The effects of pH, adsorbent amount, contact time and concentration of metal ions in the solution. The Langmuir and Freundlich isotherms models are used to investigate equilibrium data. The adsorption mechanisms of Pb^{+2} ions onto Cane Papyrus are also evaluated in terms of kinetics and thermodynamics

Experimental Section

Preparation of Adsorbent Cane Papyrus was collected from farmlands in the marshes of Messan, south of Iraq . The leaves were carefully detached from the stem of the plant and washed thoroughly with tap water to remove dirt, soil particles and debris and subsequently sun dried for l0 days. The dry biomass was ground to fine powder using a hammer mill and weighed. The resulting powder was fractionated using analytical sieves. Particles of l0-200 µm were used for simulated wastewater samples. The adsorbent showed a fluffy and highly porous and rough microstructure containing some voids and cracks which is suitable for the adsorption of Pb^{+2} ions . The concentration of Pb^{+2} ions in aqueous solution was analyzed using Atomic Absorption Spectrometer (AAS). Mechanical shaker with adjustable speed, time was used for agitation and pH meter was used for all pH measurements. The chemical composition of the adsorbent was analyzed using X-ray Fluorescence spectrometer. The chemical composition of the adsorbent is presented in Table 1.

Table (1) Chemical Composition of Cane Papyrus.

Compound	Wt %	Compound	Wt %
Na_2O	1.17	K_2O	11.7
MgO	6.93	CaO	23.9
Al_2O_3	6.15	SiO_2	23.6
TiO_2	1.33	P_2O_5	2.42
MnO	0.778	Fe_2O_3	12.8
SO_3	5.68	SrO	1.24
Cl	1.09	BaO	0.521

Surface area of the adsorbent was 1.96 m^2 /g (Table 2). This is comparable to 2 m^2 /g reported by Mousavi for waste rubber ash used for the removal of lead ions from aqueous solutions. The average pore diameter of Cane Papyrus was within the range of $10 < d < 1000 \times 10^{-8}$ cm and the adsorbent were classified as a mesoporous material. Similarly, BET surface areas of 1.083 m^2 /g and 2.52 m^2 /g for activated carbon from macadamia nuts used for phenol removal and maize tassels for heavy metal removal from polluted waters, respectively although adsorbents with higher surface areas have been widely reported in literature [15].

Table (2) Characteristics of Cane Papyrus.

Physical Parameters	Result
BET surface area (m^2 /g)	1.96
Micropore surface area (m^2 /g)	1.75
Total pore volume (cm^3/g)	0.01
Micropore volume (cm^3/g)	0.0095
Average pore diameter(Ao or 10^{-8} cm)	500

One gram of powdered Cane Papyrus was used for the adsorption of Pb^{+2} ions onto the surface of Cane Papyrus using mechanical shaker with the speed of 200 rpm at 25C°. The effect of adsorbent dosage was investigated by varying the initial mass of the adsorbent between 0.01–2.0 gm. The optimum dosage obtained was used for subsequent processes. Similarly, the effects of pH, initial lead (II) ion concentration and equilibration time were varied between 2–12 and 1–50 mg/l and 5–120 min, respectively. The percentage removal of Pb^{+2} ions from aqueous solution was estimated by using Equation (1):

$$\mathbf{Adsorption}(\%) = \frac{[\mathbf{Ci-Cf}]}{\mathbf{Ci}} \times \mathbf{100} \qquad \mathbf{(1)}$$

Where C_i and C_f are the initial and final metal ion concentrations, respectively.

$$\mathbf{qe} = \frac{\mathbf{(Co-Ce)V}}{\mathbf{w}} \qquad \mathbf{(2)}$$

Where qe is the amount of metal adsorbed in mg/g, C_i and C_e represent initial and equilibrium concentrations of metal ions in aqueous phase. V is the volume of the solution in liters (l) and W is the weight of the adsorbent used in grams.

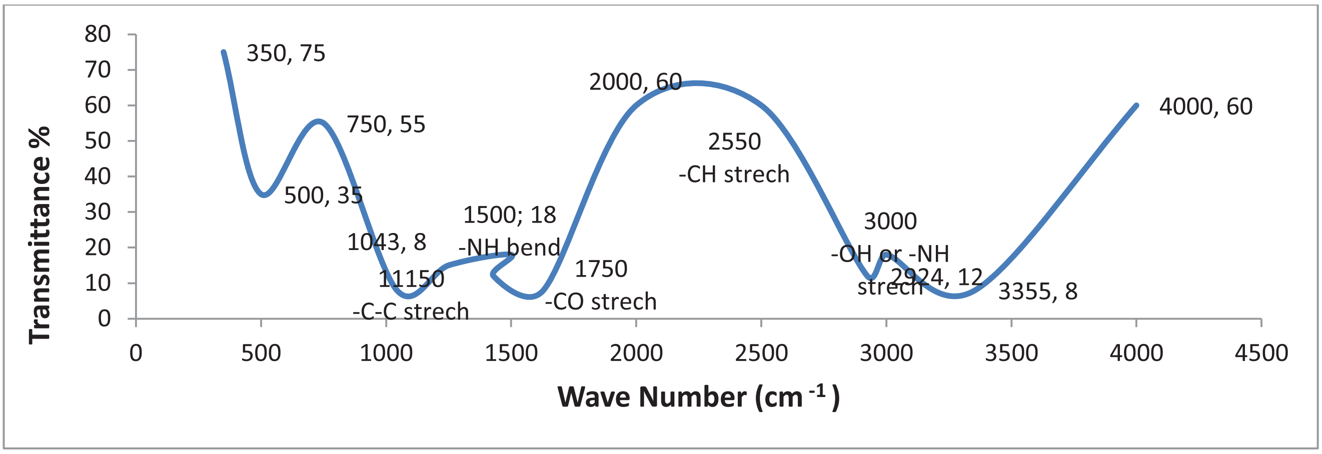
Studies of Desorption

One gram of adsorbent was introduced into a 100 ml Teflon container containing 10 mg/l Pb^{+2} ions. After equilibration for 60 min, the adsorbent was recovered. Residual Pb^{+2} ions on the surface of the used adsorbent were removed by washing it three times with ultra-pure water. De-ionized water, 1M NaOH and 1M HNO_3 were tested as potential desorbing agents. 40ml of the desorbing agents were introduced into a 100 ml Teflon container containing the recovered adsorbent and equilibrated for 60 min at a speed of 200 rpm and T = 25C°. The aqueous solutions after equilibration were centrifuged and the supernatant were analyzed to determine the concentration of Pb^{+2} ions after desorption.

Results and Discussion

Infra-Red Spectroscopy Results

The results from the Fourier transform infra-red showed a broad peak at 3000 cm^{-1} with a high transmittance frequency, which can be attributed to either –OH or –NH groups [1,16]. As shown in Figure 1, the band observed at 2550 cm^{-1} is possibly due to C–H stretching vibrations of saturated aliphatic compounds while the band at 1750 cm^{-1} can be attributed to –NH bending vibration of primary amines . A small peak was observed at 1350 cm^{-1} and corresponds to v(C–C) stretching vibrations of aromatic rings . The peaks observed at 1200 cm^{-1} and 1150 cm^{-1} corresponds to the C–O stretch of alcohols, carboxylic acids, esters or ethers . The absorption band at 500 cm^{-1} can be due to the presence of an alkyl halide. Also confirmed that mucilage extracted from Diceriocaryum species contains carboxyl functional group. The presence of acidic functional groups is responsible for its adsorptive property . The stated clearly from their studies of natural plant materials that the biochemical characteristics of acidic functional groups are responsible for their metal ion uptake.



Fig(1) Infra-red spectra of the Cane Papyrus.Effect of pH

The competition between metal ions and protons for sorption sites is also affected by the pH of the solution. The effect of pH on adsorption of Pb^{+2}onto Cane Papyrus is shown in Figure (2). Lead (II) ion removal was slightly affected by changes in the pH of the solution. There was a slight increase in metal uptake 98.8 % at pH value 4. This was accompanied by a slight decrease after pH 4 (98.8%). There was a relatively constant percentage removal from pH 5–6.5 (98.8%–99%). However, a decrease in removal efficiency was observed at pH value of after 7 (96%). the maximum adsorption of Pb^{+2}ions occurred at pH 6.5. At pH values higher than 7, Pb^{+2} ions started precipitation

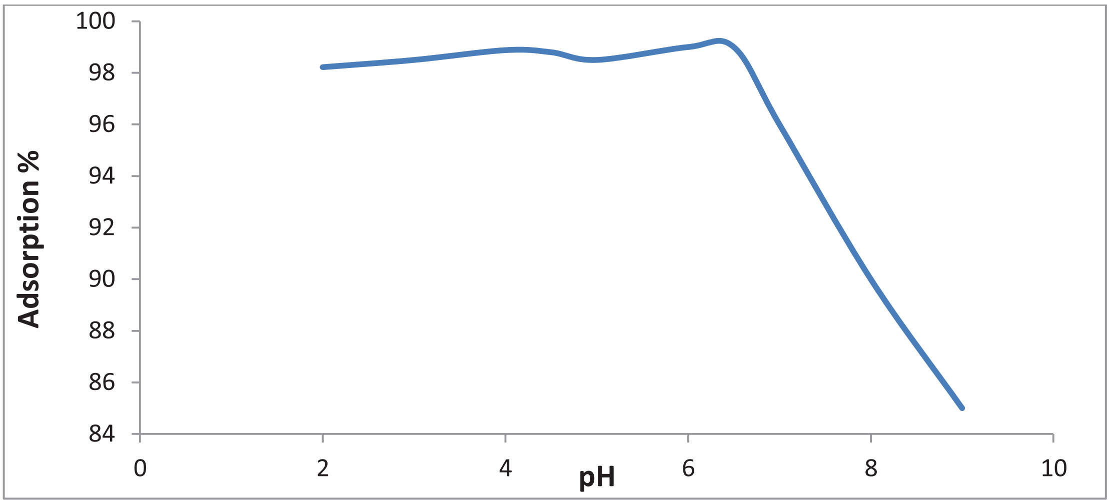


Fig.(2) Effect of pH on the adsorption efficiency of pb^{+2} ions onto Cane Papyrus.

Effect of Contact Tim

Figure (3) shows the effect of contact time on the adsorption of pb^{+2} ions onto Cane Papyrus. There was a rapid uptake of pb^{+2} ions with a removal efficiency of 85% within five minutes of equilibration. The rapid uptake was due to fast transfer of the metal ion onto the empty adsorption sites on the surface of the adsorbent. Afterwards, there was a slow additional uptake of the metal ion from 5 min up to 60 min of equilibration, accounting for 98.5% pb^{+2} ions removal. There was no significant increase in the removal of pb^{+2} ions after 60 min indicating that equilibrium condition has been reached. This shows that the remaining empty sites on the adsorbent has been occupied leading to repulsive forces between adsorbed pb^{+2} ions on the adsorbent and those in the aqueous phase.

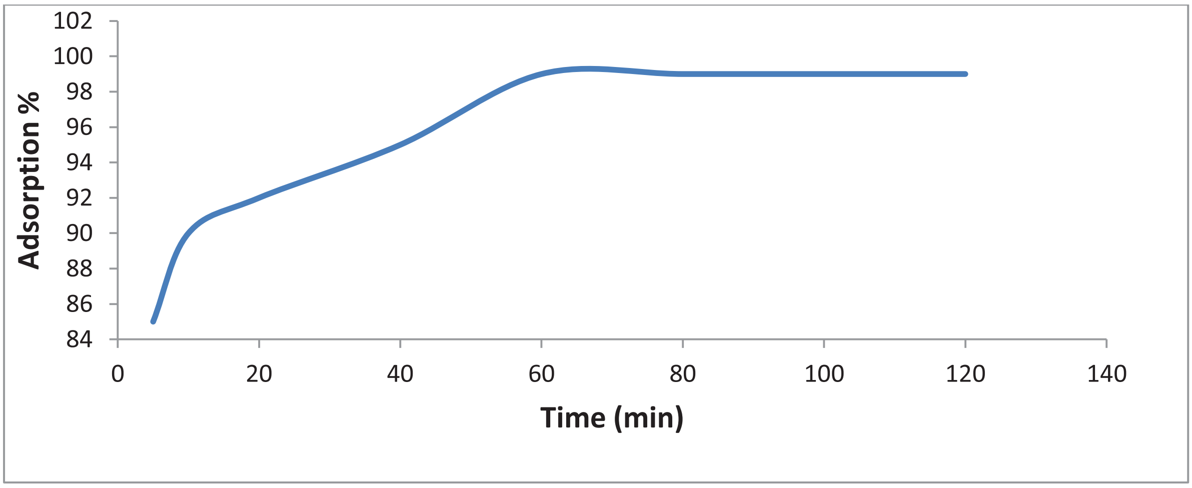


Fig. (3) Efficiency adsorption of pb^{+2} ions with contact time onto Cane Papyrus.

Effect of Adsorbent Dosage

The effect of adsorbent dosage on the adsorption of pb^{+2} ions was determined by varying the adsorbent dosage from l0–200 g. The percentage removal of pb^{+2} ions by the adsorbent increased sharply from 30% at adsorbent dosage of l0 g to 95% at l00 g but decreased slightly to 85% when 200 g was used. The initial rapid increase observed could be due to the increased availability of binding sites and surface area which makes the adsorption of the ions quite easy until equilibrium was reached. The subsequent decrease in the removal efficiency could be due to aggregation or overlapping of the adsorption site. Figure (4) represented these changes.

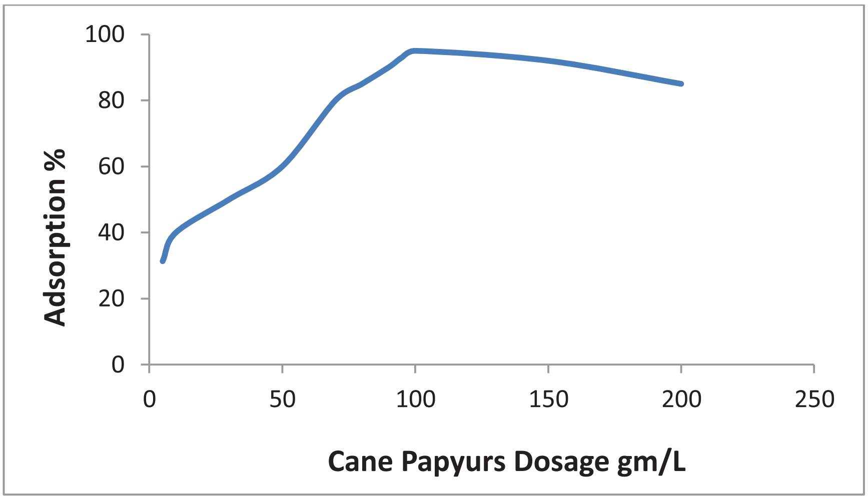


Fig. (4) Effect of Cane Papyrus Dosage on the adsorption efficiency of pb^{+2} ions.

Adsorption Isotherms

Experimental data for the adsorbed metal against initial concentration were fitted into the langmuir and Freundlich adsorption isotherms. The langmuir model assumes that the adsorption of an ideal gas on an ideal surface occurs only at fixed number of sites and each site can only hold one adsorbent molecule (monolayer). It also assumes that all available sites are equivalent and there is no interaction between adsorbed molecules on adjacent sites. The linearised equation for langmiur model is represented by Equation (3).

$$\frac{1}{qe} = \frac{1}{qmax} + \{\frac{1}{bqmax}\}\frac{1}{Ce} \qquad (3)$$

where Ce is the equilibrium concentration of the metal ion (mg/l), q_e is the quantity of pb^{+2} ions adsorbed at equilibrium (mg/g), q_{max} is the maximum amount adsorbed (mg/g) and b is the adsorption constant (l/mg). The plot of l/q_e against l/Ce gave a straight line with a regression coefficient of 0.9733 Figure (5) indicating that the adsorption conforms to langmuir model. The maximum concentration of pb^{+2} ions adsorbed and the adsorption capacity was calculated from the slope and intercept of the plot and are shown in Table (3). The conformity of the adsorption process to langmuir model was determined using Equation (4):

$$Rl = \frac{1}{(1+bCo)} \quad (4)$$

Where R_l is the separation factor, Co is the initial metal concentration (mg/l) and b is the langmuir constant (l/mg). $R_l > 1$ indicates an unfavorable monolayer adsorption process, $R_l = 1$ linear, $0 < R_l < 1$ favorable and $R_l = 0$ irreversible. The result obtained from this study has an R_l value between zero and one, indicating a favorable adsorption process. This implies that chemisorptions process duly explains the adsorption of pb^{+2} ions onto Cane Papyrus.

Table (3) Freundlich and Langmuir constants for adsorption of pb^{+2}ions on Cane Papyrus.

Langmuir model	q_{max} mg/gm	b	R_l l/mg	R^2
	45.5	0.213	0.0-1.0	0,9733
Freundlich model	K_f	n	R^2	
	0.2	0.0906	0.9869	

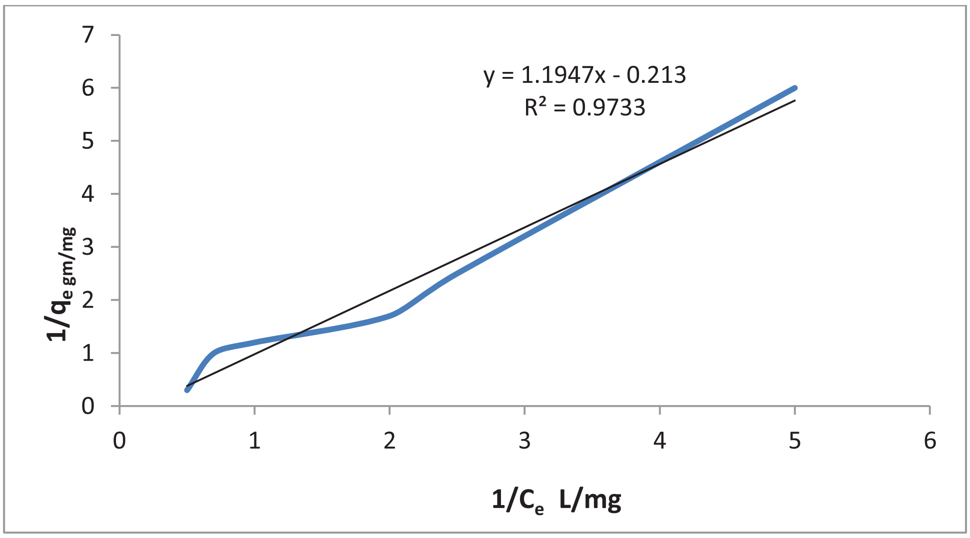


Fig.(5) Langmuir plot for pb^{+2} ions adsorption onto Cane Papyrus.

The Freundlich isotherm model describes a multi-site adsorption for heterogeneous surfaces and can be represented by Equation (5);

$$q_e = K_f\, Ce^{l/n} \quad (5)$$

where K_f is the adsorption capacity (l/mg) and l/n is the intensity of the adsorption showing the heterogeneity of the adsorbent site and the energy of distribution . Equation (6) was obtained by taking the logarithm of Equation (5):

$$\log q_e = \log K_l + \frac{l}{n} \log C_e \qquad (6)$$

A plot of logqe against logCe gave a linear graph with a regression coefficient of 0.9869 (Figure 6), indicating that the adsorption also fits into Freundlich model. From the linearised coefficients obtained from both models, the langmuir model best described the adsorption process than the Freundlich model. This suggests a chemisorptions process rather than a physisorption process. The constants obtained for the Freundlich and langmuir plot is presented in Table (3). A maximum adsorption capacity of 45.5 mg/g was obtained in this study for the adsorption of pb^{+2} ions. The use of Cane Papyrus is therefore a potential candidate for the removal of pb^{+2} ions in water and wastewater.

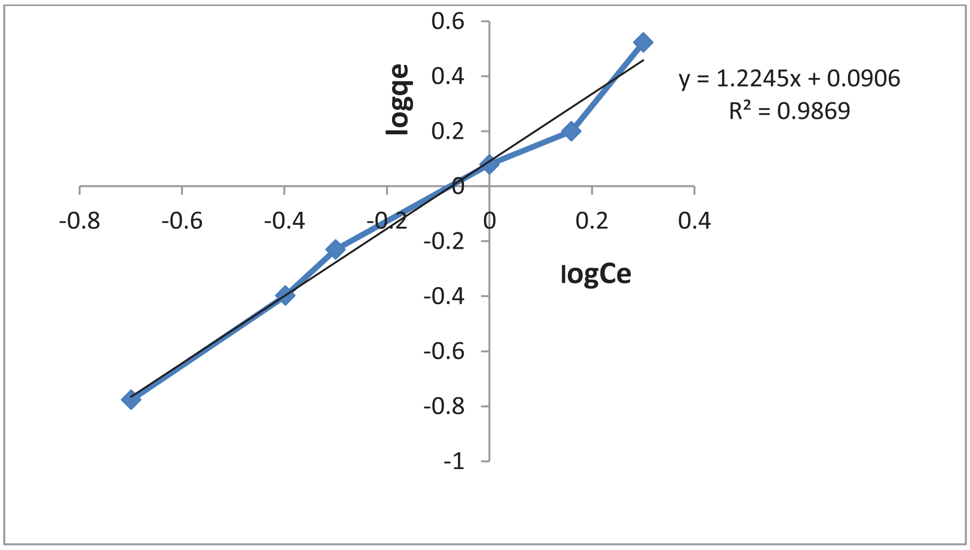


Fig.(6) Freundlich plot for pb^{+2} ions adsorption onto Cane Papyrus.

The Models of Adsorption Reaction :

The mechanism adsorption reactions are usually carried out using adsorption reaction models and adsorption diffusion models. Both models are used to understand the kinetics of the reaction. The linearised equations for the pseudo first and pseudo second order kinetics are presented in Equations (7) and (8), respectively.

$$\log(qe - qt) = \log qe - \left\{\frac{Kt}{2.303}\right\} \qquad (7)$$

$$\frac{t}{qt} = \left\{\frac{1}{K2qe2}\right\} + \frac{1}{qe} \qquad (8)$$

where q_e and q_t are the amounts of pb^{+2} ions adsorbed at equilibrium and at a given time t; k_l and k_2 are the rate constants of pseudo first and pseudo second order models. The pseudo first order kinetic model was used to treat the experimental data obtained by plotting $\log(q_e–q_t)$ vs. equilibration time (Figure 8). A linearity coefficient of 0.8681 was obtained. Similarly, a linear graph (R_2 = 0.9885) was obtained by plotting t/q_t values against time t (Figure 7). The pseudo second order best describes the kinetics of the adsorption process and this agrees with other results reported in the literature. The result obtained from the kinetic plot favors chemisorptions mechanistic pathway rather than physisorption.

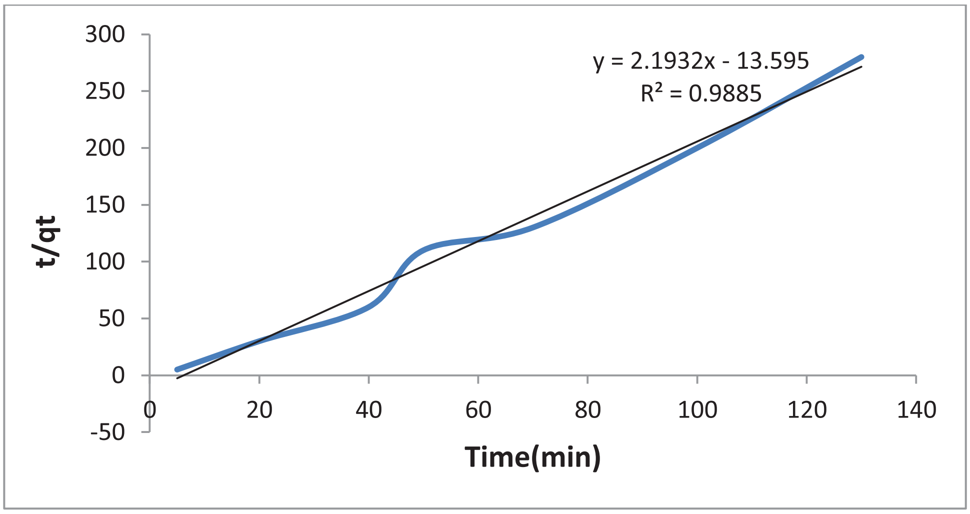


Fig.(7) Pseudo second order kinetics for pb^{+2} ions adsorption onto Cane Papyrus.

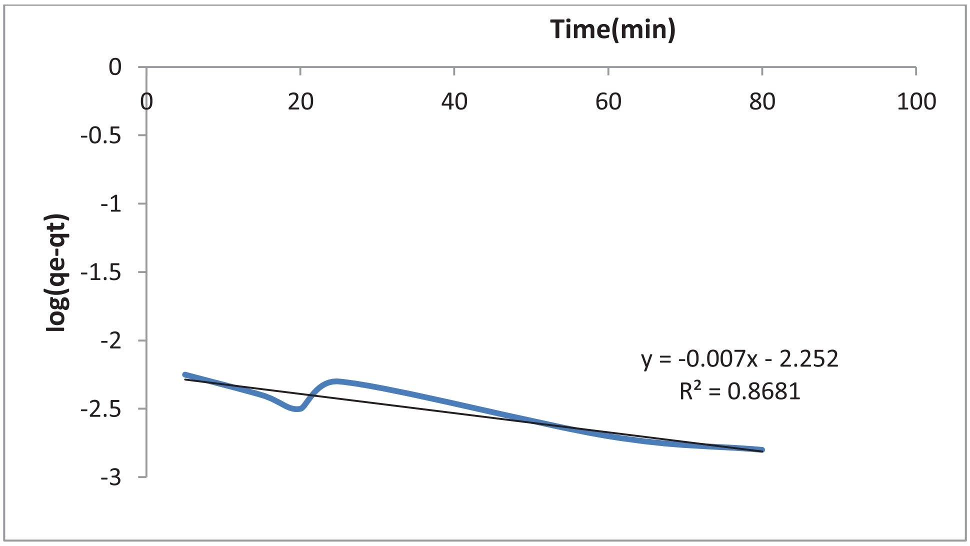


Fig.(8) Pseudo first order kinetics for pb^{+2} ions adsorption onto Cane Papyrus.

Mechanism Based Model Weber-Morris mechanistic model in Equation 9 was used to ascertain whether intra-particle diffusion or film diffusion (external diffusion) is the rate-controlling step.

$$qt = Kd(t)^{1/2} + I \quad (9)$$

Where k_d is the intra-particle diffusion rate constant (mg/g $min^{-0.5}$) and I (mg/g) is a constant describing the thickness of the boundary layer. A linear plot of qt versus $t^{1/2}$ passing through the origin will suggest intra-particle diffusion as the sole rate-determining step. However, if a linear plot was obtained that is not passing through the origin; it means the adsorption process is controlled by more than one mechanism. In this study, a linear plot was obtained that did not pass through the origin (Figure 9), suggesting that the mechanism of the reaction is multi-linear and the rate-limiting reaction is controlled both through film diffusion and intra-particle diffusion.

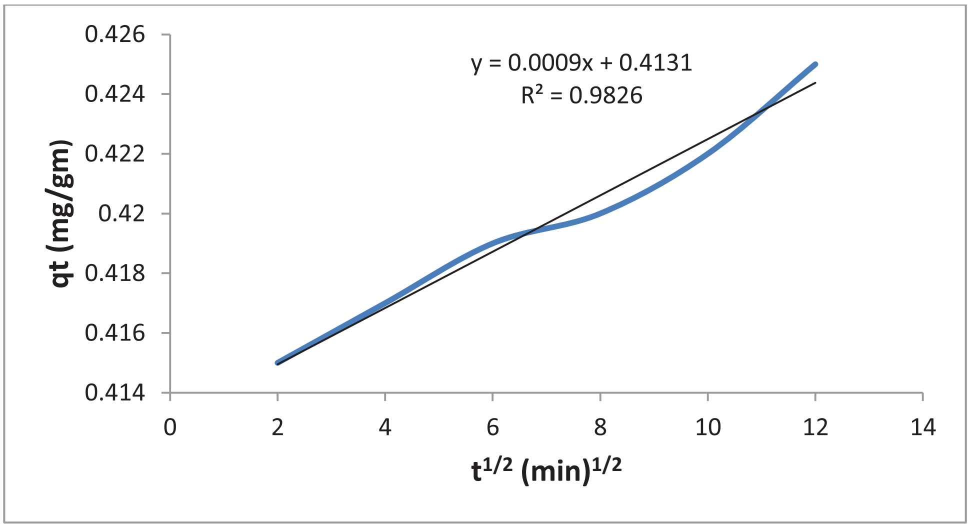


Fig.(9) Intra-particle diffusion model plot for pb^{+2} ions adsorption onto Cane Papyrus.

Desorption Studies

This study was carried out to assess the most suitable desorbing agent for eluting adsorbed pb^{+2} ions from the surface of Cane Papyrus. The effects of de-ionized water, 0.2M NaOH and 0.2M HNO_3 solutions were tested for their ability to remove the adsorbed pb^{+2} ions from the surface of the adsorbent. HNO_3 was a better desorbing agent and was able to recover 50% of pb^{+2} ions adsorbed to the surface of the adsorbent. NaOH and de-ionized water showed desorption efficiencies of 25% and 2%, respectively. Desorption is beneficial for the separation and enrichment of pb^{+2} ions as well as the regeneration of the adsorbent.

Conclusions

The adsorption ability of powdered Cane Papyrus has been investigated and found effective

for the removal of pb^{+2} ions from wastewater. Acidic functional groups present on the surface Sustainability of the adsorbent is believed to be responsible for the removal of pb^{+2} ions from aqueous media. The Freundlich isotherm model gave a better description of the adsorption process than the langmuir isotherm model. Pseudo-second order kinetics best described the kinetics of the reaction while 0.2 M HNO_3 was a better desorbing agent than 0.2 M NaOH and de-ionized water.

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