

Preparation and Characterization of Activated Carbon from Palm Tree Leaves Impregnated with Zinc Chloride for the Removal of Lead (II) from Aqueous Solutions

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Abstract: Removal of Lead (II) from aqueous solution onto Activated carbon derived from Palm tree leaves (*Phoenix dactylifera*) as a novel precursor by chemical activation with ZnCl_2 , at specific condition of carbonization temperature at 500°C and 1 hour as a holding time and detonated as AC(PTL)ZnCl_2 . The obtained material was submitted to measurements of active surface area, Fourier Transform Infrared Spectroscopy (FTIR) analysis and scanning electron microscope (SEM). Batch-adsorption studied had been carried out to examine the adsorption capacity of the AC(PTL)ZnCl_2 for the removal of Lead (II) from aqueous solution. The effect of various process parameters like pH, initial metal concentration, adsorbent dose, contact time, and temperature on the efficiency of Pb (II) removal was investigated. Maximum adsorption of Pb (II) on AC(PTL)ZnCl_2 (86.4%) was observed at pH 5.81. The optimum conditions for adsorbent dose and temperature were determined as 0.030 g and 25°C , respectively. Initial Pb (II) concentrations has important effect on AC(PTL)ZnCl_2 in the studied range (25–125 mg/L) where the removal percentage increases as the metal ion decrease. The highest percentage removal of concentration corresponding to the maximum adsorption was found to be 82.75 ± 3.65 . The adsorption equilibrium data was well explained by Langmuir, Freundlich and Dubinin-Radushkevich isotherm. The parameters suggested that the adsorption of Pb (II) on prepared AC(PTL)ZnCl_2 is physical adsorption. The Langmuir isotherm which fitted best for the experimental data obtained showed (Correlation Coefficient, $R^2 = 0.9463$) higher than the (Freundlich isotherm, $R^2 = 0.7554$), but more close to (Dubinin-Radushkevich isotherm, $R^2 = 0.9260$). The porous characteristics and adsorption efficiencies of prepared AC(PTL)ZnCl_2 were also investigated.

Keywords: Adsorption Isotherms, Activated Carbon, Palm Tree Leaves, Lead (II), Surface Area, Pore Size, SEM, FTIR

1. Introduction

The lack of clean drinking water and rise in environmental water pollution are a growing global concern. So availability of safe drinking water is still distance dream to many around the world, especially in developing countries. Increasing of human activities and industrialization have led to a wide range of physical, chemical and biological pollutants entering water, bodies and affecting human lives, thousands of

chemicals have been identified in drinking water supplies around the world hazardous to human health.

Nowadays water pollution by heavy metals is fast growing due to natural processes and increasing human activities which include mining, agriculture, and manufacturing industries [1]. There for, must be work to create a healthier, safer, and cleaner environment for everyone by helping to guarantee clean drinking water, preserving raw water sources and ensuring the optimal operation water purification processes. Heavy metals which

are natural components of the Earth's crust are usually associated with toxicity. Exposure to heavy metals, even at trace level, is known to be a risk for human beings [2]. There are 59 elements classified as heavy metals and out of these five are considered to be highly toxic and hazardous heavy metals [3]. These are lead (Pb) cadmium (Cd), chromium (Cr), copper (Cu), and zinc (Zn), have a potentially damaging effect on human physiology. Metal toxicity can result from drinking-water contamination (e.g. lead pipes), increased ambient air concentrations near sources of emission, or ingestion via the food chain [4]. The increased use of heavy metals in industry has resulted in increased availability of metallic substances in natural water sources [5, 6].

Lead, Pb (II) is among those contaminants that must be removed from water, due to its high toxicity and tendency to accumulate in tissues of living organisms [7]. Lead can occur in different forms such as organic and inorganic forms. Lead is the most significant toxin of the trace metal ions, and human exposure to the inorganic forms is through ingestion of food and water. As the result, there has been a great deal of attention given to new technologies for removal of heavy metal ions from contaminated water. Many technologies like adsorption, precipitation, membrane filtration, and ion-exchange have been used to remove metal pollutants from water [8]. However, adsorption has proven to be economical and efficient for removing heavy metals, organic pollutants and dyes from polluted waters [9].

Numerous researchers have extensively studied the preparation of activated carbon from various types of precursors and evaluate the performance of such developed materials by adsorbing of different heavy researches have been accomplished on converting low cost raw materials and agricultural waste to activated carbon and evaluate their performance by removing different heavy metal ions. Prepared activated carbon from low cost biosorbent was used to remove several metal ions [10], and A wide variety of activated carbons have been prepared from agricultural waste such as coconut shells, cotton stalk, sugarcane bagasse, coir pith, straw [11-13] and also from non-renewable materials like coal, wood, peat [14], and many others.

The present study is mainly focused on preparing the micro-porous activated carbon from palm tree leaves (as novel material) by chemical activation method using Zinc Chloride (ZnCl_2) as a chemical agent. Also, evaluated the removal efficiency of Pb (II) ions from the aqueous phase using the prepared activated carbon.

2. Materials and Methods

The carbonaceous precursor used for preparation of activated carbon (AC) was Palm tree leaves, collected from Alsalam Park in Riyadh, Kingdom of Saudi Arabia. Prior to use, sample was washed gently with water to remove impurities present on the surface and then dried for one

week. All chemical reagents used in this work are procured from Pharmchem Haryana and General Drug House (p) Ltd Daryagani, New Delhi, (India).

2.1. Preparation of Activated Carbon

Palm tree leave, collected, dried, crushed and grinded in a ball mill. The grinded sample was sieved to obtain the particles of uniform size, 1.0– 1.5 mm. The precursor obtained was washed to remove surface bounded impurities and dried at 105°C for 24 h. Raw material of about 100 g was impregnated with ZnCl_2 for 24 h in impregnation ratio of 1: 1.5 at 50°C to achieve well penetration of the chemical into the interior of the precursor.

About 10 g of the Palm tree leave impregnated with the activating agent ZnCl_2 and the impregnation was transferred to a stain less steel reactor (150 mm length and 40 mm diameter) with narrow ports at both ends. The tube is placed inside an electric horizontal tubular furnace (Bysakh & Co) controlled by the proportional integral derivative (PID) controller. The furnace tube dimensions are 800 mm length and 50 mm in diameter. The temperature (500°C) of the reaction zone was measured by the chromel – alumel (K-type) thermocouple. The pyrolysis of the samples was carried out under continuous flow of N_2 gas (200 ml/min). The carbonized samples were cooled to room temperature under inert atmosphere and washed with water followed by 0.1 M hydrochloric acid (HCl) to remove the residual chemical agents until the pH value of the rinsed water was neutral. The adsorbents prepared was denoted as AC(PTL) ZnCl_2 throughout the work.



Figure 1. Images of activated carbon obtained from palm tree leave after carbonization process.

2.2. Evaluation of Activated Carbon

The activated carbon sample was evaluated three ways:

2.2.1. Specific Surface Area Measured by Liquid Nitrogen Adsorption

Nitrogen (N_2) gas adsorption-desorption isotherms on prepared AC(PTL) ZnCl_2 at liquid nitrogen temperature (-195.6°C) were carried out using an automatic adsorption unit, Autosorb – 1(Quanta chrome). The samples were degassed at 200°C for 3h prior to analysis so as to remove any adsorbed moisture or other impurities bounded to the surface of the sample. Surface area (ST) values were calculated from the experimental adsorption isotherm over a relative pressure range of 0.01 to 0.3 using the standard BET (Brunauer, Emmett and Teller) method. The accuracy of

measurements performed by this equipment was $\pm 5\%$. The BET equation is given as [15].

$$P/V(P^0 - P) = (1/V_m C) + (C-1) P/P_0 V_m C \quad (1)$$

where, V is the volume adsorbed at STP ($\text{cm}^3 \text{g}^{-1}$), V_m is the volume of monolayer capacity at STP ($\text{cm}^3 \text{g}^{-1}$), and the term C , the BET constant, is related to the energy of adsorption in the first adsorbed layer and its value is an indication of the magnitude of the adsorbent-adsorbate interactions. The total pore volume (V_T) of the samples was determined as the total volume of N_2 gas adsorbed at high relative pressure (0.995) [16].

2.2.2. Fourier Transform Infrared Spectroscopy

The surface functional groups of the ACs were estimated by Fourier Transform Infrared (FTIR) spectroscopy (Nicolet 6700, Thermo Sciatic, USA). FTIR spectra of the activated and inactivated AC(PTL)ZnCl₂ samples were recorded within 400 – 4000 cm^{-1} . The transmission spectra of the samples were recorded using the KBr pellet. About 1.0 – 2.0% of the sample was mixed with dry KBr and grinded in mortar. Then the samples were transferred to hydraulic press. The pellets which are homogeneous and transparent in appearance were dried overnight at 100°C, and then inserted into the IR sample holder for the analysis.

2.2.3. Scanning Electron Microscopy (SEM)

SEM analysis of samples was performed by using (JSM-6380LA) scanning electron microscope. The SEM instrument was operated at 5 kV/SE (Accelerating Voltage Machine), and 50°C inclination. Before analysis, all samples were ground and coated in a sputter coating unit (Edwards Vacuum Components Ltd., Sussex, England) to reduce charging and improve the secondary electron signals for imaging. The micrographs were recorded using photographic techniques.

2.3. Effect of Process Parameters

Batch adsorption experiments for adsorption of Pb (II) on AC(PTL)ZnCl₂ were conducted using aqueous solutions of the metal. A stock solution of 1000 mg/L of Pb (II) was prepared by dissolving appropriate weight of Pb (NO_3)₂ (General Drug House(p)Ltd. Daryagani, New Delhi (India) in 1% (v/v) nitric acid solution in a 1.0 L volumetric flask. The stock solution was diluted as required to obtain different concentrations of Pb (II) solutions. For each run, a definite amount of AC(PTL)ZnCl₂ was added to 25 ml of Pb (II) solution taken in 100 ml Erlenmeyer flasks. All the adsorption experiments were carried out at constant temperature of 25°C.

2.3.1. Effect of pH

The effect of pH on metal adsorption was monitored over a pH range of 1.5 to 9, using electronic pH - Meter (pH 211). In this study, 25 ml of separate solutions 25 mg/L Pb (II) was transferred into 100 ml conical flasks agitated at 100 rpm for

180 min with 0.03g AC(PTL)ZnCl₂ at 25. The mixture was filtered and the filtrate analyzed for residual metal ions using FAAS (model 932AB).

2.3.2. Effect of Contact Time

The investigation was done to determine the optimum time for adsorption of lead ions using AC(PTL)ZnCl₂. The biosorbent (0.03g) was contacted with 25 ml separate solutions of 25 mg/L Pb (II) ions adjusted to pH 5.81. The solution was agitated at 100 rpm for different contact times (1-1440 min) at 25°C. The mixtures were filtered and residual metal ions in filtrate analyzed using FAAS.

2.3.3. Effect of Adsorbent Dosage

The effect of quantity of AC(PTL)ZnCl₂ used was investigated by equilibrating 25 ml solutions of 25 mg/L Pb (II) ions adjusted to pH 5.81, with different masses of the adsorbent (0.01-0.05 g) agitated at 100 rpm for 180 min at 25. The mixture was filtered and the residual metal ions in filtrate analyzed using FAAS.

2.3.4. Effect of Initial Metal Concentration

Separate 25 ml solution of lead ions with different initial concentrations (25-125mg/L) were contacted with optimized adsorbent dosage 0.03 g pH 5.81. The mixtures were agitated at 100 rpm for 180 min at 25°C. The mixtures were filtered and filtrate analyzed for residual metal ions.

2.3.5. Effect of Temperature

The effect of temperature of 25 ml solutions, 25 mg/L Pb (II) ions on adsorption was monitored over a range of 25 to 55°C. The investigations were carried out at optimized adsorbent dose, contact time, pH, and agitation time. The mixtures were filtered and filtrate analyzed for residual lead ions using FAAS.

2.4. Equilibrium Adsorption Studies

The adsorption isotherms for the adsorption of Pb (II) onto AC(PTL)ZnCl₂ were investigated by varying the initial Pb (II) concentration from 25 to 125 mg/L at optimized adsorbent dose, contact time, pH, temperature, and stirring speed (established after optimization of working parameters). The equilibrium data were investigations using Langmuir, Freundlich, Dubinin – Radushkevich Isotherms models.

The data obtained in the batch modes were used to calculate the equilibrium metal ion adsorptive amounts (mg/g) were calculated using the following expressions [17, 18]:

$$q_e = (V/w) (C_o - C_e) \quad (2)$$

$$\% \text{ Removal} = 100 (C_o - C_e) / C_o \quad (3)$$

Where q_e is the amount of the heavy metal ion adsorbed by the AC(PTL)ZnCl₂ sample in (mg/g), C_o and C_e are the initial and equilibrium concentrations of the metal ion respectively in (mg/L), V is the volume of the solution treated in (L) and w is the adsorbent mass of (AC(PTL)ZnCl₂) in (g).

3. Results and Discussion

3.1. Evaluation of Activated Carbon

3.1.1. Specific Surface Area Measured by Liquid Nitrogen Adsorption

Surface area and pore properties of the prepared AC(PTL)ZnCl₂ are tabulated in Table 1. Figure (2 & 3) represents the incremental mesopore volume and Micropore size distribution for the prepared AC(PTL)ZnCl₂ respectively. BET surface plot for N₂ gas adsorption on the activated prepared sample is shown in Figure 4.

Table 1. Surface area and pore properties of the prepared AC(PTL)ZnCl₂ based on N₂ adsorption isotherms.

Physical properties of the prepared AC(PTL)ZnCl ₂	
BET Surface Area	299.8424 ± 5.0495% m ² /g
Langmuir Surface Area	370.8677 m ² /g
q _m (at STP)	68.8786 m ³ /g
Pore volume	0.129132 cm ³ /g
Pore Size (Adsorption average pore width)	17.2267 Å
Correlation Coefficient, (R)	0.999585

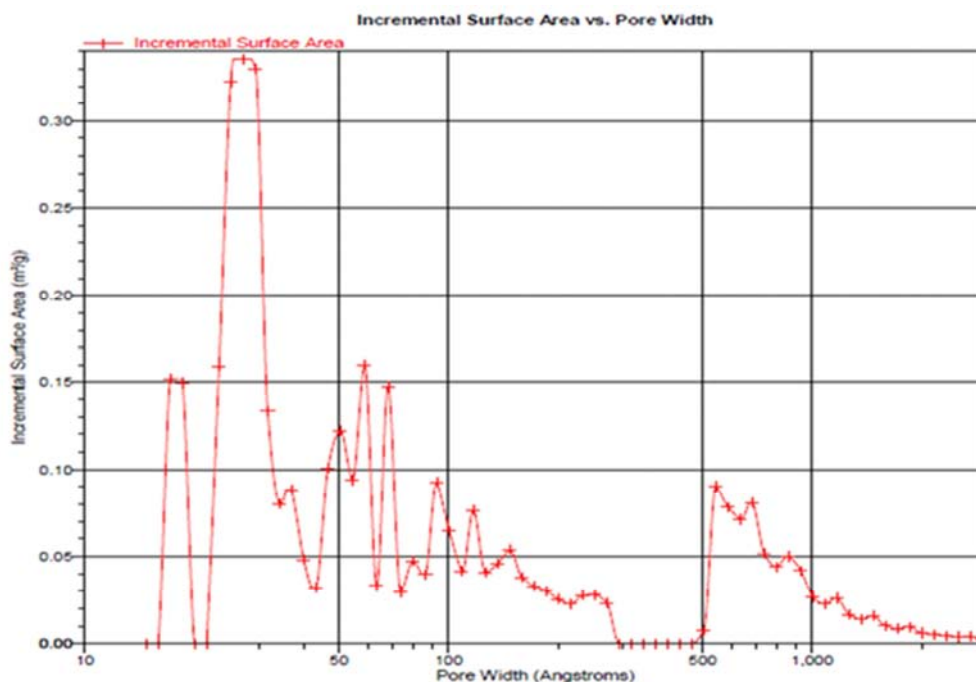


Figure 2. Incremental mesopore volume for prepared AC(PTL)ZnCl₂

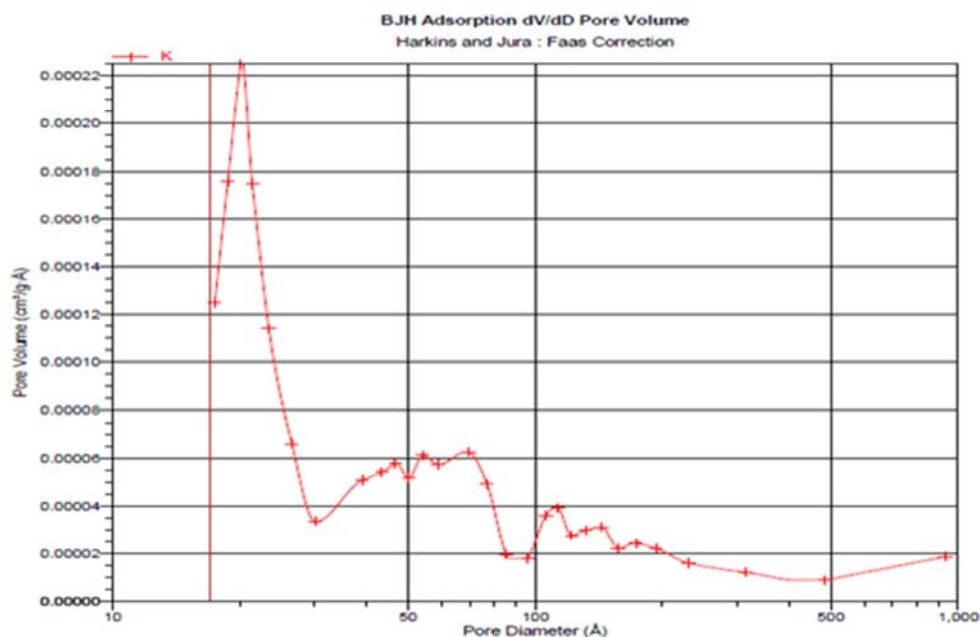


Figure 3. Micropore size distribution for AC(PTL)ZnCl₂.

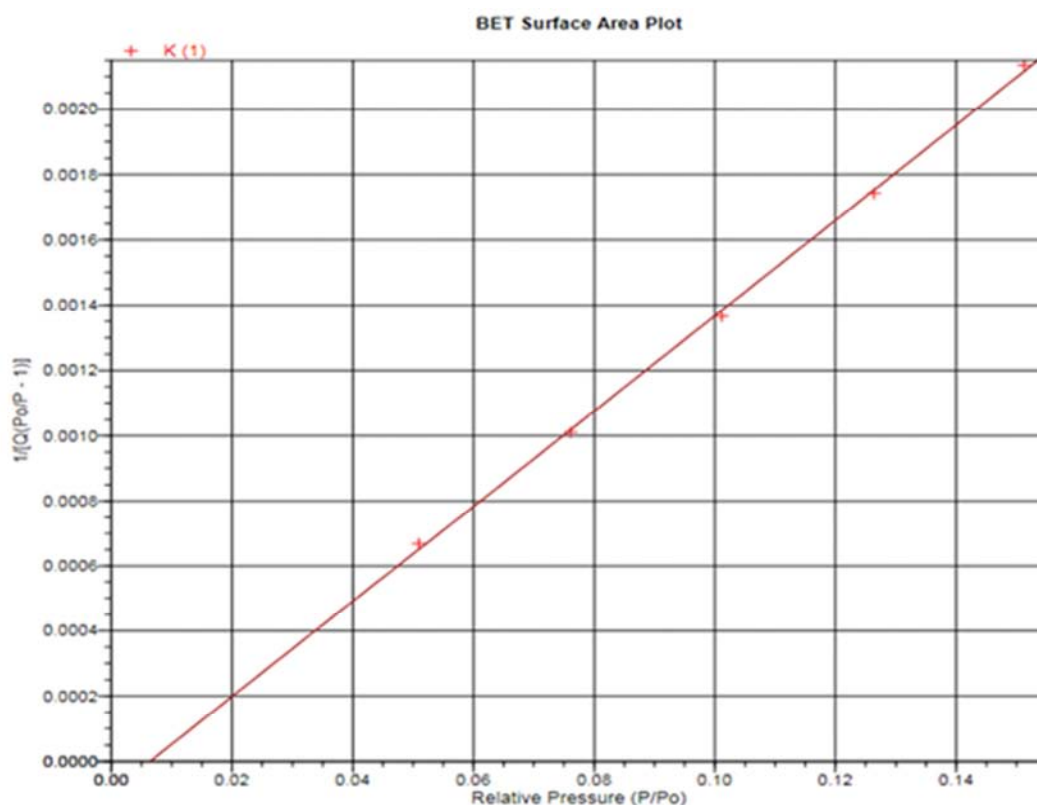


Figure 4. BET plot for N_2 gas adsorption on the activated prepared sample.

3.1.2. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR analysis of prepared AC(PTL) $ZnCl_2$ reveals a simple spectrum, shown on figure 5. The broad peaks at around 3423.43 cm^{-1} is assigned to presence of OH groups (adsorbed moisture) on surface. Silane (Si – H) groups in prepared AC(PTL) $ZnCl_2$ were confirmed by the peak at

around 2368.66 and 2368.74 cm^{-1} respectively. A little shift of the bands corresponding to silane groups was observed in prepared ACs. The presence of amine groups are confirmed by the peaks observed at 1612.39 and 1570.40 cm^{-1} while the band at 1108.13 cm^{-1} is due to the C – N stretching.

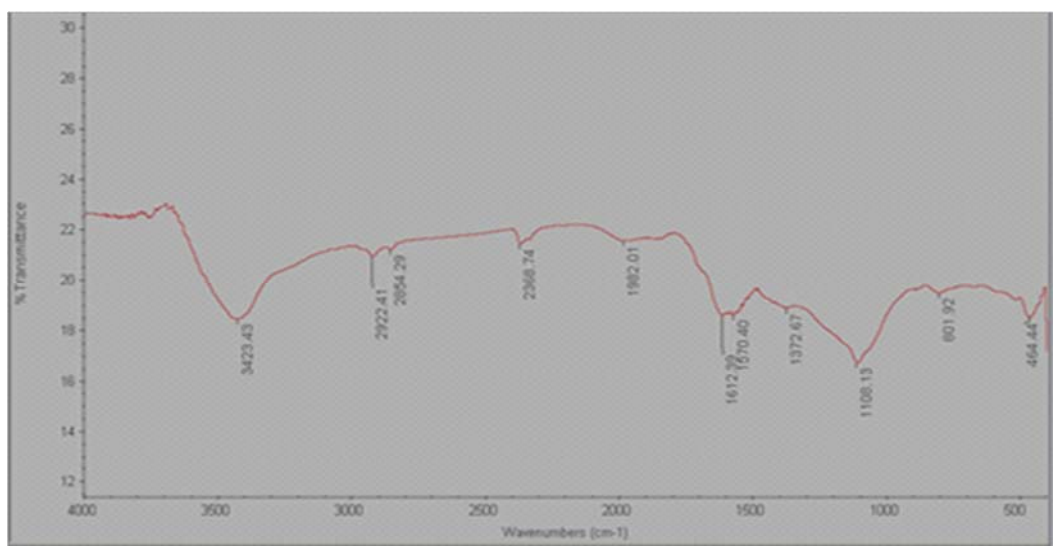


Figure 5. FTIR spectrum of prepared AC(PTL) $ZnCl_2$.

3.1.3. Scanning Electron Microscope (SEM)

The prepared activated carbon AC(PTL) $ZnCl_2$ was examined by Scanning Electron Microscope (SEM) to analyze the surface of the adsorbents. SEM micrographs of

the chemically activated carbons by $ZnCl_2$, was presented in Figure 6 respectively. Well-developed porous surface was observed at higher magnification. The pores observed from SEM images are having diameter in micrometer (μm) range.

These pores are considered as channels to the microporous network. From the figure, it can be observed that all the

adsorbents have rough texture with heterogeneous surface and a variety of randomly distributed pore size.

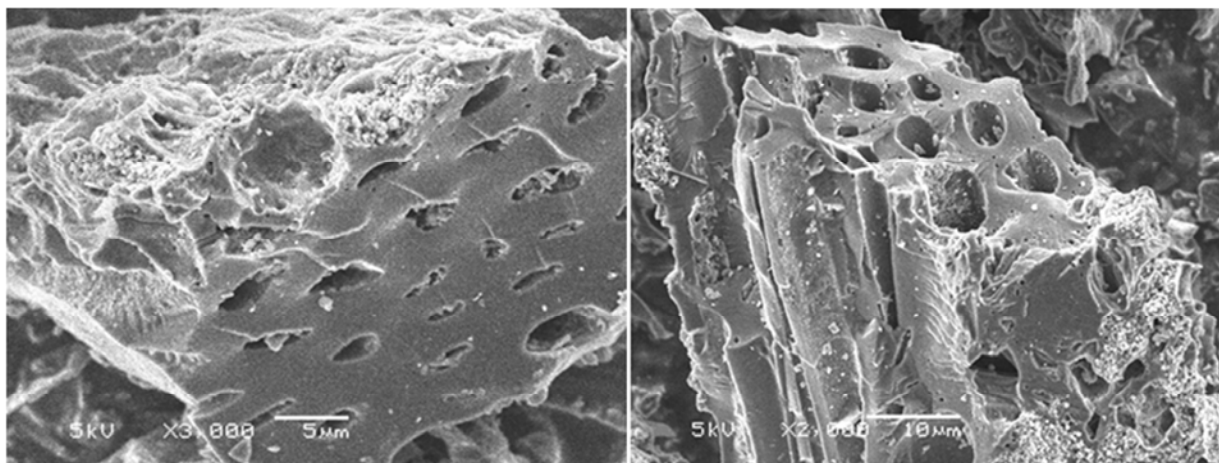


Figure 6. SEM images of the prepared AC(PTL)ZnCl₂, Magnification X3000, and X2000.

3.2. Effect of Process Parameters

3.2.1. Effect of pH

Solution pH is one of the important process parameters that significantly influences the adsorption of Pb (II) on adsorbent [19, 20]. AC(PTL)ZnCl₂ was employed for Pb (II) removal at different pH values (1.5 – 9.0). The preliminary experiments were performed at definite experimental conditions (initial Pb (II) concentration – 25.0 mg/L, adsorbent dose – 0.030g, contact time – 3.0 h, and temperature – 25°C). Figure 7 shows the higher removal of Pb (II) at 5.81 pH.

It is evident from the figure that the percentage adsorption is higher at acidic pH (5.5 – 5.81), reaching maximum of about 86.4% ± 4.2. But it decreased gradually with the decrease in pH. The maximum adsorption capacities observed at pH 5.81.0 (18.00mg/g). Adsorption values at pH greater than 6.9 gives rise to lead precipitation, so that active sites would have achieved saturation above a certain range of pH values. The results obtained are in close agreement with reported studies [19, 21].

These obtained results could be explained as, in acidic media i.e. when the pH of solution less than 4, the elevated hydrogen ions (H⁺) will rival the Pb (II) ions from reaching the free available sites on the adsorbent surface and prevent the Pb (II) ions from bounding with activated carbon surface due to the repulsive forces. Besides that, it is also noted when the pH values reaches 5.81, the adsorption process enhanced and removal percentage get maximum quantities regarding the lower hydrogen ions (H⁺) exist, and on the sense the Pb (II) ions will get better chance to occupy the free sites of the active surface. Later on, when the pH precede toward basic region and elevated above 5.81, the recorded values of removal ions increase significantly specially at 7 and 9 pH to record higher values. This is attributed to Pb (II) ions precipitated regarding to the formation of lead hydroxide anions due to the dissolution of Pb(OH)₂ as a result [18, 21].

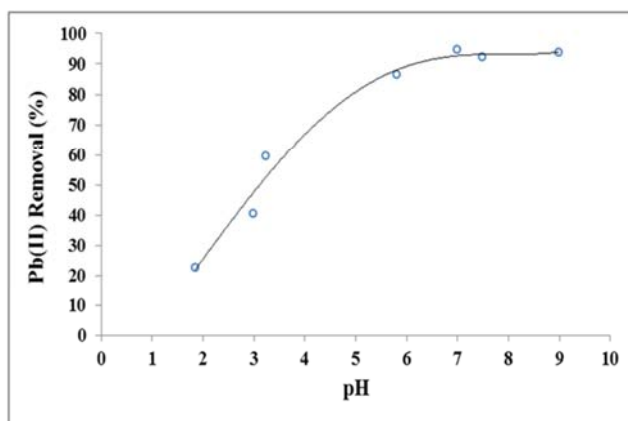


Figure 7. Effect of pH on Pb (II) removal by AC(PTL)ZnCl₂ (Initial concentration – 25 mg/L, adsorbent dose – 0.030 g, Agitation speed – 100 rpm, contact time – 3.0 h, and temperature – 25°C).

3.2.2. Effect of Adsorbent Dose

The effect of adsorbent dose on removal percentage of Pb (II) using AC(PTL)ZnCl₂ was illustrated in Figure 8. Different doses of adsorbents ranging from 0.01 – 0.050 g were considered and other process parameters were maintained constant (pH – 5.81 Pb (II) concentration – 25.0 mg/L, Agitation speed – 100 rpm, contact time – 3.0 h, and temperature – 25°C).

An increase in adsorption capacity with increasing adsorbent dose up to a maximum of 0.03 g giving the corresponding optimum percentage removal of 78.48%. On the other hand, it is found that any further addition over the above mentioned weight (0.03g) will not make any enhancement in the adsorption process, where almost negligible increase of removal efficiency over the specific adsorbent dose. The initial increase in adsorption capacity with increasing adsorbent mass is explained by the increase in the number of exchangeable sites for metal ion adsorption, after which equilibration was attained [18, 22].

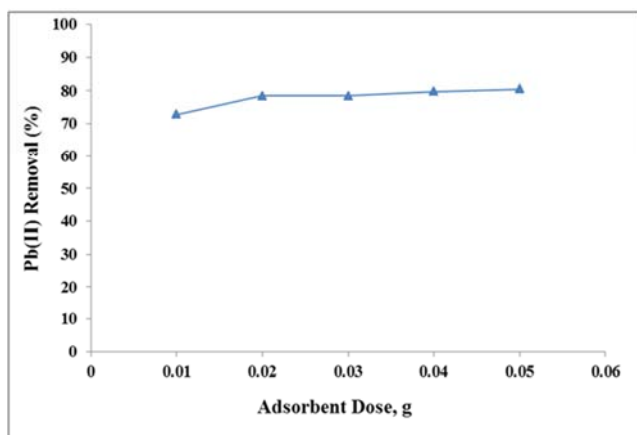


Figure 8. Effect of adsorbent dose on Pb (II) removal by AC(PTL)ZnCl₂ (pH-5.81, Initial concentration - 25 mg/L, Agitation speed - 100 rpm, contact time - 3.0 h, and temperature -25°C).

3.2.3. Effect of Contact Time

The effect of contact time on the removal of lead (II) is shown in Figure 9. The amount of the adsorbed metal ions increases with increasing time until it levels off after some (180 min). A constant adsorption is indicative of equilibration due to saturation of adsorption sites. Rapid adsorption of metal ions during the initial stages was due to the large initial concentration gradient between the adsorbate in solution and the number of available vacant sites on the adsorbent surface [18, 19, 23].

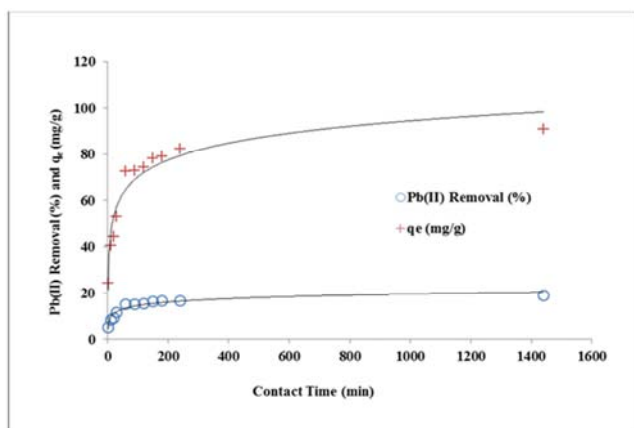


Figure 9. Effect of contact time on Pb (II) removal by AC(PTL)ZnCl₂ (pH-5.81, Initial concentration - 25 mg/L, adsorbent dose - 0.030 g, Agitation speed - 100 rpm, and temperature -25°C).

3.2.4. Effect of Initial Lead (II) Concentration

The initial concentration of metal ions in the solution is an important parameter since the metal ions concentration change over a broad range in effluents applications.

The batch adsorption experiments were carried out with different initial concentrations (C_i) (25, 50, 75, 100, and 125). The variation of percentage removal of Pb (II) ions with different initial concentration for the prepared activated carbon AC(PTL)ZnCl₂ was clarified in Figure 10. The figure shows an excellent performance of the prepared activated carbon at equilibrium state and clarifies the optimum Pb (II) ions initial concentration used at confined experimental

conditions.

It is also evidently observed that the percentage removal of the Pb (II) ions is sufficiently high, (86.4%) at low concentration (25 mg/L) and gradually decreases as the concentration increases [18]. This could be attributed to the fact that after the formation of mono-ionic layer at low concentration over the activated carbon surface, further formation of the layer is highly hindered at higher concentration and is due to interaction between Pb (II) ions on the surface and in the solution [18, 23].

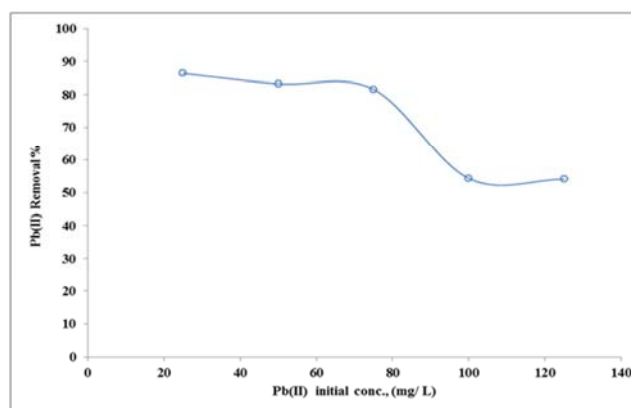


Figure 10. Effect of Pb (II) initial concentration on its removal by AC(PTL)ZnCl₂ (pH-5.81, contact time - 3h, adsorbent dose - 0.030 g, Agitation speed - 100 rpm, and temperature -25°C).

3.2.5. Effect of Temperature

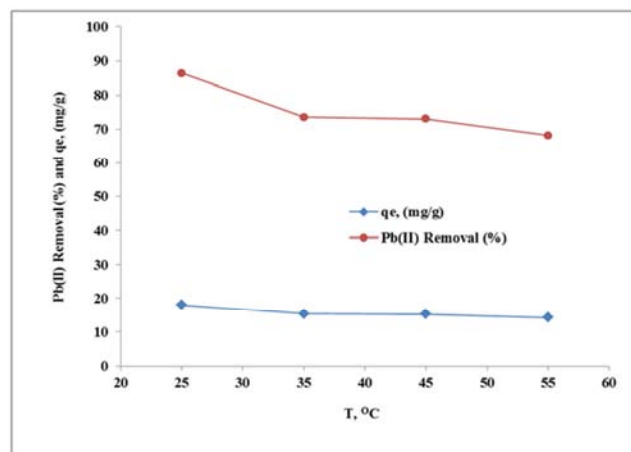


Figure 11. Effect of temperature on Pb (II) removal and q_e (mg/g) by AC(PTL)ZnCl₂ (pH-5.81, Initial concentration - 25 mg/L, adsorbent dose - 0.030 g, Agitation speed - 100 rpm, and contact time - 3.0 h).

Effect of temperature on Pb (II) removal percentage on AC(PTL)ZnCl₂ was shown in Figure 11. Experiments were performed in the temperature range 25–55°C at constant Pb (II) concentration (25.0 mg/L), adsorbent dose (0.030 g), contact time (3.0 h) and pH (5.81) for AC(PTL)ZnCl₂. Adsorption of Pb (II) on the adsorbent witnessed the increase in removal percentage and adsorption capacity (q_e) at 25°C, while in the range from 35 to 55°C, no significant change with further increase of temperature. The figure represents high rate of adsorption at 25. However low

rate of Pb (II) adsorption was observed at 55°C within studied range of temperatures. The adsorption of Pb (II) on AC(PTL)ZnCl₂ decreased from 83.3 to 11.0%, with the rise in temperature from 25 to 55. This indicates that the removal of Pb (II) onto AC(PTL)ZnCl₂ is exothermic [18, 19, 24].

The high removal percentage of Pb (II) by AC(PTL)ZnCl₂ may be due to the high diffusion rate of metal ions into the pores as the surface area and pore volume of the adsorbent were large, However, at high temperature the kinetic energy of Pb (II) species is low and hence contact between the metal ions and the active sites of AC is in sufficient, resulting in reduced removal efficiency [25, 26, 27].

3.3. Adsorption Isotherms

The successful representation of the dynamic adsorptive separation of solute from solution by an adsorbent depends upon a good description of the equilibrium between the two phases. Adsorption equilibrium is established when the amount of solute being adsorbed onto the adsorbent is equal to the amount being desorbed [28]. The equilibrium adsorption isotherms were depicted by plotting solid phase concentration (q_e) against liquid phase concentration (C_e) of solute.

Adsorption isotherm explains the interaction between adsorbate and adsorbent and is critical for design of adsorption process. The Langmuir, Freundlich, and D-R isotherms are the most frequently used models to describe the experimental data of adsorption. In the present work these four isotherms were applied to investigate the adsorption process of Pb (II) on prepared AC(PTL)ZnCl₂ at different conditions of process parameters.

3.3.1. Langmuir Isotherm

The Langmuir isotherm is applicable to homogeneous sorption where the sorption of each sorbate molecule on to the surface has equal sorption activation energy and is represented as follows [29, 30]:

$$q_e = K_L C_e / (1 + a_L C_e) \quad (4)$$

Where q_e is the solid phase sorbate concentration at equilibrium, K_L and a_L are the Langmuir isotherm constants.

The linear form of Langmuir equation is given as:

$$C_e/q_e = 1/K_L + (a_L/K_L) C_e \quad (5)$$

The adsorption data were analyzed according to the linear form of equation (equation 5). The plots of C_e/q_e versus C_e are linear which indicate that the adsorption data fitted reasonably to the Langmuir isotherm (Figure 12). The constants were evaluated from the slope a_L/K_L and intercept $1/K_L$, where K_L/a_L gives the theoretical monolayer saturation capacity Q_0 . The Langmuir constants obtained are summarized in Table 2.

The positive value of a_L (0.166), obtained for AC(PTL)ZnCl₂ indicates the efficiency of Langmuir model to explain the adsorption process. The adsorption data for

AC(PTL)ZnCl₂ was well fitted to the Langmuir equation with reasonably high regression coefficient (0.9463).

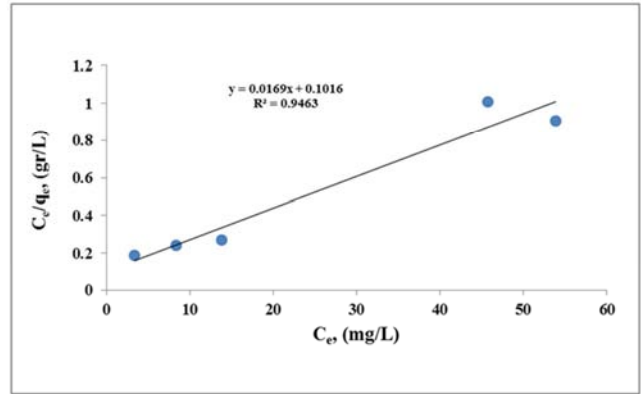


Figure 12. Langmuir isotherms of AC(PTL)ZnCl₂ for the Pb (II) removal at 25°C.

3.3.2. Freundlich Isotherm

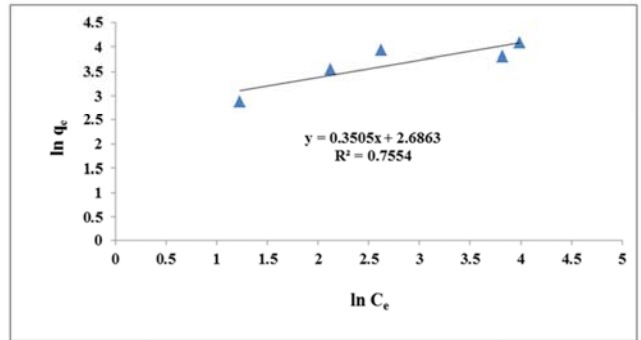


Figure 13. Freundlich isotherms of AC(PTL)ZnCl₂ for the Pb (II) removal at 25°C.

The most important multilayer adsorption isotherm for heterogeneous surfaces is the Freundlich isotherm which is characterized by the heterogeneity factor $1/n$, and is represented by the equation:

$$q_e = K_F C_e^{1/n} \quad (6)$$

where, q_e is the solid phase concentration in equilibrium, C_e is the liquid phase sorbent concentration at equilibrium, K_F is the Freundlich constant and $1/n$ is the heterogeneity factor. The magnitude of n gives an indication on the favorability of adsorption. It is generally stated that the values of n in the range 2 – 10 represent good, 1 – 2 moderately good, and less than 1 poor adsorption characteristics [31]. The Freundlich isotherm is an empirical equation based on an exponential distribution of adsorption sites and energies. The linear form of Freundlich equation is:

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad (7)$$

where, the intercept $\ln K_F$ is a measure of adsorption capacity, and the slope $1/n$ is the adsorption intensity. The values of K_F and n were calculated from the intercept and slope of the plots $\ln q_e$ against $\ln C_e$ (Figure 13). The Freundlich isotherm describes reversible adsorption and was

not restricted to the formation of monolayer. The Freundlich isotherm showed a poor fit to the adsorption data than Langmuir isotherm, with regression coefficient of 0.7554 compared to 0.9463 in Langmuir. This indicates that Pb (II) adsorption on AC(PTL)ZnCl₂ was monolayer adsorption. Freundlich sorption isotherm constants were determined and are summarized in Table 2.

3.3.3. Dubinin – Radushkevich Isotherm

The linear form of Dubinin – Radushkevich (DR) isotherm equation is presented as [32]:

$$\ln q_e = \ln q_D - 2B_D RT \ln (1 + 1/C_e) \quad (8)$$

A plot of $\ln q_e$ against $RT \ln (1+1/C_e)$ in Figure 14 showed straight line and indicates a good fit of the isotherm to the experimental data. The apparent energy (E) of adsorption from DR isotherm model can be estimated using the equation given below:

$$E = 1/ (2B_D)^{1/2} \quad (9)$$

The DR isotherm constants and mean free energy were presented in Table 2. It was found that the DR isotherm model gives a satisfactory fit for Pb (II) adsorption data for AC(PTL)ZnCl₂ with good regression coefficient (0.926). The

magnitude of the activation energy can be used to determine the type of adsorption process. It easy to have a general insight into the undergoing process. If the value of $E < 8$ kJ/mol, the adsorption type can be explained by physisorption, and if E is in the range of 8 – 18 kJ/mol then the adsorption type is ion exchange [33], and chemical-reaction-controlled when $E > 50$ kJ/mol [23, 34]. The low value of apparent energies obtained (0.09414 kJ/mol) confirms that the adsorption of Pb (II) on prepared AC(PTL)ZnCl₂ is physical adsorption [35].

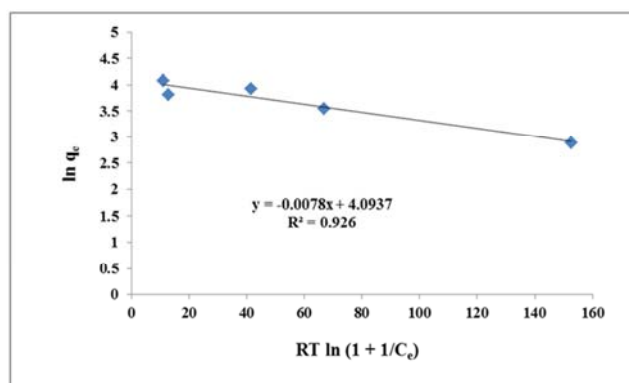


Figure 14. Dubinin – Radushkevich isotherms of AC(PTL)ZnCl₂ for the Pb (II) removal at 25°C.

Table 2. Langmuir, Freundlich, and Dubinin – Radushkevich isotherm constants for the Pb (II) removal on the prepared AC(PTL)ZnCl₂ at 25°C.

Langmuir				Freundlich			Dubinin Radushkevich			
K_L (L/mg)	a_L (L/mol)	Q_0 (mg/g)	R^2	$K_F[(\text{mg/g})/(\text{L/mg})^{1/n}]$	$1/n$	R^2	$B_D \times 10^{-3} (1/(\text{J/mol})^2)$	q_D (mg/g)	E (J/mol)	R^2
9.843	0.166	59.30	0.9463	0.988	0.351	0.7554	3.9	1.41	94.14	0.926

4. Conclusion

The main conclusions which are achieved from this research are:

1. The prepared activated carbon, AC(PTL)ZnCl₂, used in this study is found to have a high capability for removing the Pb (II) ions from aqueous solution.
2. The adsorption method is successfully applied to remove Pb (II) ions from aqueous solution. The removal efficiency of lead (II) ions was found to be dependent on various parameters such as pH of the solution, initial lead concentration, mass of adsorbent and contact time.
3. The results obtained showed that the removal efficiency of the Pb (II) ions by the prepared activated carbon, AC(PTL)ZnCl₂, increased with time, which is significant in the first stage with an instantaneous removal of Pb (II) ions, after that the curves become as plateau after 180 minutes.
4. The experimental results showed that the removal efficiency of the Pb (II) ions by AC(PTL)ZnCl₂ activated carbon decreases with increase in initial Pb (II) ions concentration, and increases with increase in mass of adsorbent.
5. The pH of the solution played an important role in influencing the ability of adsorbents towards the metal

ion. The increase in the pH of solution from 2 to 5.81 led to increase in the removal efficiency.

6. The optimum conditions which have been obtained in adsorption process for treating the aqueous phase were 50ppm for initial lead concentration, 5.81 pH for solution acidity, and 15 g/L for mass of adsorbent.
7. The equilibrium data obtained for the prepared activated carbon, AC(PTL)ZnCl₂, is fitted to the Langmuir and Dubinin – Radushkevich models more than the Freundlich model.

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