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Preparation and Characterization of Activated Carbon with ($ZnCl_2$ - Activated) from (PET) Bottle Waste for Removal of Metal ions (Cu^{+2}) in Aqueous Solution

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Abstract. The power of activated carbon resides from polyethylene terephthalate (PET) by chemical and physical activation to adsorption of metal ions (Cu^{+2}) on certain conditions, such as (Concentration of metal ion in the solution, and contact time). Its chiefly objective is to reduce the poisonousness by the metal mentioned above and reducing the surrounding contamination resulting from the bottle waste after throwing them. In this work, activated carbons were prepared from bottle waste by carburizing and activation methods. The Carburizing temperature were 500ºC and 900ºC under Argon gas with flow rate (150 cm^3 min^{-1}). activating agents ($ZnCl_2$) were utilized. The isotherm models of Langmiuir and Freundlich were studied and Langmuir isotherm model was more appropriate when Carburizing temperature was 900ºC, in contrast to carbonization in 500ºC were studied the Freundlich isotherm model was best. Pseudo-first-order, Pseudo-seconds order kinetics also studied. The pseudo-seconds-order was more suitable to describe the adsorption properties for (Cu^{+2}) when Carburizing temperature was 900ºC. In general, the (PET) west activated with $ZnCl_2$ and temperature of 900ºC was best adsorption from activated with temperature of 500ºC.
Keywords. A. Activated carbon, C. Adsorption; metal ions (Cu^{+2}), D. isotherm models of Langmuir and Freundlich.

1. Introduction

A well-known method of recycling polymer waste is to manufacture inexpensive products or consumer goods. The alternative is to treat a fundamentally new product, such as activated carbon, which is effective and cheap [1]. AC is used for advanced technology and to meet many water quality requirements. For thousands of years, AC has been used to improve the quality of the drinking water, it has been utilized as an adsorption medium. various forms (powder and granules), AC was used for that improvement, as it is used to remove colour-producing heterocyclic compounds as well as pollutant precursors when cleaning, and to track pollutants, whether organic or inorganic and compounds (taste and odor) [2]. Organic materials of biological origin have been used to obtain activated carbon and use it in various forms, in other words converting organic materials such as (wood, banana pitch, coconut shells, and corncobs) to activated carbon [3].

The rapid expansion of heavy metal related industries such as those involved in electroplating, mining, smelting, battery manufacture, tanneries, paint, pesticides, printing, and photographic had caused a serious environmental problem due to incomplete heavy metal treatment [4]. Because of its acute toxicity and persistence in nature, heavy metals have proven harmful to both the environment and

human health [5]. Heavy metal is a metallic chemical element with a relatively high density. Most heavy metals are toxic even in low concentrations, they tend to bio-accumulate then they are dangerous [6]. On the other hand, the problem of increasing plastic waste in large quantities does not threaten directly the environment, but it is a problem of great concern due to the amount of solid waste generated that cannot be decomposed [7]. Usually, a person obtains important minerals, including heavy metals, through various nutrients, in which case the person obtains the minerals necessary for the metabolism or strengthening of the immune system. It has been reported that some minerals such as (Copper, Selenium, and Zinc) play some important and beneficial roles in human metabolism. For example, copper in low concentration acts as cofactors for various redox cycle enzymes; However, in high concentrations, the human metabolism is disrupted leading to anemia, irritation of the liver, stomach, kidneys, and intestines. Heavy metal toxicity can also disrupt or damage the mental and central nervous system, alter blood composition, and damage the lungs, kidneys, liver, and other important organs. It has also been found that damage to the human respiratory system develops after exposure to a high level of minerals. [8].
A common treatment method is to remove metal ions from industrial water or wastewater, either through adsorption, bio-absorption, chemical precipitation, solvent extraction, reverse osmosis, or filtration, and other processes. Among these treatments, it is adsorption, so because adsorption is efficient, at the same time economical and inexpensive method, this method is used to remove heavy metal ions from aqueous solutions. An adsorbent that can be used to remove heavy metals from industrial wastewater or sewage is activated carbon due to its high surface area as well as the chemical nature of its surface, the small permeable structure, and the Ease of manufacture at low cost [9].
The aim of the research project study was to prepare the physically and chemically activated carbon material and to characterize the carbonaceous materials obtained from PET waste, and to apply for adsorptive removal of (Cu^{+2}) from the aqueous solution.

2. Experimental

2.1 Preparation of the activated carbon

PET (Polyethylene terephthalate) from drink bottles was used as the raw material for the carbonization process. After good washing and drying, the bottle is cut into small pieces (2 – 0.1 cm). Then it was burned in the electric oven at 500ºC and holding at 2 hours to obtain the carbon. The burning shall be in an oxygen-isolated atmosphere under with flow rate (150 cm^3 min^{-1}) from Argon gas. The carbon that the result from the carbonization through mesh number 80-160 (about 0.2 - 0.098 mm) is (B1), and then Impregnation with the $ZnCl_2$ and mixing in the magnetic starrier for 4 hours (C1).
Carbon produced from carbonization (B1) and activated carbon resulting from the impregnation of $ZnCl_2$ (C1) was also treated with carbonization at 900ºC, so the resulting carbon (B2 and C2), respectively as the table 1.

2.2 Preparation of metal solution

The aqueous solution (Cu^{+2}) was prepared by dissolve (1g) of Cu in (50 cm^3) of 5M HNO_3. Diluted to (1 L) into a volumetric flask with deionized water. Preparing was different concentrations of each solution containing metallic ions (5, 10, 15, 20, 25, 30) ppm, the equilibrium concentration of the solutions was determined by the atomic absorption spectrometer (the flame used for acetylene-air). Where the calibration curve was drawn amongst adsorption and concentrations (ppm) of (Cu^{+2}) as shown in Figure 1.

Table 1. The formulations of specimens using in the research.

Sample	Prepare the sample	Time agent
B1	Heating at 500°C	2 hours
C1	(5g) B1 + (250 ml) $ZnCl_2$	48 hours
B2	B1 at 9000C	2 hours
C2	C1 at 9000C	2 hours

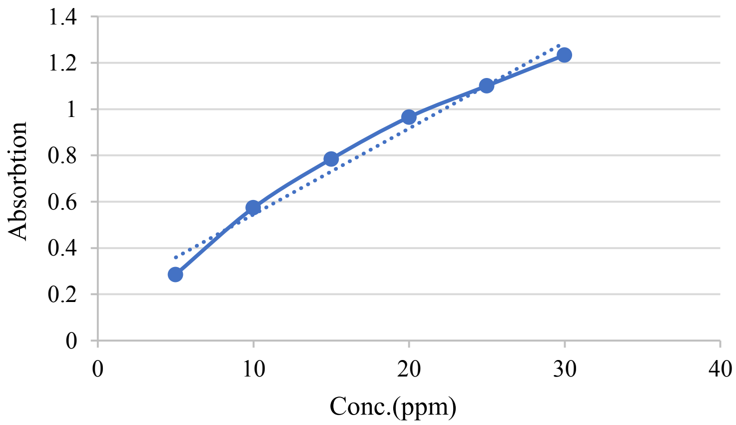

Figure 1. Calibration curve for Cu^{+2} metal solution.

3. Adsorption studies

3.1. Adsorption equilibrium and isotherms

To determine Adsorption amount by the changes were monitored by changing the mineral concentration (mg / L), as well as the adsorption time (hour) using the balance equations [10, 11]:

$$q_e = \frac{V}{m}(C_0 - C_e) \quad (1)$$

$$\text{Removal efficiency}(\%) = ((C_0 - C_e)/C_0) * 100\ \% \quad (2)$$

Here V is the volume of the metal ions solution (L),
m is the weight of the prepared carbons (g),
C_0 is the initial concentricity of the adsorbate (mg/L),
C_e is the concentricity of the adsorbate at equilibrium (mg/L),

Langmiuir isotherm model. This model proposed by Langmuir was based on a homogeneous surface. It assumes that the surface of the sorbent forms a layer of monomolecular sorption, and that the active sites on the surface of the sorbent are energy identical. It believes adsorption to be a chemical phenomenon [12].

The formulation for Langmuir is defined as follows:

$$q_e = \frac{q_{max} b\ C_e}{1 + b\ C_e} \quad (3)$$

and the linear form of Langmuir formula is defined as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{1}{q_{max}} C_e \quad (4)$$

Where; q_e represents the amount of metal accumulated (mg/g),
q_{max} is the maximum metal sorption (mg/g),
b is the ratio of adsorption and desorption rates (mL/mg).

3.2. Freundliche isotherm model. The model proposed by (Freundlich , 1906) was based on an equation that encompasses the heterogeneity of wide-ranging affinity surface or surface support sites. It's based on the active sites and their energies being distributed exponentially. It is implicit that the stronger binding sites are engaged for sorption first and that the binding force decreases with the increasing occupancy of the site [11, 13].

The formulation for Freundlich is defined as follows:

$$q_e = K_f\ C_e^{1/n} \tag{5}$$

The famous linear formula of the Freundlich isotherm is known by equation:

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right)\ C_e \tag{6}$$

Where K_f and (1/n) are empirical constants dependent on several environmental factors.

3.3. Adsorption kinetics

3.2.1. Pseudo-first-order kinetic model. The pseudo-first-order rate expression, commonly recognized as the Lagergren equation, in general defined by the subsequent equation [14, 15]:

$$\frac{dq_t}{dt} = K_2\ (q_e - q_t) \tag{7}$$

Using the initial condition qt = 0 at t = 0, can integrate this equation.

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{8}$$

Where; k_1 (1/h) is the constant for kinetic of pseudo-first - order adsorption,
q_e and q_t are representing the amounts of adsorbed tetracycline at equilibrium (mg/g of AC) at time t (h).

3.2.2. Pseudo-second-order kinetic model. The pseudo-second-order rate expression, in general defined by the subsequent equation [15, 16]:

$$\frac{dq_t}{dt} = K_2\ (q_e - q_t)^2 \tag{9}$$

Integrating Eq. (9) and using again the initial condition $q_t = 0$ at $t = 0$, the following equation is obtained

$$q_t = \frac{q_e^2\ K_2\ t}{1+q_e\ K_2\ t} \tag{10}$$

In which q_e and q_t have the same meaning as before, and K_2 (g/mg. h) is the corresponding kinetic constant.

4. Results and discussion

4.1. Equilibrium studies

When calculating the (PET-AC) adsorption capacity of the metal ions (Cu^{+2}) by using equation (1) for 4 samples (B1, C1, B2, C2) found to increase with an increase in initial metal ion concentrations as shown in figure 2. This is due to an increase in the saturation of adsorbent surface with an increase in initial metal ion concentrations [17].

The relationship between contact time and adsorption capacity of heavy metals with activated carbon prepared from (AC-$ZnCl_2$) are shown in figure 3. From the result obtained, it is obvious when contact time increases will be metal ion removal increased. The adsorption capacity for (Cu) ion concentration prepared at 30 ppm and 48 hr contact time was (41.752, 22.086, 16.144, and 7.700) mg/g for sample C2, B2, C1, and B1 respectively. Increasing the contact time to the removal of heavy metals will not result in any changes to the removal percentage, but will result in desorption of the metal ions from the AC surface. The results show at different times that metal ions achieved different equilibrium (B1 and C1) because of their specific properties [18].

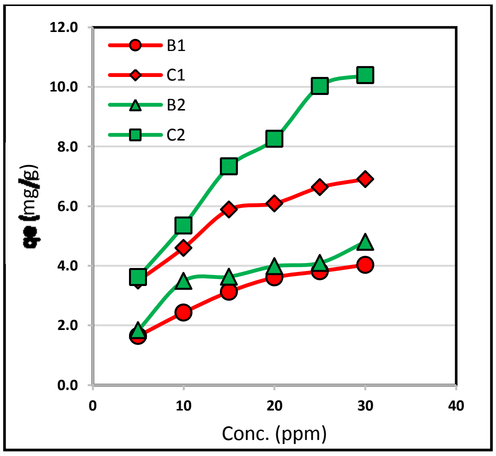

Figure 2. Effect of initial metal ion concentration on the adsorption capacity of ACs for adsorption of (Cu^{+2}), at time=1 hr., pH=3, temp.=30ºC and ACs dosage=50 mg.

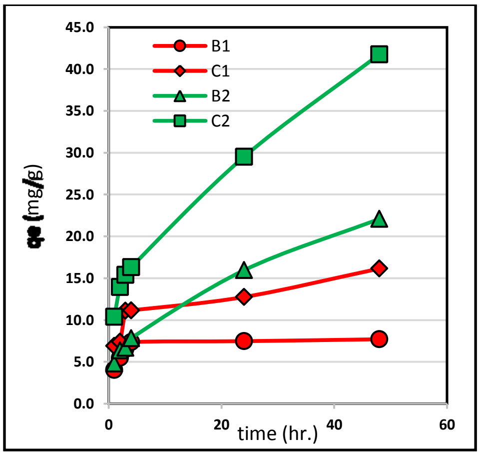

Figure 3. Effect of contact time on the adsorption capacity of ACs for adsorption of (Cu^{+2}), at metal ion concentration =30 ppm, pH=3, temp.=30ºC and ACs dosage=50 mg.

4.2. Adsorption Isotherm results

The shape of the isotherms is an experimental tool to diagnose the type of the adsorption. To describe the adsorption data of the equilibrium isotherm model is used, the thermodynamic parameters underlying these models give insight into the adsorption mechanism, the adsorbent affinity, and the surface properties. Because of more applications are developed, the importance of obtaining the best equilibrium isotherm becomes more important, more precise and detailed isotherm descriptions are required for the design of the adsorption system [19]. Langmuir Isotherm to predict if an adsorption system is "favourable" or "unfavourable", which is defined as [20]

$$R_L = \frac{1}{1+b\,C_0} \qquad (11)$$

The Langmuir constant, b, was used to calculate the separation factor, R_L When:
($0 < R_L < 1$) Type of Isotherm is Favourable, ($R_L>1$) Type of Isotherm is Unfavourable, ($R_L = 1$) Type of Isotherm is Linear and when ($R_L = 0$) Type of Isotherm is Irreversible.
It was found that quantities R_L (0.259, 0.173, 0.152, 0.285) for (B1, C1, B2, C2) respectively, the adsorption abilities of metallic ions (Cu^{+2}) is desirable as figure 4.
In all types of activated carbons, the linear plot of (log C_e) versus (log q_e) in Freundlich isotherm showing in figure 5 offers a high rate of correlation coefficient (R^2) was (0.979, 0.991, 0.986, 0.881) for (B1, C1, B2, C2) respectively. [21].

4.3. Kinetic study

Two kinetics models were utilized to calculate the percentage of the adsorption process. These kinetic models are pseudo-first-order and pseudo-second-order. This kinetics were utilized for studying of adsorption of (Cu^{+2}) onto the surface of (B1, C1, B2, and C2). This study was under the following conditions: initial concentration of metallic ion is (30 mg/L), temperature (30ºC), pH=3, and ACs dosage (50 mg). Applicability of a particular type of rate equation is selected based on the value of the correlation coefficient R^2. Both the values of R^2 for the "pseudo-first-order" and "pseudo-second-order" was close value showing in figure 6. But, the values of R^2 for the pseudo-first-order adsorption model aren't satisfactory. Therefore, the more suitable describe the adsorption kinetics is the pseudo-seconds-order adsorption model [22].

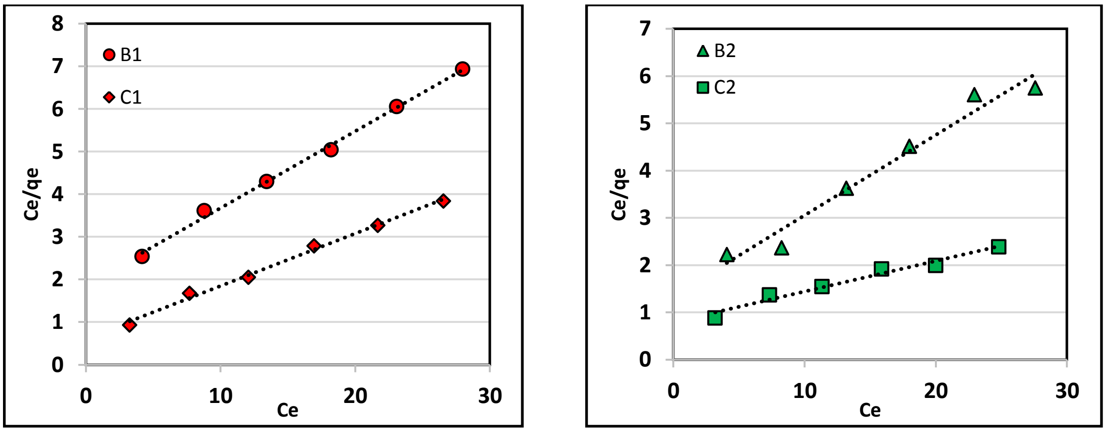

Figure 4. Adsorption isotherm Langmuir model for (Cu^{+2}).

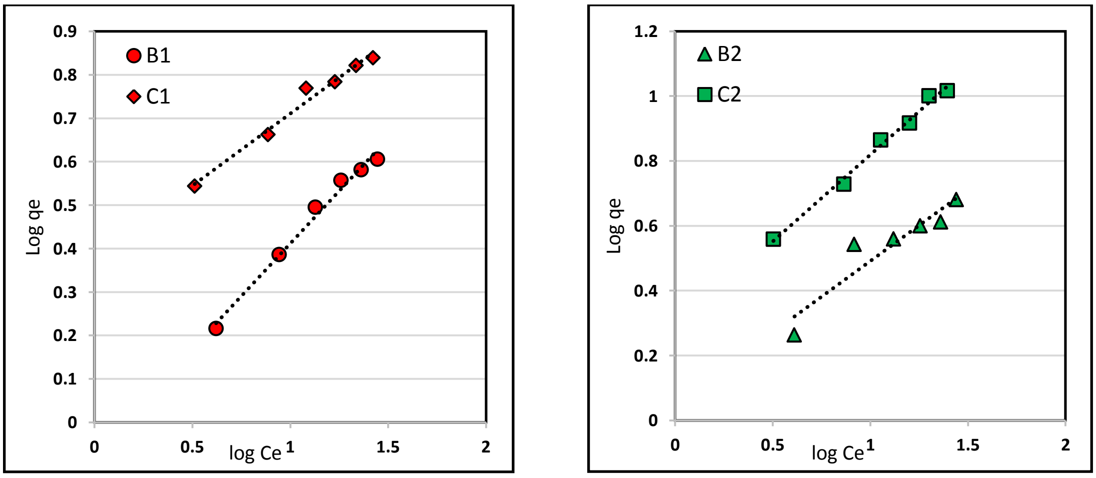

Figure 5. Adsorption isotherm Freundlich model for (Cu^{+2}).

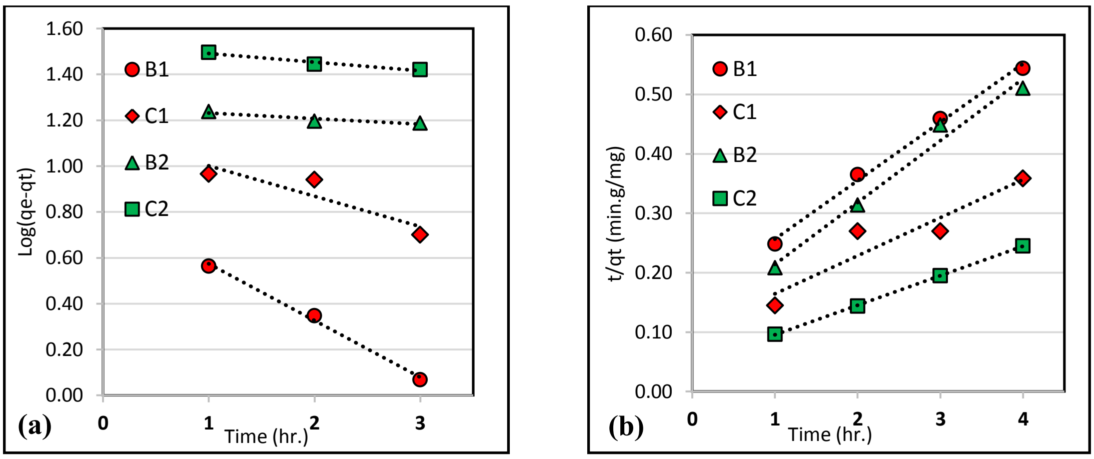

Figure 6. (a) Pseudo-first-order (b)Pseudo-first-order Adsorption (Cu^{+2})

5. Conclusions

The polyethylene terephthalate activated carbons were prepared to estimate the adsorption of heavy metal ions (Cu^{+2}). By using physical and chemical activation. In the preparation process of carbon, 500, and 900 ºC were chosen as the optimal pyrolysis with $(ZnCl_2)$ activation. Form (PET) bottle waste-derived carbon was the adsorption metal ions (Cu^{+2}) onto ACs rises with increasing contact time and higher adsorption was at 48 hours. The Langmuir model was best for adsorption (Cu^{+2}) when used the sample was treated at 900 ºC. The pseudo-second-order was more suitable for the adsorption of metal ions.

6. References

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