Modification of Activated Carbon Prepared From Pigeon Pea Husks with Eriochrome Black T for Removal of Copper (II) Ions

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Abstract— *Wastewater pollution due to heavy metals is one of the most important problems facing humanity today. The current study showed a sensitive and effective method for removal of copper (Cu) from aqueous solutions using activated carbon (AC) modified with Eriochrome Black T (EBT). The AC was prepared from pigeon pea husks, since this is an abundant and inexpensive natural resource, using chemical activation with phosphoric acid solution (70%), then physically modified with EBT. Surface properties of the AC-EBT phase were characterised by scanning electron microscopy (SEM) analysis and Fourier transmission infrared (FT-IR) spectroscopy. The high adsorption of AC-EBT is due to the well-developed pores on the fabricated AC-EBT, which lead to high Cu uptake, and the maximum monolayer adsorption capacity of 158.73 mg g^{-1} after 1 hour contact time. The experimental data fitted well to the Langmuir adsorption isotherm. Results demonstrated that AC-EBT would be a useful and valuable method for controlling water polluted with copper ions.*

Index Terms—Activated carbon; Copper ion; Eriochrome Black T; Pigeon pea husks.

I. INTRODUCTION

Heavy metals commonly found in wastewater come from industries such as paints, pigments, glass production, mining operations, and battery manufacturing processes. Heavy metals can contaminate groundwater resources and cause groundwater pollution. Heavy metals can also be introduced via acidic rain, which breaks down soils and releases heavy metals into streams, rivers, lakes, and groundwater [1]. High concentrations of copper (Cu), the metal considered in this study, have a strong toxic effect, are non-biodegradable, can bio-accumulate in organisms, and have a direct effect on plants, animals, and people. [2-4]. It can cause many health problems; for example, cancer, brain and kidney damage, and metabolic acidosis. In addition, it can cause poisoning effects like mucosal irritation, central nervous system irritation, and necrotic changes in the liver. Therefore, removal of this metal from wastewater is vital [5]. Different techniques have been used for the removal of pollutants from wastewater; for example, precipitation, electrochemical treatment, coagulation, precipitation, solvent extraction, membrane filtration, and advanced oxidation processes [6]. However, these methods are high in energy consumption, result in the incomplete removal of ions, produce toxic materials, and have high operating costs; as a result, they are not suitable for developing countries and small-scale industries in developed countries [7].

Adsorption, on the other hand, has been an effective separation process for a wide variety of applications. A common, and promising, adsorbent is activated carbon (AC) because of its large surface area, high adsorption capacity, and porous structure [8]. It has been proven to remove pollutants, dyes and heavy ions from aqueous solutions and gaseous environments. Due to the high cost and the difficulty involved in its regeneration, many researchers are focusing on the production of low cost agricultural wastes for the elimination of heavy metals from contaminated water. In recent years, AC has been prepared from inexpensive materials of little economic value such as wood, bagasse, coir pith, orange peel, bamboo dust, corncobs, palm shells, coconut shells, tobacco stems, and hazelnuts [9-11]. Recently, modification of the surface of activated carbon with functional groups for selectivity is a subject of growing interest [12]. Modification of the surface of activated carbon with coordinated ligands has been performed in order to improve the selectivity and binding properties of AC [13-16]. The aim of this work was to prepare activated carbon from pigeon pea husks (PPH), followed by modification of the surface of the prepared activated carbon with Eriochrome Black T (EBT). (Figure 1) EBT is commonly used as an indicator in complexometric titration and for biological staining [17]. The fabricated material was characterised using SEM analysis, and FT-IR spectroscopy before and after modification with EBT. The removal of copper ion from aqueous solution using pigeon pea husk-based activated carbon modified with EBT was investigated in this study.
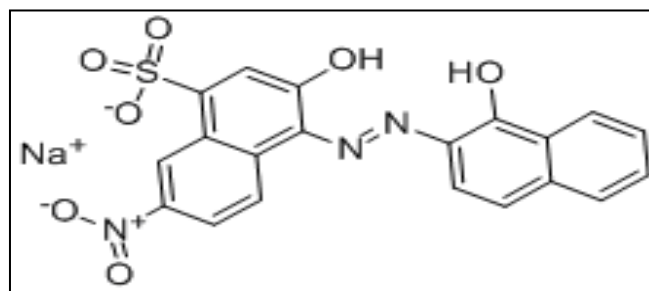

Fig. 1 Chemical Structure of 1-(1-Hydroxy-2-Naphthol azo) 6-Nitro-2-Naphthol-4-Sulphonic Acid Sodium Salt

II. EXPERIMENTAL

2.1. Chemicals and Materials

Pigeon pea husks were collected from an agricultural area near Taif, KSA. Eriochrome Black T ($C_{20}H_{12}N_3NaO_7S$), MW= 461.38 g mol^{-1}, was purchased from Sigma-Aldrich (Poole, UK).

Copper sulphate was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The Whatman filter paper (pore size 25 μm and diam. 15 cm) was purchased from Sigma-Aldrich (Poole, UK). Distilled water was employed for preparing all the solutions and reagents.

2.2. Instrumentation

A hot plate-stirrer from VWR International LLC (West Chester, PA, USA), a scanning electron microscope (SEM) Cambridge S360 from Cambridge Instruments (Cambridge, UK), UV-Vis spectrophotometer from Thermo Scientific™ GENESYS 10S (Toronto, Canada), a furnace (WiseTherm high temperature muffle furnaces, Wisd Laboratory Instrument, Wertheim, Germany) were used in the study. The FT-IR spectra were collected in the attenuated total reflectance (ATR) mode using a PerkinElmer RX FT-IR ×2 with diamond ATR, DRIFT attachment from PerkinElmer (Buckinghamshire, UK).

2.3. Fabrication of Activated Carbon

Activated carbon was prepared from pigeon pea husks. They were ground and sieved and the powder was soaked in H_3PO_4 solution (70 %) for 24 h. Then it was filtered and washed with deionised water and dried in a furnace for 30 min at 400 ℃, followed by 10 min at 800 ℃.

2.4. Coating of AC with EBT dye

The surface of the prepared activated carbon was modified with EBT. This was performed by mixing 10 g of AC with 0.5 g of EBT dissolved in 1L of deionised water and leaving the mixture for 72 h at room temperature. The mixture was filtered and the AC-EBT was washed with deionised water until colourless to ensure that the unadsorbed EBT were removed. The material was dried in an oven for 24 h at 60 ℃.

2.5. Characterisation of Fabricated Materials

Scanning electron microscopy was utilised in order to identify the surface physical morphology for AC, activated carbon-modified Eriochrome Black T (AC-EBT), and AC-EBT sample after adsorption of copper ions onto its surface, AC-EBT-Cu (II). The chemical functionality of the prepared materials was qualitatively identified using Fourier transmission infrared spectroscopy (FT-IR). Spectra between 4000 and 650 cm^{-1} were recorded.

2.6 Removal of Cu (II)

Experiments were carried out at 25 °C. Adsorption experiments were performed by adding 15 mg of AC-EBT to 80 mL of metal ion solution of the desired concentration in a 100 mL Stoppard conical flask. The flasks were agitated at 200 rpm, using a stirrer for 1 h to attain equilibrium. After filtration, the final concentration of metal ion in the filtrate was estimated spectrophotometrically by monitoring absorbance using the UV-Vis spectrophotometer. Langmuir isotherms were used to study the adsorption capacity of the adsorbent. The amount of Cu present in the sample solution was obtained from the standard calibration curve [18, 19]. The adsorption capacity of metal ion, q_{eq} (mg g^{-1}), was calculated using the following equation:

$$q_{eq} = \frac{(C_i - C_{eq}) \times V}{m}$$

Where C_i and C_{eq} are the initial and equilibrium concentrations of metal ion (mg L^{-1}), respectively. V is the volume of solution (mL), and m is the mass of activated carbon sample (g).

III. RESULTS AND DISCUSSION

3.1. Preparation of Activated Carbon

Activated carbon is known as a very effective adsorbent because of its high porosity and large surface area. However, due to its high production costs, AC tend to be more expensive than other adsorbents, so many researchers have been fabricating AC from conventional waste (agriculture and wood industry), and non-conventional waste (municipal and industrial activities). Using the biomass waste as a raw material for the preparation of AC has many advantages, mainly of an economic and environmental nature, low ash contents, and reasonable hardness [20, 21]. In this study, AC was fabricated from pigeon pea husks due to their abundance and low economic value. The activated carbon was prepared using a chemical activating agent, which was (70%) H_3PH_4 solution. Chemical activation was used rather than physical activation as it produces higher yields, needs lower temperature of activation, less time, and results in a higher porosity [22]. The fabricated material was studied using SEM analysis, a well-known technique for studying the morphological features and surface characteristics of adsorbent materials. The SEM images of the prepared AC show a porous morphology and pores of different shapes and sizes (Figure 2).
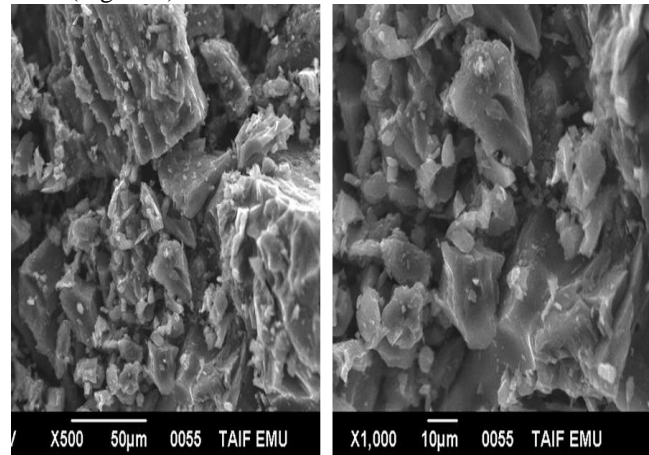

Fig. 2 Scanning Electron Micrographs of Activated Carbon Prepared from Pigeon Pea Husks

3.2 Modification the Surface of AC with EBT

The surface of AC was modified with a chelating agent, EBT. It contains one azo nitrogen atom and two oxygen atoms for binding and coordination with heavy metals [23]. In addition, there is a potential participation of sulfonic group (-SO$_3$H) as strong ion exchange group [12]. After modifying the pigeon pea husk-based activated carbon, the material was characterised using SEM analysis. As can be seen in Figure 3, the surface morphology of AC was significantly changed after modification of the surface of AC with EBT. Due to covering of AC with EBT, large and well-developed pores were formed on the surface of the AC.

It was concluded that the AC-EBT had more possibilities for adsorbing heavy metals since it had uniform porosity with a significant number of pores compared to AC, which had uneven porosity and a rough surface.
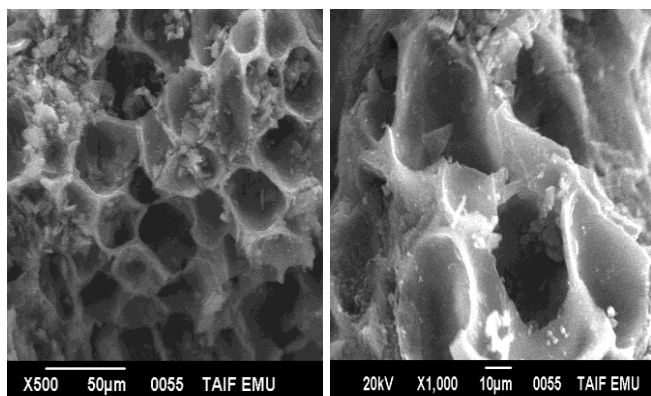

Fig. 3 Scanning Electron Micrograph of the Prepared Activated Carbon Modified with EBT

The prepared activated carbon and activated carbon modified with EBT were studied using an FT-IR spectrometer within the range of 4000 to 650 cm^{-1} were taken to get information on the nature of functional groups at the surface of the fabricated materials. The FT-IR technique is useful for the identification of constituents of the AC sample [24]. Figure 4 shows the FT-IR spectra of (A) AC and (B) AC-EBT. The broad band at 3450 cm^{-1} was attributed to the absorption of water molecules as a result of an O-H stretching mode of hydroxyl groups and adsorbed water. The band at 2900 cm^{-1} was assigned to C-H interaction with the surface of the carbon [25]. The spectra displayed bands at 1569 cm^{-1}, which corresponded to C=C vibration in aromatic rings [26]. The band at 1141 cm^{-1} corresponded to the C-O-H stretching vibration. In Figure 4 (B), the new band at 1046 cm^{-1} in the FT-IR spectrum of AC-EBT was attributed to S-O stretching in the sulfonate group [27], which confirmed the coating of AC with EBT.
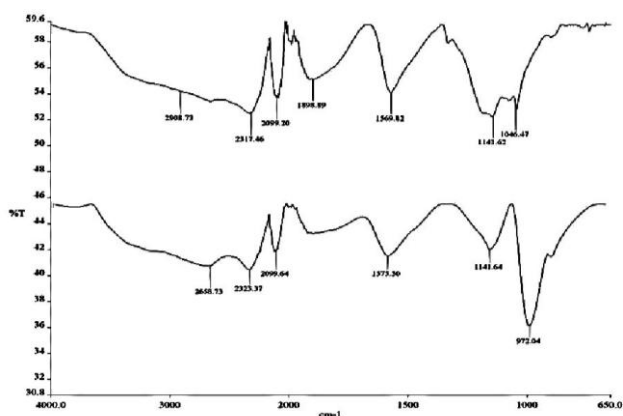

Fig. 4 FT-IR Spectra of (A) AC, and (B) AC-EBT Samples

3.3 Removing of Copper ions

The adsorption process results from the interaction between the surface of AC and the adsorbate. In this study, the adsorbate was copper ion. The effect of initial concentrations of copper ion on adsorption onto AC and AC-EBT was investigated at different concentrations, as can be seen in Figure 5. It was found that AC and AC-EBT

manifested the same behaviour until 100 mg L^{-1}, then AC-EBT was better than AC when using high concentrations of copper ion. This result confirms that modification of the surface of AC with EBT leads to an improvement in the properties of AC by forming a porous structure containing several functional groups; as a result, capacity for adsorption is enhanced.
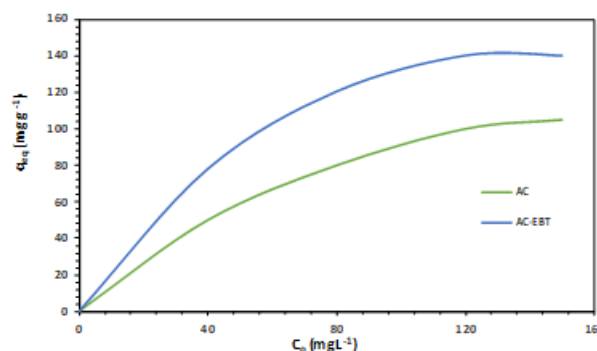

Fig. 5 Adsorption Capacity of Copper Ions onto AC and AC-EBT (T =25 °C, Shaking Time = 1 h, Adsorbent Mass =15 mg, Solution Volume = 80 mL)

Figure 6 shows the SEM micrographs of AC-EBT after uptake of copper ion. It was observed that there was a significant difference in the SEM morphology of AC-EBT before and after using the material for uptake of copper ion. Adsorption of copper ion on the surface of the prepared material caused changes in the morphology of AC-EBT, and the pores on the surface of AC are not distinct due to the adsorption of copper into the materials.
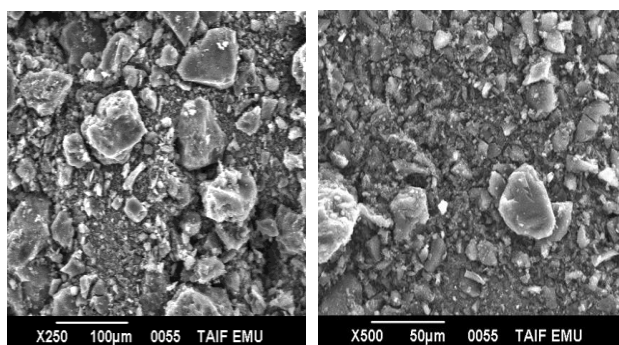

Fig. 6 SEM Image of AC-EBT after Uptake of Copper Ions

3.4 Adsorption Isotherm

The adsorption capacity of AC-EBT for copper was investigated for different copper concentrations. It was found that the adsorption capacity increased by increasing the initial concentration of copper ions. This is probably due to the driving force for mass transfer [28]. Adsorption isotherm was utilised to represent how copper ions interact with AC-EBT. The common known of all isotherms is the Langmuir isotherm. It is established in the following hypotheses: uniformly energetic adsorption sites, monolayer coverage, and no lateral interaction between adsorbate molecules. Therefore, the Langmuir adsorption model is applied to homogeneous adsorption process [28, 29]. The linearised form of the Langmuir isotherm is expressed as:

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{Q_o b} + \frac{C_{eq}}{Q_o}$$

Where C_{eq} is the equilibrium concentration of Cu in solution (mg L^{-1}), q_{eq} is the amount of Cu adsorbed per unit weight of adsorbent (mg g^{-1}), the constants Q_o and b are the characteristics of the Langmuir equation. Q_o is the maximum adsorption capacity (mg g^{-1}) and b is the energy of the adsorption (L mg^{-1}). The data for plot Langmuir is given in Table 1, and the modelled adsorption isotherm is plotted in Figure 7.

Table 1: Effect of Initial Concentration on the Equilibrium Concentrations

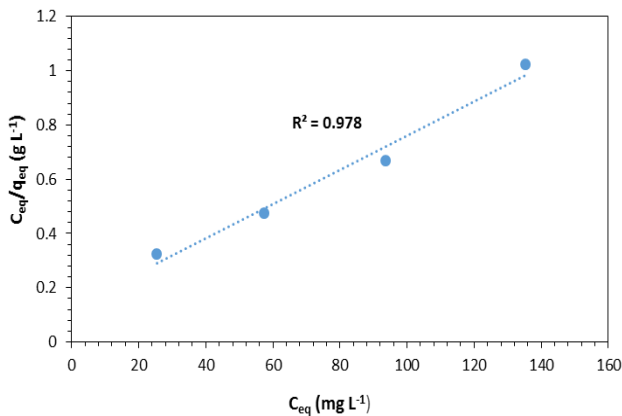| C_i (mg L^{-1})	C_{eq} (mg L^{-1})	q_{eq} (mg g^{-1})	$\frac{C_{eq}}{q_{eq}}$ (g L^{-1})
40	25.35	78.13	0.324
80	57.4	120.53	0.476
120	93.7	140.26	0.668
160	135.2	132.26	1.022

Fig. 7 Langmuir Sorption Isotherm of Copper (II) onto AC-EBT

The correlation coefficient ($R^2=0.978$) indicated that the adsorption data of copper on AC-EBT fitted well to the Langmuir isotherm and confirms the formation of a monolayer coverage of copper ion at the surface of AC-EBT. A plot of $\frac{C_{eq}}{q_{eq}}$ versus C_{eq} yields a straight line with slope $\frac{1}{Q_o}$ and intercept $\frac{1}{Q_o b}$. From the figure, it was found that the maximum experimental adsorption capacity was 158.73 mg g^{-1}. The Q_o value is higher than the value of adsorption capacity of previous study [29].

The essential features of the Langmuir isotherm are expressed in terms of a dimensionless constant separation factor, or equilibrium parameter (R_L) [30], which is defined by the following relationship:

$$R_L = \frac{1}{1 + b\,C_o}$$

Where b is the energy of the adsorption (L mg^{-1}) and C_o is the initial concentration of metal ion (mg L^{-1}). The value of R_L indicates the type of the isotherm system; if linear ($R_L = 1$), unfavourable ($R_L > 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$). The values of

R_L in Table 2 indicate the nature of isotherm. In this study, the value of R_L was found to be between 0 and 1, confirming that AC-EBT is favourable for the adsorption of copper under the conditions used in this study.

Table 2: Separation factor (R_L) at different copper concentrations

C_i (mg L^{-1})	R_L
40	0.347
80	0.210
120	0.150
160	0.117

IV. CONCLUSION

The present investigation showed that pigeon pea husks, a cheap and abundant material, can be utilised as a raw material for the fabrication of activated carbon. It was found that the process of fabrication of AC was considered economically feasible and yielded highly activated carbon. Modification of the surface of fabricated activated carbon with EBT was performed for the removal of copper ions. Copper ions are found to adsorb strongly on the surface of AC-EBT. Adsorption behaviour is described by a monolayer Langmuir type isotherm, and the maximum adsorption capacity was determined from the Langmuir equation and found to be 158.73 mg g^{-1}. It concluded that AC-EBT can be an effective adsorbent for removal of copper ions from wastewater.

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