



# Effect of Emeraldine, Metal Organic Frameworks and Modified Animal Charcoal on Potassium Ferrocyanide

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## Abstract

*The drawback of animal charcoal (easy saturation, polymerization risk etc) on adsorption has really called for a modification of carbon. In an effort to bridge the gap, Emeraldine supported with MOF-199 Hong Kong University of Science and Technology MOF (HKUST-1) metal organic frameworks (POLYMER/Metal Organic Frameworks) composite were used to modify animal charcoal. The effect of Bare Animal Charcoal (BB), Bare Animal Charcoal modified with Emeraldine (BE), Bare Animal Charcoal modified with HKUST-1 metal organic frameworks (BH), Bare Animal Charcoal modified with Emeraldine / HKUST-1 metal organic frameworks (BEH) supported with HKUST-1 metal organic frameworks composite on adsorption were studied using Ultraviolet-visible spectroscopy (UV-vis), scanning electron microscopy (SEM). The UV-vis analyses showed that Emeraldine fiber was in contact with HKUST-1MOF and both complemented the animal charcoal composite. SEM results revealed that BB and MOFs were well-dispersed and anchored tightly on the polymer composite. The adsorption capacity of the Bare Animal Charcoal and synthesized materials was studied by UV-vis spectroscopy analysis. The pH at which the composite works at optimum is 8, the optimum dosage was found to be 0.3g at a contact time of 100 mins all analysis was carried out at room temperature. Potassium ferrous cyanide as a known probe was used as an adsorbate. The Langmuir isotherm equation fitted the equilibrium data for Potassium ferrous cyanide sorption.*

**Keywords:** Animal Charcoal, Emeraldine, Hkust-1, modification and optimization

## 1. Introduction

Animal charcoal is primarily made from cattle and pork bones; however, to prevent the spread of Creutzfeldt–Jakob disease, the skull and spine are no longer used. (Medellin.C. et al. 2007). The bones are heated in a sealed vessel at up to 700 °C (1,292 °F); the oxygen concentration must be kept low while doing this, as it affects the quality of the product, particularly its adsorption capacity. Most of the organic material in the bones is driven off by heat, and was historically collected as Dippel's oil; that which is not driven off remains as activated carbon in the final product. Heating bones in an oxygen-rich atmosphere gives bone ash, which is chemically quite different. The tricalcium phosphate in Animal charcoal can be used to remove fluoride (Horowitz HS. Et al. 1967) and metal ions from water, making it useful for the treatment of drinking supplies. Animal charcoal is the oldest known water defluoridation agent and was widely used in the United States from the 1940s through to the 1960s. (Miangera H. & Mkongo G. 2003). As it can be generated cheaply and locally it is still used in certain developing countries, such as Tanzania. (Dannny, C. et al 2000). Animal charcoal usually have lower surface areas than activated carbons, but present high adsorptive capacities for certain metals, particularly those from group 12 (copper, zinc, and cadmium).

Because of the low surface area of animal charcoal, metal organic frameworks and polymer were used to increase the surface area making it have a higher adsorptive capacity. Metal-organic frameworks are a class of porous materials which are synthesized through the self-assembly of metal ions and organic linkers. MOFs have crystalline structures and typically are characterized by large internal surface areas, uniform but tunable cavities



and tailorable chemistry. These characteristics make them very promising for a variety of applications, including gas storage (Li, J. 2009) chemical separation (Lee, J. 2009), catalysis (Ma, L. 2009 & Allendof, M. 2009), sensing (Horcajada, P. 2010) and drug delivery (Chae, H. 2004). By serving as unique host matrices for various functional species, MOFs also offer the opportunity to develop new types of composite materials that display enhanced (gas storage) or new (catalytic, optical and electrically conductive) behaviours (Bureekaew, S. 2009 & Zhao, D. 2010) in comparison to the parent MOF counterparts.

The type of organic materials, called conjugated polymers, has attracted a lot of attention lately, as materials for possible applications in micro-electronic devices (Larsen R.W. 2011). The reasons for this are their unique properties and versatility. The emeraldine form of Polyaniline, often referred to as emeraldine base (EB), is either neutral or doped, with imine nitrogens protonated by an acid (Palys, T. et al. 2000)

In this work we modified Animal charcoal with Hkust-1 MOFs and Emeraldine to increase the surface area of Animal charcoal as such increase its adsorptive capacity.

## 2. Materials and Method

### 2.1 Reagents

In this work all chemical reagents were purchased from Sigma-Aldrich (of analytical grade) and used without further purification: MOF-199 (HKUST-1), Animal charcoal, Copper(II) Nitrate Trihydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ), Benzene-1,3,5-tricarboxylic acid ( $\text{H}_3\text{BTC}$ ), Ethanol (EtOH), Dimethylformamide (DMF), Ammonium persulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) (Sigma Aldrich, Germany), Hydrochloric acid (HCl) (Alpha), Sulfuric ( $\text{H}_2\text{SO}_4$ ) (Fisher chemicals, United Kingdom).

#### 2.1.1 Instrumentation

Ultra Violet Spectroscopy (UV-vis), Scanning Electron Microscopy (SEM).

### 2.2. Method

To prepare the composite, Animal charcoal mixed with Emeraldine and Hkust-1, (200mg) Emeraldine powder and 200 mg of Hkust-1 were mixed with animal charcoal (800 mg) and mixture was transferred to the mortar and pestle and then homogenized.

#### 2.2.1 Optimization procedures

##### 2.2.1.1 Determination of optimum composite dosage, pH and Contact time

In order to find out the optimum composite dosage, same amounts of bared, Emeraldine modified, Hkust-1 modified and Emeraldine + Hkust-1 modified animal charcoal: 0.1 g – 1.0 g were measured different from every composite into a Vial containing 2ml of 0.1M  $\text{K}_3\text{Fe}(\text{CN})_6$ . Ten samples of each composites were analyzed using UV-vis.

In order to improve the performance of the modified composite, the pH may influence the response of the composite. Therefore, the effect of pH was studied. The effect of the pH of supporting composite response was tested in the range of 1.0 to 10 using the pH meter electrode at the optimum dosage. The rate of adsorption on composite has effect on the performance of the modified composite. Therefore, the amount of adsorbate on composite depends on the contact time. So that, the contact time was optimized. The modification was carried out

at different contact time of 10 -140 mins. To determine the influence of time at which the contact was optimum, each modified composite was deposited in 0.1M  $K_3Fe(CN)_6$ . This is in agreement with (Pardieu, E. 2009)

### 3 Result and discussion

#### 3.1 Characterisation of Composite

The morphology of the Homogenised samples was carried out using the Scanning Electron Microscopy (SEM) as shown below:

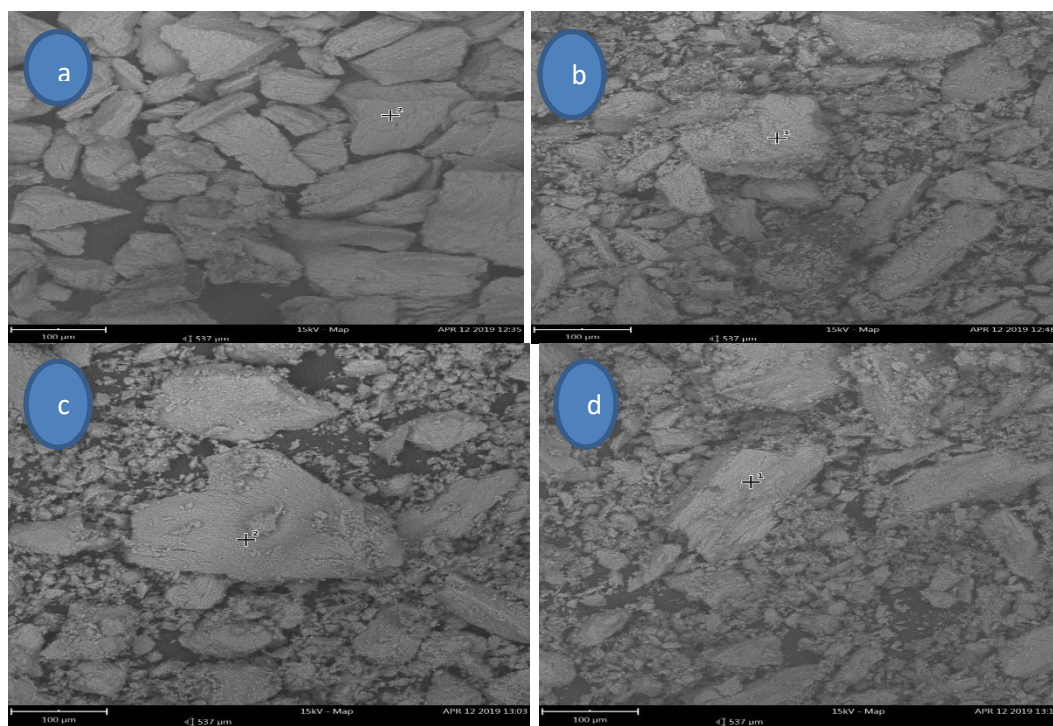


Figure 1: Shows the SEM Analysis of (a) Bare Animal charcoal (BB) SEM analysis (b) Animal charcoal mixed with Emeraldine (BE) SEM analysis (c) Animal charcoal mixed with Hkust (BH) SEM analysis (d) Animal charcoal mixed with Emeraldine and Hkust (BEH) SEM analysis

#### 3.2 Optimization of composite

##### 3.2.1 Effect of Dosage

The effect of dosage of the composite was studied with UV-vis. Dosage is an important parameter in adsorption studies as it gives the optimum dose at which maximum adsorption occurs. Figure 2 shows the effect of composite dose on the adsorption of analyte (ferrous cyanide). The percentage adsorbed first increased with an increase in composite dose due to increased surface area and more adsorption sites available for binding to analyte (Ahalya, N. et al. 2006). Maximum removal was obtained at 0.3 g hence it was considered the optimum dose for adsorption experiments. After 0.3 g of sorbent dosage there was no significant change in the amount of analyte.

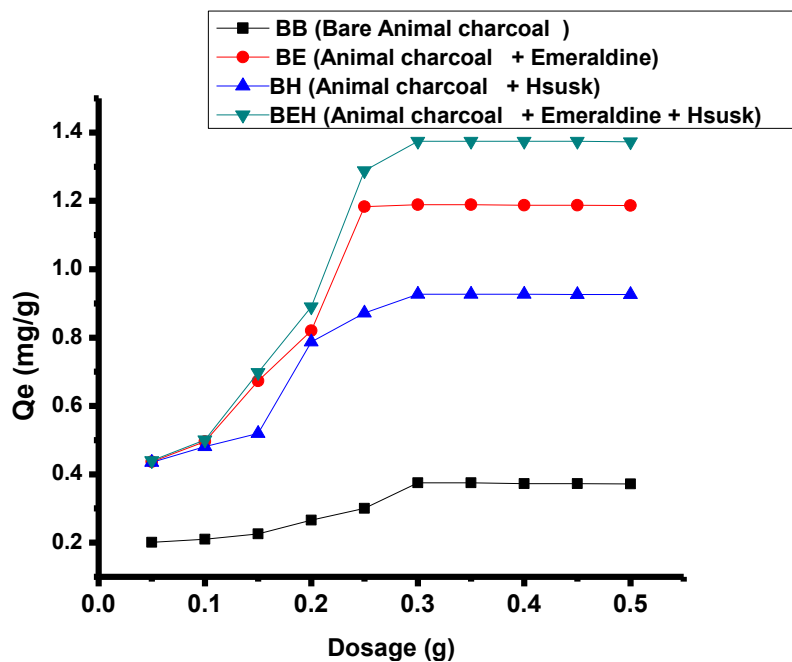


Figure 2: The effect of modifiers on bared animal charcoal in 0.1 M  $K_3Fe(CN)_6$ .

### 3.2.2 Effect of pH

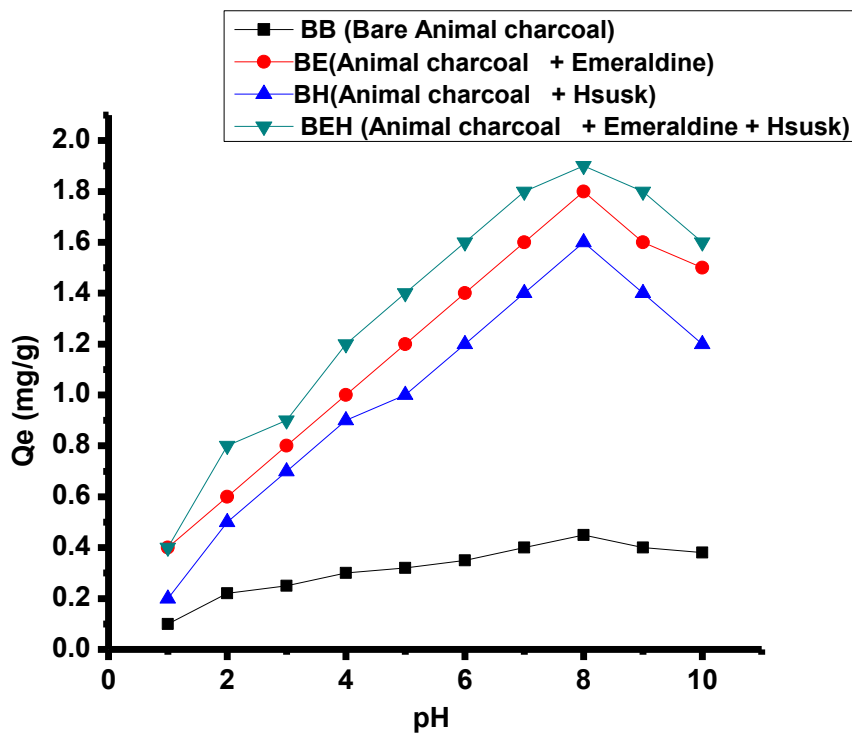


Figure 3: The effect of pH at which the modified composite is at optimum

pH is an important parameter in adsorption as it affects both the degree of ionisation of the sorbate and the surface charge of the sorbent during the adsorption process. pH influences adsorption by a way of modifying the functional groups of the MOFs and Hkust-1 adsorbent. Figure 3 shows the effect of pH on the adsorption of ferrous cyanide. The amount adsorbed decreases after pH 8, and a maximum adsorption of 0.36 mg/g, 1.6 mg/g, 1.8 mg/g and 1.9 mg/g at animal charcoal, animal charcoal+ Hkust-1, animal charcoal + Emeraldine and animal charcoal+ Hkust-1 + Emeraldine respectively. Doping of emeraldine with hydrochloric acid developed acidic surface sites which had a high affinity for the ferrous cyanide and hence the ability to adsorb ferrous cyanide. The results are in agreement with findings (Pardieu, E. 2009).

### 3.2.3 Effect of Contact time

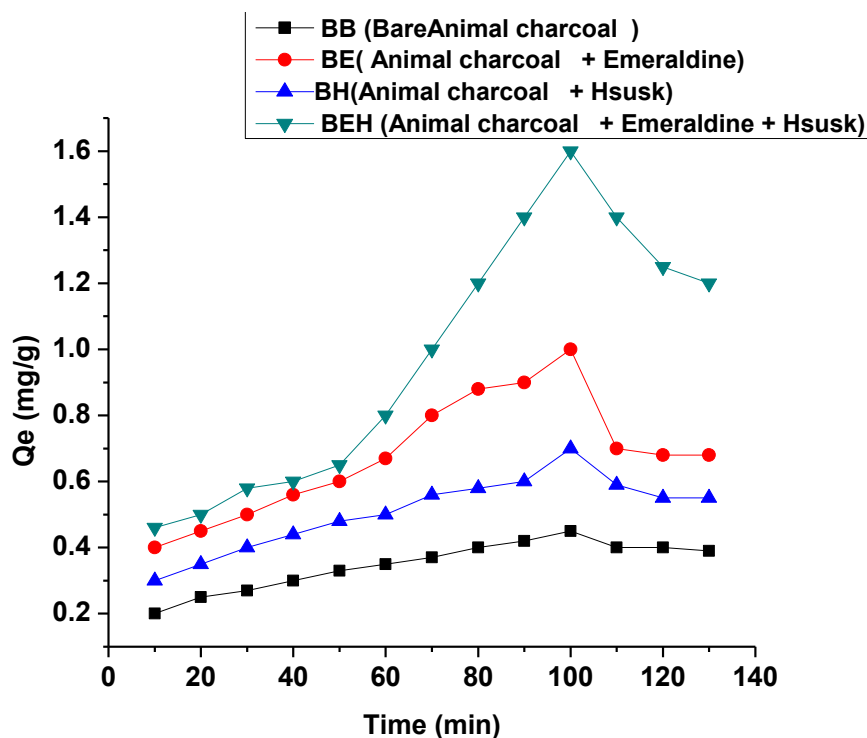


Figure 4: The effect of contact time at which the composite adsorbs 0.1 M  $K_3Fe(CN)_6$ .

The effect of contact time on biosorption was investigated from 10-130 min. Figure 4 shows the effect of contact time on the adsorption of ferrous cyanide. The adsorption rate of ferrous cyanide increased with an increase in contact time. The rate of adsorption is higher in the beginning due to a large available surface area of the adsorbent. The fast-initial uptake is also due to the rapid accumulation of ferrous cyanide on the surface of the adsorbent. As these sites become exhausted the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles, hence more time is then consumed on diffusion of ferrous cyanide to binding sites. However, it decreases after an equilibrium time of 100 min, which indicates that the adsorption had reached saturation. Therefore, the adsorption time was set at 100 min in each of the next experiments. Further increase in time after 100 min did not bring about any improvement. This is in agreement with the work done by (Neera, S. 2009).

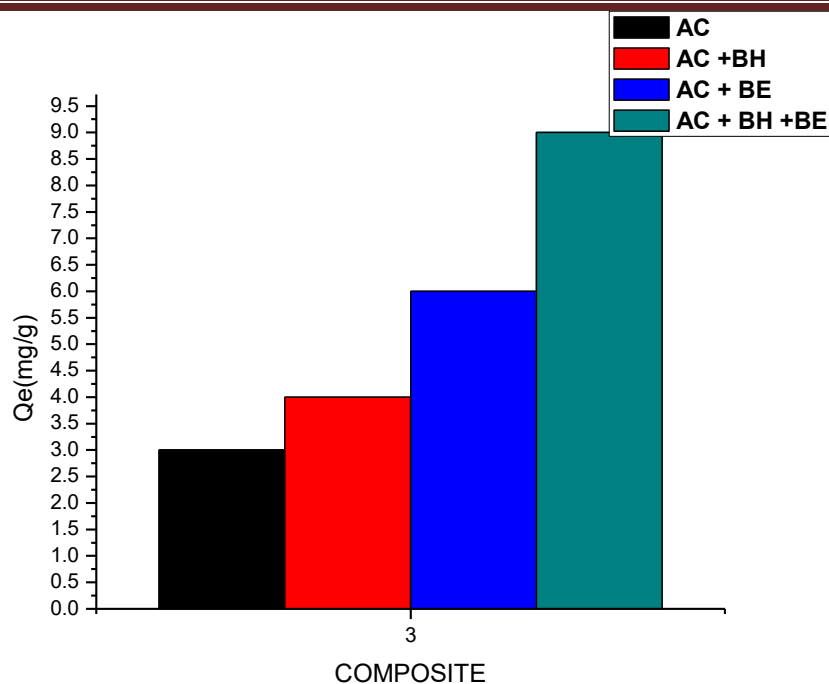


Figure 5: Shows a histogram of the study being repeated at the same laboratory giving no significant difference.

### 3.3 Repeatability Study

Same experiment was repeated in the same laboratory and the increase in the surface area of the composite (figure 5) was found to be the same as the one optimized therefore the surface area increased on addition of modifies on animal charcoal as well increased the adsorption capacity of the composite.

## 4 Conclusion and Recommendations

In this work, we introduced Bare Animal Chacoal (BB), Bare Animal Chacoal modified with Emeraldine (BE), Bare Animal Chacoal modified with HKUST-1 metal organic frameworks (BH), Bare Animal Chacoal modified with Emeraldine / HKUST-1 metal organic frameworks (BEH) supported with HKUST- 1 metal organic frameworks composite which increased the surface area of the bared animal charcoal upon modification with polymer and MOF. Furthermore, the modification procedure is less expensive and more convenient which increase the surface area for adsorption there by solves the problem of blockade in animal charcoal. In order to fully assess the application potential and added value of the developed composite, future/or further research is required on adsorption of other analytes.

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