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Research Article

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Adsorption of Cr^{6+} and Fe^{3+} from hospital wastewater using activated carbon from epicarp of *Detarium microcarpum* and *Balanitea egyptiaca* shells

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ABSTRACT

In this study, the adsorption behaviour of some adsorbents; ACDMPA, ACDMZC, ACBAPA, ACBAZC and CAC with respect toCr^{6+} and Fe^{3+}has been investigated in order to consider its application for the removal of metal ions in Hospital wastewater. The batch adsorption studies parameters such as adsorbent dosage, agitation time and pH were employed. The influence of pH on Cr^{6+} and Fe^{3+} uptake by different adsorbents used were carried out between pH 2-8. The optimum pH for the removal of Cr^{6+} by all the adsorbents was 2, the optimum pH for the removal of Fe^{3+} was 4 by ACDMPA and CAC. At pH 6, the maximum adsorption of Fe^{3+} occur when ACDMZC, ACBAPA and ACBAZC was used. An equilibrium time of 30 minutes was required for the adsorption of Cr^{6+} and Fe^{3+} by CAC, while 45minutes was the equilibrium time for the adsorption of the two metal ions onto ACDMPA, ACDMZC, ACBAPA and ACBAZC. The optimum dosage for removal of Fe^{3+} was 0.4g when CAC and ACDMPA was used, and 0.6g when other adsorbents were used. For Cr^{6+} the optimum dosage for its removal was 0.4g when ACDMPA was used, while 0.6g is the required optimum dosage for other adsorbents. Adsorption parameters for ACDMPA were determined using both the Langmuir and Freundlich Isotherms, but the data for Fe^{3+} adsorption were well fitted into the Langmuir equation, while the adsorption of Cr^{6+} was well fitted into the Freundlich than the Langmuir equation. The results proved that all the carbon produced has the ability to remove heavy metal specie in wastewater.

Key words: Adsorption, heavy metals, dosage, contact time and pH.

INTRODUCTION

Recently, the control of heavy metals pollutants has been a problem to man, especially in Nigeria. The pollution of water bodies due to the discharged of non-degradable hazardous compounds was causing worldwide concern. The heavy metals are the most important constituents among toxic compounds in the effluent [1]. These heavy metals are discharged into the environment through industrial activities and also through Hospital wastewater. These metals are known to accumulate in our ecosystem once they are discharged; from very low level to a level above the threshold in the environment. Most of these metals such as iron, lead, cadmium, chromium, cobalt, nickel, mercury, and arsenic are very toxic. They are carcinogenic and at a very high concentration may cause bad health condition [2- 4]. Hospital effluent contains enormous quantities of inorganic and organic chemical wastes, which are steadily becoming more complex and difficult to treat by conventional technologies. Adsorption onto activated carbon has been found to be superior to other techniques of wastewater treatment because of its capability for adsorbing a broad range of different types of absorbates efficiently, and its simplicity of design [5,6].

Moreover, some of the conventional techniques employed for treatment of wastewater include; coagulation and flocculation, reverse osmosis, chemical oxidation, membrane separation process, electrochemical methods, aerobic and anaerobic microbial degradations [7]. The above method suffer from one or more limitations (Efficiency, cost , effectiveness, availability and management, except “Adsorption” [7]. In addition, the world economic today is focusing on better waste management policies so as to reduce waste and “to protect the environment” [8].

The purpose of this research is to study the adsorption behaviour of heavy metal ($Fe^{3+}$and Cr^{6+}) ions from Hospital wastewater, using activated carbon derived from epicarp of *Detarium microcarpum* and *Balanitea egyptiaca* shells. This aim will be achieved by evaluating equilibrium adsorption using adsorbent dosage, agitation time and pH of the solution in order to ascertain the optimum conditions for the adsorption of these heavy metal ions onto the activated carbon.

1.1. Sample Collection and Treatment

Detarium microcarpum and *Balanitea egyptiaca* fruits were collected from Dutsin-Ma Local Government area of Katsina State. After collection, it was taken to the Department of Biological Science, Ahmadu Bello University Zaria, where it was authenticated and identified. The Epicarp shells were removed and washed several times with tap water and then with distilled de-ionized water to remove impurities and salts. The precursors were sun-dried and later dried in an oven at 110^{o}C for 24 hrs. The dried shells were pulverised and sieved to 850μm particle size.

1.2. Preparation of Activated carbon from the precursors

Activated carbon were produced using $ZnCl_2$ and H_3PO_4 as activating agents. Standard methods were followed for the carbon production as described by [6]. The Carbon produced were ACDMPA (Activated carbon from *Detarium microcarpum*, using H_3PO_4 as activating agent), ACDMZC (Activated carbon from *Detarium microcarpum*, using $ZnCl_2$as activating agent), ACBAPA (Activated carbon from *Balanitea egyptiaca*, using H_3PO_4 as activating agent) and ACBAZC (Activated carbon produced from *Balanitea egyptiaca*, using $ZnCl_2$ as activating agent). Commercial activated carbon (CAC) was purchased, which served as standard.

1.3. APPLICATION OF ACTIVATED CARBON TO RAW HOSPITAL WASTEWATER

Activated carbon produced from the Epicarp of *Balanitea egyptiaca* and *Detarium micropcarpum* seed shell was used for the removal of heavy metals ions from wastewater. Samples of the wastewater (10cm^3) were mixed with 0.1g carbon, in 250cm^3 Erlenmeyer flasks, then Standard methods were followed to ensure proper removal as described by [9].

1.4. Batch Adsorption studies

1.4.1.Effect of adsorbent dosage on the adsorption of $Cr^{6+}$and Fe^{3+}.

Effect of adsorbent mass was studies by using different masses (0.2, 0.4, 0.6, 0.8, and 1.0 g) of the adsorbent for the batch experiment described above.

1.4.2.Effect of agitation time on adsorption of *$Cr^{6+}$and Fe^{3+}*

The effect of agitation time on the removal efficiency of different heavy metal ions were investigated at 15, 30, 45 and 60minutes time of contact.

2.4.3. Effect of initial solution pH on adsorption of $Cr^{6+}$and Fe^{3+}.

The pH of solution is important in adsorption study, in that pH of a solution determines the speciation of the metal ion in solution and also dictates the surface charge of adsorbents with variable charge characteristics. Using constant concentration of 0.6 g adsorbent dose and agitation time of 45 mins at ambient temperature, the pH of the solution was varied. The pH values, at which the adsorption behaviour was investigated were 2, 4, 6 and 8.

2.5.1. Calculation

From the measured concentration of Cr^{6+} and Fe^{3+} ions, amount of the metal adsorbed (qe) was calculated using equations 1 [10].

$$Qe= \frac{V(Co - Ce)}{100M} \quad (1)$$

where qe is the amount of adsorbate ion adsorbed in milligram per gram of the adsorbent, Co is the initial concentration of the metal ion before the adsorption process, Ce is the equilibrium concentration of the metal ion in the filtrate after adsorption process, M is the mass in gram of the adsorbent and V is the volume of the solution in mL.

RESULTS AND DISCUSSION

Preamble: ***Effect of Process Parameters***
The effect of different process parameters such as adsorbent dosage, contact time and pH were strongly studied on the adsorption of Cr^{6+} and Fe^{3+} onto the activated carbon produced.

3.1. Effect of adsorbent dosage on the adsorption of Cr^{6+} and Fe^{3+}

Presented in Figures 3.1- 3.2 below, illustrated the variation of metal ions adsorbed at adsorbent dosage of 0.2,0.4, 0.6, 0.8 and 1.0g.

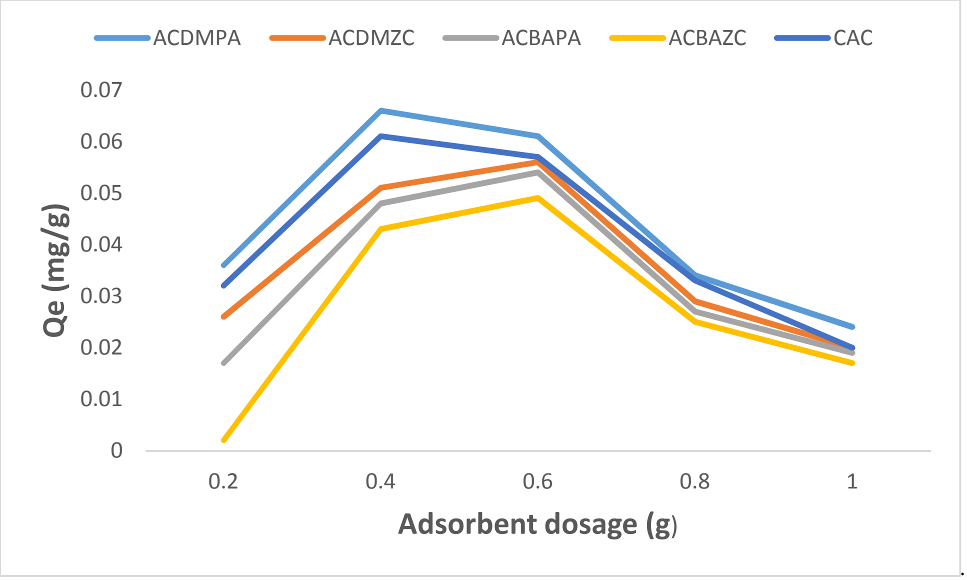
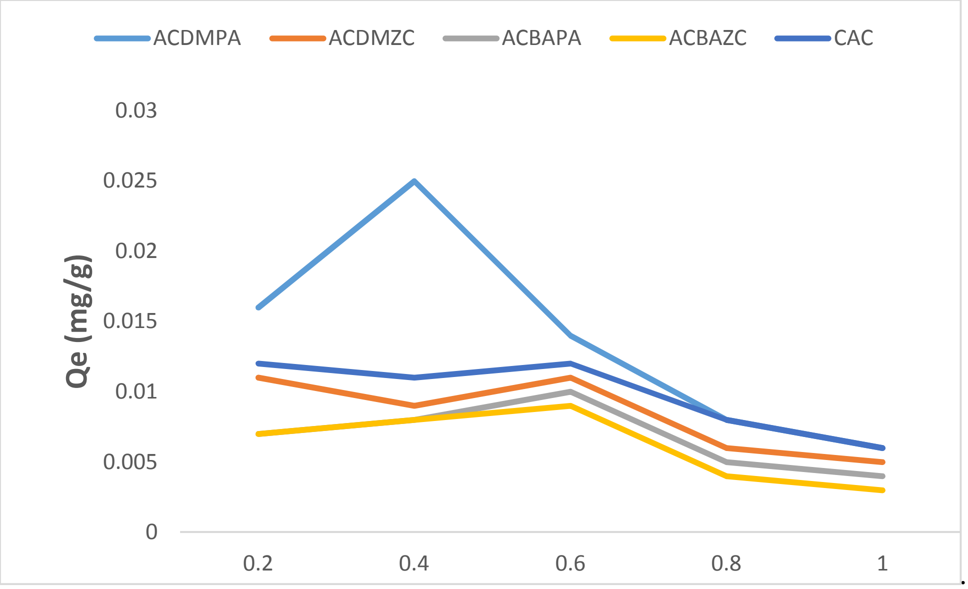


Figure1. Effect of dosage on adsorption of Fe^{3+} by all the adsorbents



Adsorbent dosage (g)

Figure 2. Effect of adsorbent dosage on adsorption of Cr^{6+}onto the carbons

DISCUSSION

Figures 1 and 2 shows the adsorption of Fe^{3+} and Cr^{6+} onto all the prepared adsorbents at different dosage of 0.2, 0.4, 0.6, 0.8 and 1g respectively. A trend of increment in adsorption capacity of Fe3+ occur with increment in adsorbent of 0.4g for ACDMPA and CAC, while ACDMZC, ACBAPA and ACBAZC recorded the highest adsorption when the dose was 0.6g. The adsorbents ACDMPA and CAC recorded a maximum adsorption capacity of 0.066 mg/g and 0.061mg/g for Fe(III) respectively. The adsorbents ACDMZC, ACBAPA and ACBAZC recorded a maximum adsorption capacity of 0.056, 0.054 and 0.049mg/g Fe^{3+} respectively. On the other hand Figure 2 shows the maximum adsorption capacity of Cr^{6+} as 0.025, 0.012, 0.011, 0.010 and 0.009mg/g for ACDMPA, CAC, ACDMZC, ACBAPA and ACBAZC respectively at carbon dosage of 0.6g, with the exception of ACDMPA at 0.4g. Further increment of adsorbent above 0.6 g resulted in a decline in adsorption capacity for bothFe^{3+} and Cr^{6+}. The initial increment in adsorption capacity with increase in adsorbent dosage was expected, since the number of adsorbent sites increased and thus more surface area was available for metal attachment. Same trend has been reported by earlier researchers [11,12].

3.2.Effect of agitation time (contact time) on the adsorption of Cr^{6+} and Fe^{3+}

Figures 3.3 and 3.4 represented the effect of contact time on the adsorption of Cr^{6+} and Fe^{3+}onto the adsorbents. The contact time of 15, 30, 45 and 60 minutes was used to monitor the adsorption pattern.

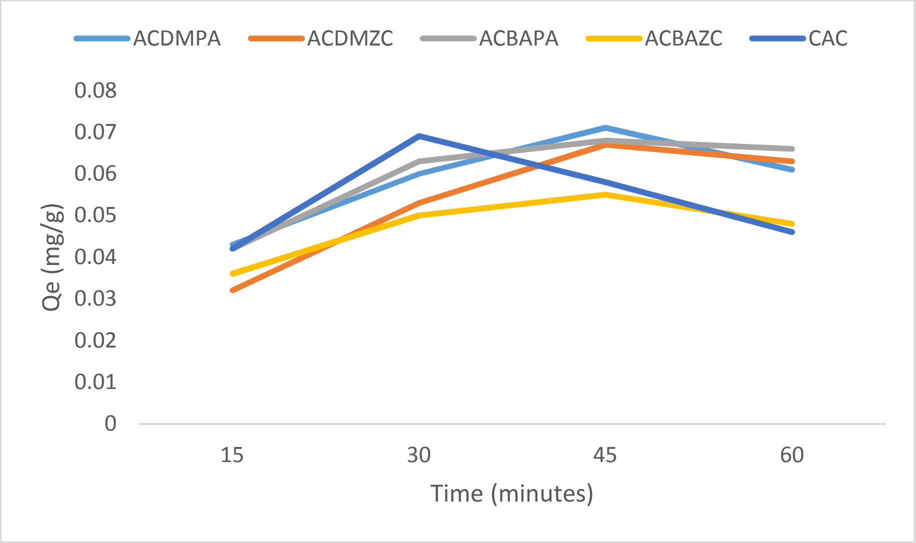


Figure 3. Effect of agitation time on adsorption of Cr^{6+} by all the adsorbents

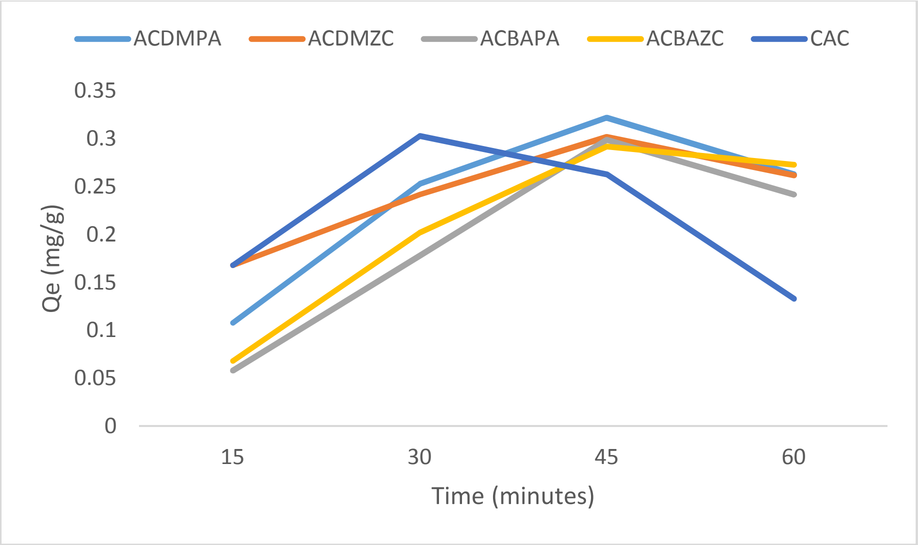


Figure 4. Effect of agitation time on adsorption of Fe^{3+} by all the adsorbents

The effect of contact time on the adsorption efficiency of the adsorbents forCr^{6+} and Fe3+ were studied. The results were presented in Figures 3 and 4. The rate of metal ions uptake was rapid in the first 30 minutes by all the adsorbents. The removal efficiency of CAC for both ions decreases as the contact time exceeded 30minutes, while the other adsorbents adsorbed optimally at contact time of 45mimutes. The results is in agreement with the one obtained by Sharma et al., [13] for the removal of chromium in wastewater by fly ash.

3.3. Effect of pH on the adsorption of Cr^{6+} and Fe^{3+}

The pH of the solution that contains the adsorbate plays a vital role on the adsorption of adsorbate. Figures 3.5 and 3.6 illustrated the adsorption behaviour of the metal ions, at pH 2, 4,6 and 8.

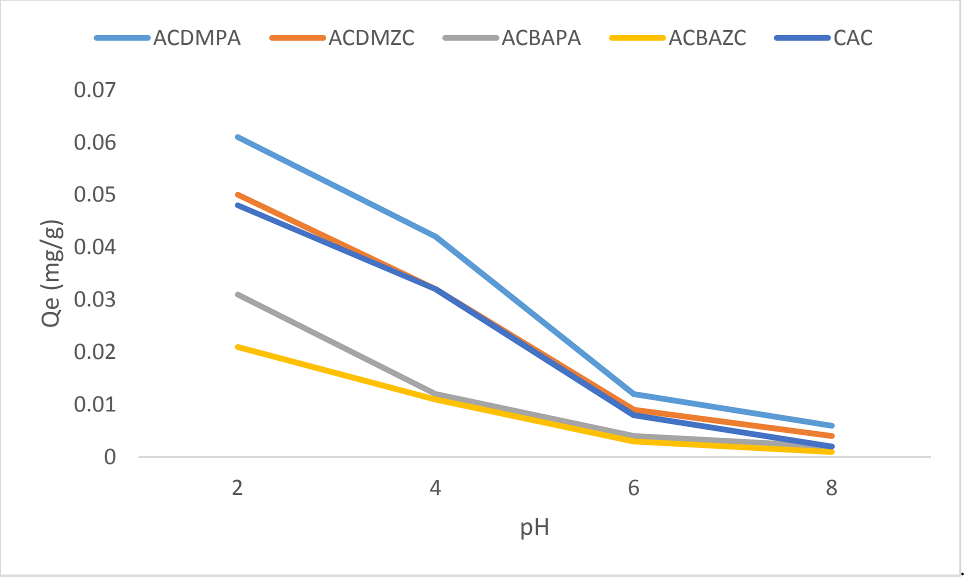


Figure 5. Effect of pH on the adsorption of Cr^{6+} by all the adsorbents

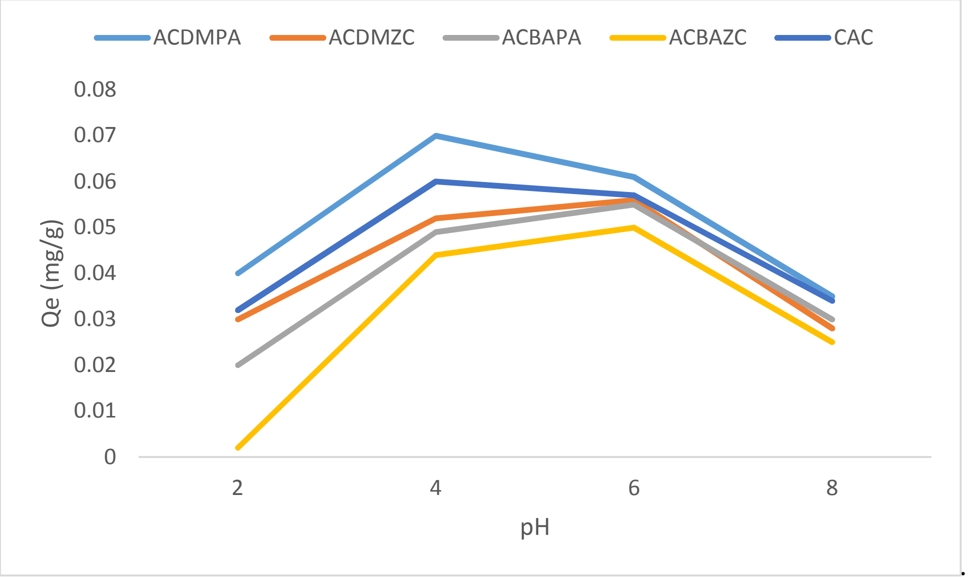


Figure 6. Effect of pH on the adsorption of Fe^{3+} by all the adsorbents

The pH of a solution plays a vital role on the adsorption of heavy metals since it estimate the surface charge of the adsorbent and the extent of ionization and speciation of the adsorbate. Presented in Figure 5, is the effect of pH on the adsorption of Cr^{6+} at various pH values. It was observed that the adsorption of Cr^{6+} on all the carbon continuously decreases with increase in pH and the maximum adsorption was observed at pH 2. The sharp decrease in the removal of Cr^{6+} with increase in pH of the solution may be due to the fact that, low pH leads to an increase in H^+ ions on the carbon surface, which results in significantly strong electrostatic attraction between $HCrO_4^-$and the positively charged carbon surface, which is in agreement with research carried out earlier [14,15,16].Similar results were also obtained by [17] and[18].The level of adsorption by the adsorbents followed this order; ACDMPA > ACDMZC > CAC > ACBAPA > ACBAZC, which may be attributed to large BET surface area that favours adsorption. At pH greater than 6 and up to 8, there was no significant increase on the adsorption of Cr^{6+} by all the adsorbents.

On the other hand, Figure 6 shows the effect of pH on the adsorption of Fe^{3+} at various pH levels. The adsorption of Fe^{3+} increases with increase in pH range of 4-6. An increase of pH above 6 resulted in poor adsorption of Fe^{3+} by all the adsorbents. It can be deduced that at lower pH value, the surface of the adsorbent is surrounded by hydrogen ions (H^+), thereby preventing metal ions (Fe^{3+} ion) from approaching the binding sites of the adsorbents. At higher H^+ concentration, the adsorbent surface becomes more positively charged such that the attraction between adsorbents and metal cations is reduced. In contrast, as the pH increases, lesser H^+ which facilitate greater metal removal due to no availability of H+ at the surface of the adsorbent. The results is in agreement with work carried out earlier by Oladunni et al., [9].

3.4. Adsorption Modelling

The estimation of the adsorption capacity of the activated carbon with large surface area (ACDMPA) was further carried out by analysing the isotherm data using Freundlich and Langmuir adsorption isotherm models. The Langmuir and Freundlich models are the most commonly used for solid - liquid phase isotherms.

Langmuir isotherm is given as

$$Qe = \frac{QmaxbCe}{1 + bce} \qquad (2)$$

Which can be rewritten as follows

$$1/qe = 1/qmax + 1/bCe \qquad (3)$$

where qe is the amount of adsorbate adsorbed per gram of dried adsorbent at equilibrium (mg adsorbate/g of dried adsorbent), qmax is the constant relating to the maximum amount of adsorbate ion bound per g of adsorbent for a monolayer (mg/g), b is Langmuir constant or adsorption coefficient or the adsorption affinity (L/mg) for binding of adsorbate on the adsorbent sites, and Ce is equilibrium (residual) adsorbate concentration in solution after sorption (mg/L). A plot of 1/qe against 1/Ce (Figs. 5 and 6) gives intercept (1/qmax) and slope (1/qmaxb) [19]. The coefficient of determination, R^2 was used for comparison with that of Freundlich.

The Freundlich isotherm model which describe non – ideal sorption onto heterogeneous surfaces involving multilayer sorption is defined as follows [19]

$$\log qe = \log KF + \frac{1}{n} \log Ce$$

where qe is the amount of adsorbate adsorbed per unit weight of adsorbent, KF is Freundlich constant measuring adsorption capacity (L/mg), Ce is equilibrium concentration of the adsorbent in solution (mg/L), n is constant related to adsorption efficiency and energy of adsorption or adsorption intensity of the adsorbent. The co-efficient of determination R^2 was used to compare with that of Langmuir

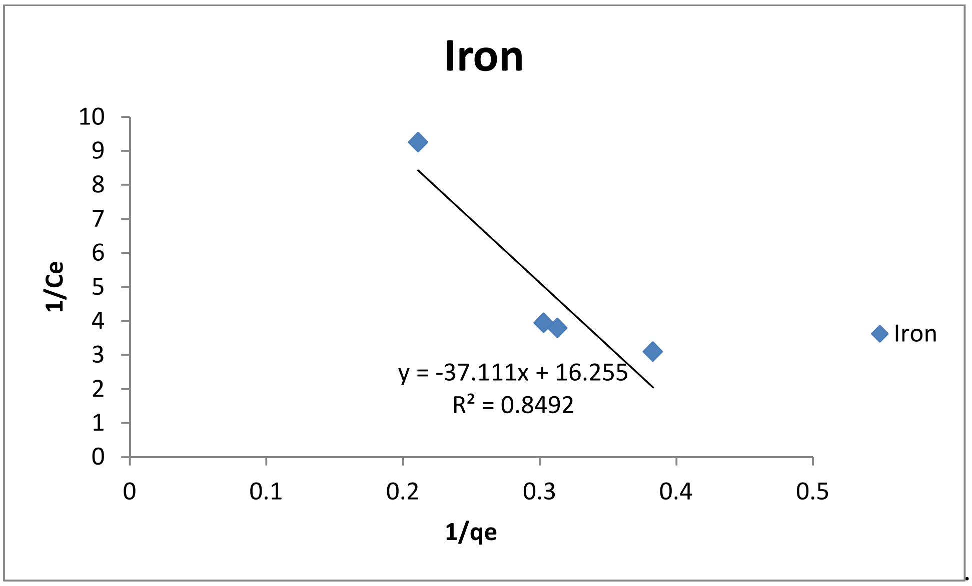


Figure 7. Langmuir adsorption isotherm of Fe^{3+} using ACDMPA

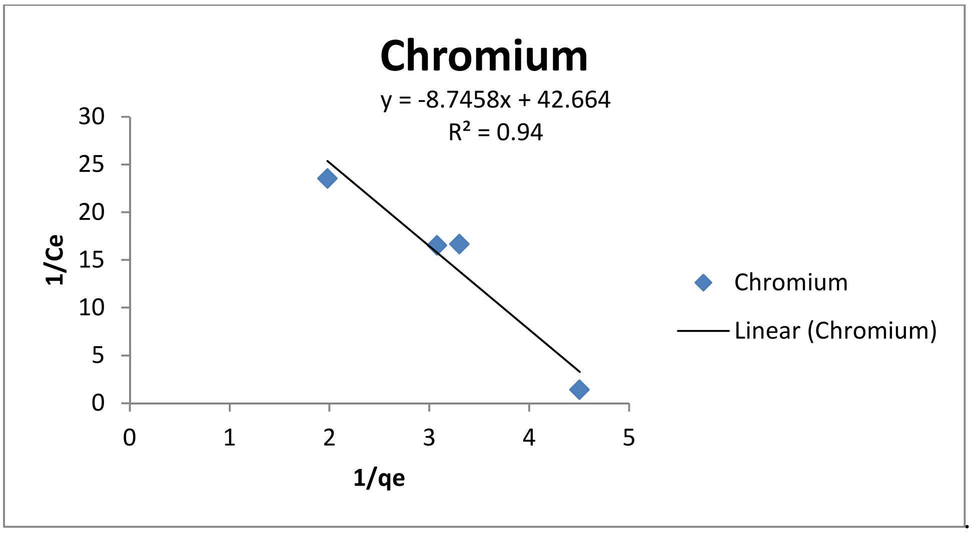


Figure 8. Langmuir adsorption isotherm for Cr^{6+} using ACDMPA

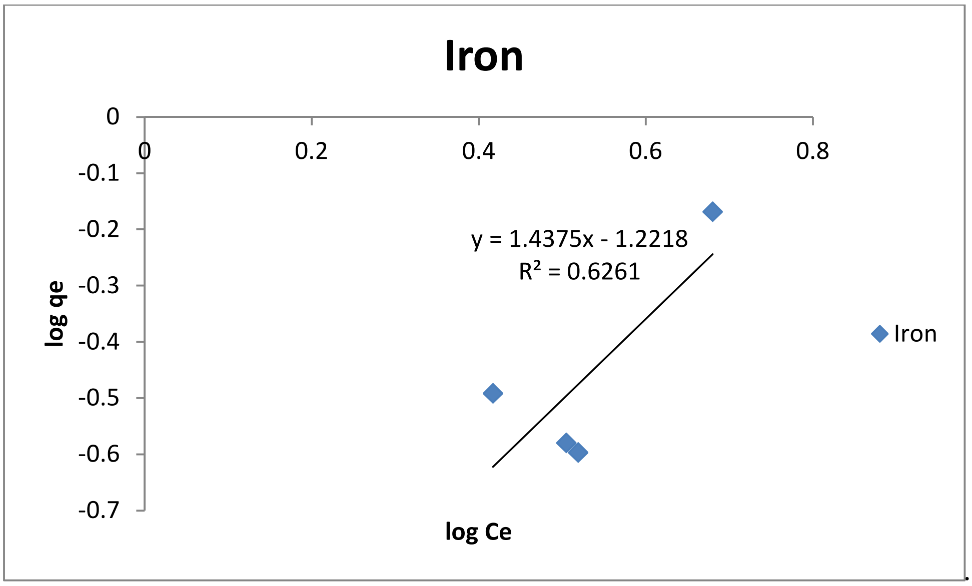


Figure 9. Freundlich adsorption isotherm of Fe^{3+} using ACDMPA

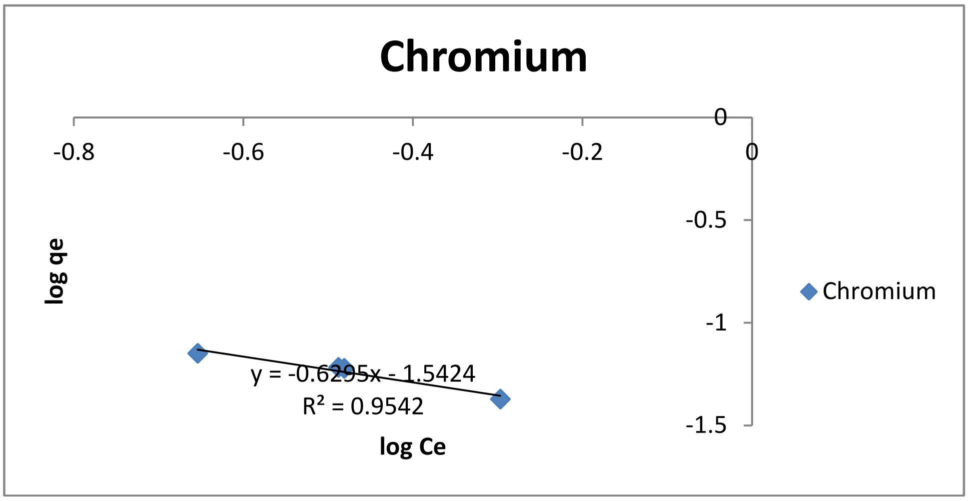


Figure 10.Freundlich adsorption isotherm of Cr6+ using ACDMPA

CONCLUSION

The adsorbents produced from *Balanitea egyptiaca* and *Detarium microcarpum* were effective and efficient for the removal of Cr^{6+} and Fe^{3+} from Hospital wastewater. The batch method of adsorption were employed by varying parameters such as adsorbent dosage, agitation time and pH of wastewater solution at room temperature. The optimum pH corresponding to the maximum removal of Cr^{6+} was 2 for all the adsorbents, while that of Fe^{3+} was 4 for ACDMPA and CAC. At pH 6, ACDMZC, ACBAPA and ACBAZC shows maximum adsorption of Fe^{3+}.The removal efficiency of CAC for both ions decreases as the contact time exceeded 30minutes, while the other adsorbents adsorbed optimally at contact time of 45mimutes. The optimum adsorption of Cr^{6+} by ACDMPA occurred when the dosage was 0.4g, while that of ACDMZC, ACBAPA, ACBAZC and CAC adsorbed optimally when the adsorbent dosage was 0.6g. The optimum dosage for removal of $Fe^{3+}$was 0.4g when CAC and ACDMPA were used, and 0.6g when other adsorbents were used. Adsorption Isotherm for ACDMPA were determined using both the Langmuir and Freundlich models. The data for Fe^{3+} adsorption were well fitted into the Langmuir model than the Freudlich with R^2 values of 0.8492 and 0.6261 respectively, while the adsorption of Cr^{6+} was well fitted into the Freundlich model than the Langmuir with R^2 values of 0.9542 and 0.9400 respectively. The results proved that all the carbon produced has the ability to remove heavy metal specie in Hospital wastewater.

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