Communication in Physical Sciences 2018, 3(1): 85-90

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Batch adsorption of Mn^{2+} and Co^{3+} from Refinery wastewater using activated carbon from epicarp of *Detarium microcarpum* and *Balanites aegyptiaca* shells

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Received 24 January 2018/Accepted 12 October 2018/Published online: 27 December 2018

Abstract *Refinery wastewater is a rich source of heavy metal ion contaminant and may not be safe if directly discharge to the environment without pre-treatment. This study seeks to implements application of various activated carbon adsorbents for the removal of cobalt and manganese ions from refinery waste water. The adsorbent produced include; 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 Balanites aegyptiaca, using* H_3PO_4 *as activating agent) and ACBAZC (Activated carbon produced from Balanitea egyptiaca, using* $ZnCl_2$ *as activating agent). Influence of initial concentration, contact time, pH and adsorbent dosages were investigated and the results indicated that optimum pH for the removal of* Mn^{2+} *by all the adsorbents was 2, while the optimum pH for the removal of* Co^{3+} *was 4 by ACDMPA and CAC. At pH 6, the maximum adsorption of* Co^{3+} *occur when ACDMZC, ACBAPA and ACBAZC was used. An equilibrium time of 30 minutes was required for the adsorption of* Mn^{2+} *and* Co^{3+} *by CAC, while 45 minutes was the equilibrium time for the adsorption of the two metal ions onto ACDMPA, ACDMZC, ACBAPA and ACBAZC. The optimum dosage for removal of* Co^{3+} *was 0.4g when CAC and ACDMPA was used, and 0.6g when other adsorbents were used. For* Mn^{2+} *the optimum dosage for its removal was 0.4g when ACDMPA was used, while 0.6g was the required optimum dosage for other adsorbents. The adsorbent produced were effective for the removal of* Mn^{2+} *and* Co^{3+}

Key words *Refinery wastewater, heavy metal contamination,* Mn^{2+} *and* Co^{3+}*remediation, bioadsorption*

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1.0 Introduction

Studies have shown that refinery sludge has a high content of petroleum derived hydrocarbon and heavy metals. Aishahri and Ther (2018) found significant concentrations of heavy metals in soil samples around the oldest and largest oil refineries located on Arabian Gulf, eastern Saudi Arabia. The results obtained indicated the following order for the heavy metal ions Cd > Mo > Tb > Ce > Hf > Eu > Yb > U > Sm > Rb > Cr > Ni > Pb > Sc > Cs > Zn > Lu > Co. Adesina and Amofe (2014) also reported significant concentrations of Pb, Sn, Fe, Zn, and Cu in soils polluted by petroleum sludge. Stanley *et al*., 2017) detected the presence of Fe (0.775 mg/L), Zn (0.750 mg/L), Pb (0.031 mg/L), Ni (0.188 mg/L), Cr (0.025 mg/L) and Cd (0.054 mg/L) ions in analysed sludge Port Harcourt refinery (in Nigeria). In view of the facts that most refinery sludge find their way to the water bodies through surface run off or direct discharge, research activities have generated impact on methods that can be useful in reducing heavy metal content of refinery waste before discharge. Consequently, several techniques have been developed at laboratory and industrial scale for heavy metal removal. Some of the methods include coagulation and flocculation, reverse osmosis, chemical oxidation, membrane separation process, electrochemical methods, aerobic and anaerobic microbial degradations (Gimba *et al*., 2001; Hajara and Muhammed, 2008). For example, Elektorowicz and Muslat (2008) adopted ion exchange and solvent methods to remove heavy metal from oil sludge and recorded 100% removal efficiency for vanadium and 99% for Cu, Zn, Fe, Ni and Cd. Hu *et al.,* (2013) reported that sludge treatment technology depends on sludge characteristics, treatment capacity, costs, disposal regulatory requirements, and time constraints. However, reports from Tripathi and Ranjan (2015) on methods available for refinery sludge treatment indicated that petroleum wastewater contains considerable amount of heavy metals and that among all available options, adsorption is one of the best and acceptable methods because it can be easily implemented, economical and can be designed to be ecofriendly. Some successes have been reported on the application of adsorption process to remove heavy metals and other contaminants from refinery sludge. Adebayo and Olayebi (2017) prepared activated carbon from coconut shell and used it to remove Cr^{3+}, Cu^{2+}, Pb^{2+} and Zn^{2+} ions from ppetroleum refinery effluent water and reported high removal efficiency. Adams *et al*. (2017) used some adsorbents of local origin to develop a filter that demonstrated good potential for removing heavy metals from crude oil polluted water.

In continuation of the search for effective adsorbent, the present study is aimed at investigating the effectiveness of activated carbon (produced from *Detarium microcarpum* and *Balanites aegyptiaca* shells) for the removal of Co^{3+} and Mn^{2+} from refinery wastewater.

The use of plant shells for the adsorption of heavy metal from aqueous solution has been widely reported and documented. Eddy (2009) used *Cyperus esculentus* shell for the removal of Zn^{2+} from aqueous solution and recorded significantly high efficiency. Odoemelam and Eddy (2009) also used modified tiger nut shell to remove heavy metal from aqueous solution and reported upto 80 efficiency. Uchechukwu *et al*. (2018) successfully decontaminated waste water by removing Cd^{2+}, Ni^{2+} and $Pb^{2+.}$ Using kolanut pot husk as adsorbent. The biosorption capacity of *Pentaclethra macrophylla shell* for the removal of Cd^{2+}, Ni^{2+} and Pb^{2+} from aqueous solution was successfully was also established by Ucheckwuku *et al*. (2015). Shells of *Cola nitida* (Okwunodulu and Eddy, 2014), Sorghum (Essien and Eddy, 2015) and others have also given good results. Therefore, the choice of *Detarium microcarpum* and *Balanitea egyptiaca* shells for the removal of heavy metal contaminants is likely supported. Influence of some parameters (such as time, adsorbent dosage, initial concentration and pH) shall be investigated in this study.

2.0 Materials and Methods

2.1 Sample collection and treatment

Detarium microcarpum and *Balanitea egyptiaca* fruits were collected from Dutsin-Ma in Katsina State The samples were authenticated and identified by a botanist in the Department of Biological Sciences, Kaduna State University Kaduna. The Epicarp shells were removed, washed several times with distilled de-ionized water to remove impurities. The precursors were sun-dried and re-dried to constant weight in an oven at 110ºC. The dried shells were pulverised and sieved to 850µm particle size (Wyasu, 2016).

2.2. Preparation of activated carbon

Activated carbon were produced using $ZnCl_2$ and H_3PO_4 as activating agents. Standard methods were followed for the carbon production described by Alau (2015). 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.

2.3 Batch adsorption study

The batch adsorption experiment was carried out as reported elsewhere (Zare *et al.,* 2014). The method was applied to study the effect of different temperatures (30 to 60 °C), adsorbent dosage (0.2 to 1.0 g), pH (2 to 10), time (15 to 60 minutes) and initial concentration. 10 g of the adsorbent was used in each case and the volume of the solution was 200 ml. The equilibrium concentration of dye adsorbed was calculated using the following equation (Oladunni *et al*., 2012).

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

where C_0, is the initial concentration of the adsorbate, C_e is the equilibrium concentration of the adsorbate, V is the volume of solution and m is the mass of the adsorbent.

3.0. Results and discussion

3.1. Effect of adsorbent dosage on the adsorption of Mn^{2+} and Co^{3+}

Figs. 1 and 2 shows plots for variation of equilibrium amount of cobalt and manganese adsorbed (by the different adsorbent) with adsorbent dosage. The plots displayed similar trend which indicate that the mechanism of adsorption experienced by the different dosage of the adsorbents is similar. In all cases, adsorption increases from initial state to a maximum before decreasing. The order of efficiency is seen to be ACDMPA>CAC>ACDMZC>ACBAPA>ACBAZC and ACDMPA>ACDMZC>CAC> ACBAPA> ACDMZC for cobalt and manganese ion respectively. The observed trend generally indicated that there is critical adsorbent dosage that can effectively give optimum adsorption of manganese and cobalt ions. Similar trend and explanation have been observed for some adsorption studies (Odionegneyi and Afangide, 2019).

The adsorption capacity of Co^{3+} with increment in adsorbent dose was 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 Co (III) respectively. The adsorbents ACDMZC, ACBAPA and ACBAZC recorded a maximum adsorption capacity of 0.056, 0.054 and 0.049mg/g Co^{3+} respectively. On the other hand,

Figure 2 shows the maximum adsorption capacity of Mn^{2+} as 0.025, 0.012, 0.011, 0.010 and 0.009 mg/g for ACDMPA, CAC, ACDMZC, ACBAPA and ACBAZC respectively at carbon dosage of 0.6g, with the exception of ACDMPA at 0.4g.

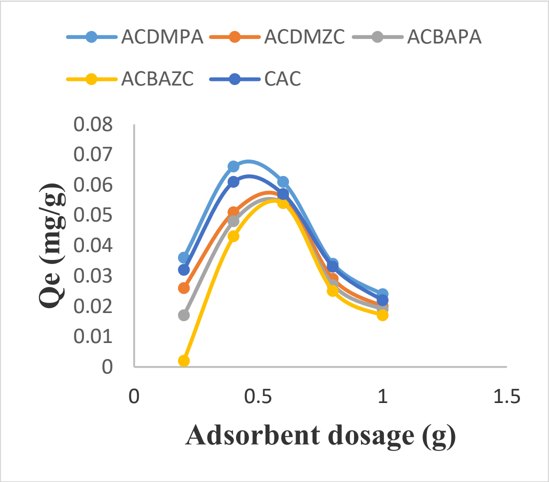

Fig. 1: Variation of Q_e with adsorbent dosage for the adsorption of Co^{3+} by the various adsorbent

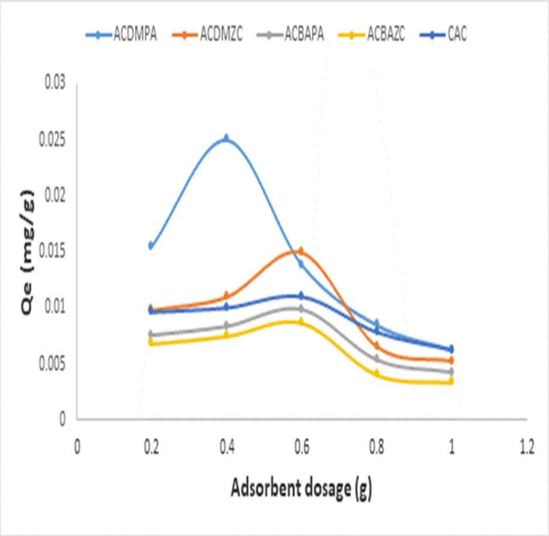

Fig. 2: Variation of Q_e with adsorbent dosage for the adsorption of Mn^{2+} by the various adsorbent

Further increment of adsorbent above 0.6 g resulted in a decline in adsorption capacity for both Co^{3+} and Mn^{2+}. The initial increment in adsorption capacity with increase in adsorbent dosage was expected, since the number of adsorbent sites increased. However, above the critical dosage, further increase led to decrease in adsorption because the available active surface might have been fully occupied and forces of desorption set in (Dakiky *et al*., 2002., Acharya et al., 2009; Odoemelam *et al.,* 2018).

3.2. Effect of agitation time

Figs. 3 and.4 represent the variation of Q_e with time for the adsorption of cobalt and manganese ions respectively.

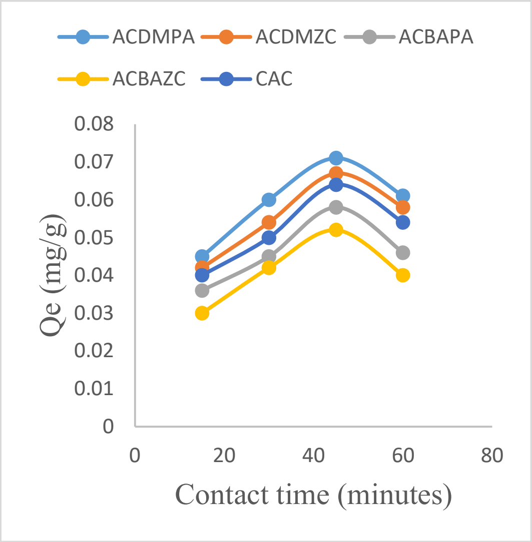

Fig. 3: Variation of Q_e with time for the adsorption of Mn^{2+} unto the surfaces of the different adsorbent

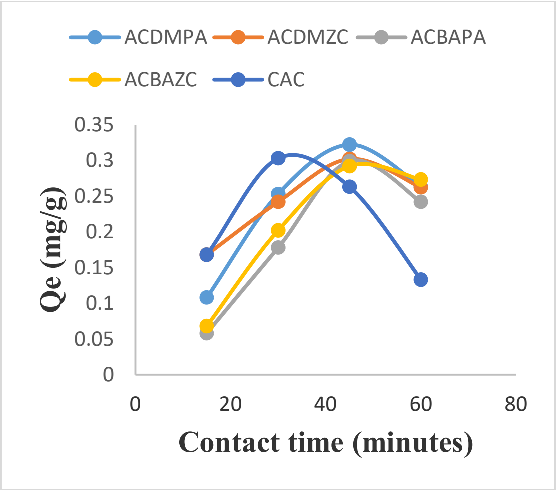

Fig. 4: Variation of Q_e with time for the adsorption of Co^{3+} unto the surfaces of the different adsorbent

Figs. 3 and 4 reveal that the Mn^{2+} and Co^{3+} increases at first to a maximum which was practically the same for the adsorption of Mn^{2+} but slightly shifted for the adsorption of cobalt unto CAC adsorbent. This also indicate that except for CAC, the mechanism of adsorption of Mn^{2+} and Co^{3+} are respectively similar. Maximum adsorption of Mn^{2+} and Co^{3+} was observed to be equilibrated at 30 and 45 minutes respectively. Period of contact can affect adsorption in three major ways. In the first option, adsorption increases with time, in the second approach, the adsorption decreases with time and in the last case, the adsorption is independent of time. In this study, adsorption depends strongly on time. Time is needed for equilibration and for activation of the available adsorption sites, once activated, adsorption will increase with time until its approached maximum adsorption capacity. Once the maximum is reached (which were 30 and 45 minutes for the adsorption of manganese and cobalt ions respectively as shown in Figs. 3 and 4), desorption can set in due to disturbance of the equilibrium due to long contact time, which establishes agitation and solution dynamic instability.

3.3. Effect of pH

The pH of the solution that contains the adsorbate plays a vital role on the adsorption of adsorbate by adsorbent. Figs. 5 and 6 illustrated the adsorption behaviour of the metal ions, at pH 2, 4, 6 and 8.

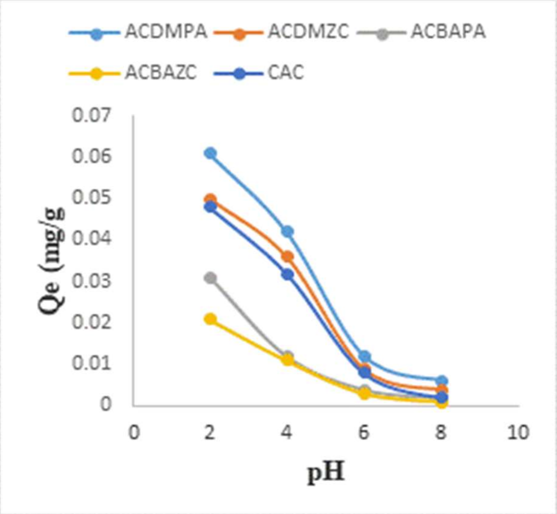

Fig. 5: Variation of Q_e with pH for the adsorption of Mn^{2+} on the various adsorbents

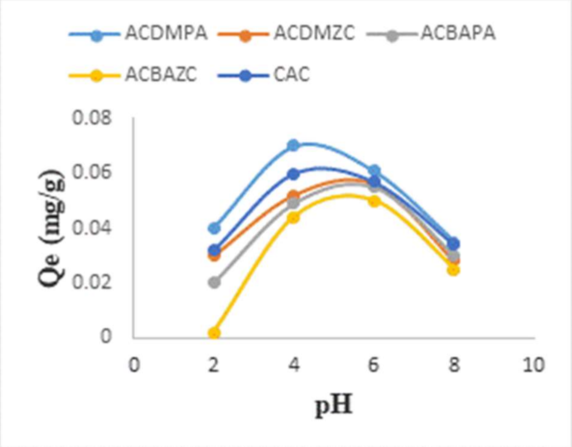

Fig. 6: Variation of Q_e with pH for the adsorption of Co^{3+} on the various adsorbents

The pH of a solution plays a vital role on the adsorption of heavy metals since it estimates the surface charge of the adsorbent and the extent of ionization and speciation of the adsorbate.

Fig. 5 reveals that the adsorption of Mn^{2+} on the adsorbents decreases with increase in pH and the maximum adsorption was observed at pH 2. The sharp decrease in the removal of Mn^{2+} 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 electrostatic repulsion with the positively charged carbon surface, which is in agreement with research carried out earlier (Stuum and Morgan, 1996; Benjamin, 2002 and Selomulva et al, 1999). Similar results were also obtained by (Goswani and Ghosh, 2005; Karthikeyan et al., 2005). 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 Mn^{2+} by all the adsorbents. However, the adsorption of Co^{3+} increases with increase in pH. An increase of pH above 6 resulted in poor adsorption of Co^{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 (Co^{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. The results agreed with work carried out earlier by Oladunni *et al*., (2012).

4.0 Conclusion

The adsorbents produced from *Balanitea egyptiaca* and *Detarium microcarpum* were effective and efficient for the removal of Mn^{2+} and Co^{3+} from Hospital wastewater. The batch method of adsorption was 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 Mn^{2+} was 2 for all the adsorbents, Co^{3+} was 4 for ACDMPA and CAC. At pH 6, ACDMZC, ACBAPA and ACBAZC shows maximum adsorption of Co^{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 Mn^{2+} by ACDMPA was at the dosage of 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 $Co^{3+}$was 0.4g when CAC and ACDMPA were used, and 0.6g when other adsorbents were used. The results proved that all the carbon produced has the ability to remove heavy metal specie in Hospital wastewater.

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