Original Research Article

Biochar versus Iron oxide-Biochar performance as adsorbents for Lead and Methyl orange from an aqueous solution

ABSTRACT

Water purification is slowly becoming a problem worldwide due to population growth. Lack of proper wastewater disposal from domestic and industrial sources has escalated water pollution in developing countries. Continuous pollution of water sources has made water purification for domestic supplies very expensive. Modern and cost-effective ways of water purification are urgently needed. One of the modern emerging technologies is adsorption using nano-materials. The aim of the study was to prepare an engineered iron oxide-biochar (Fe_2O_3-BC), a nano-composite using pyrolysis and microwave activation. The efficiency of the nano-composite was evaluated in the removal of the heavy metal lead (Pb) and the dye methyl orange (MO) in aqueous solutions. Infrared spectroscopy was used to identify the functional groups present in the synthesized biochars before and after adsorption. The adsorption properties of the synthesised Fe_2O_3-BC and biochar (BC) were determined by application in lead metal and methyl orange aqueous solutions on known concentrations. FAAS and UV/VIS Spectrophotometry were used for Lead and Methyl Orange concentrations measurements respectively. Batch adsorption experiments were conducted to investigate the capacity of Fe_2O_3-BC and BC to remove MO and Pb in aqueous solutions. A dose of 50 mg Fe_2O_3-BC had the highest percentage MO removal of 89.81% at pH 2 while 50 mg of BC had a highest of 11.55% at pH 12. A dosage of 100 mg of Fe_2O_3-BC had 100% MO removal and 250 mg BC achieved a maximum of 30.61% removal in 30 minutes. Maximum MO removal concentrations were 70 mg/L and 55 mg/L respectively for Fe_2O_3-BC and BC adsorbents. Both Fe_2O_3-BC and BC had Pb^{2+} removal of 97% in 30 minutes. A dose of 65 mg for both Fe_2O_3-BC and BC adsorbents had 100% removal of Pb^{2+}. The adsorption studies of both MO dye and Pb^{2+} on Fe_2O_3-BC nano-composite fit the Langmuir isotherm (R^2 value of 0.999) and Temkin isotherm (R^2 value of 0.919). The Fe_2O_3-BC nano-composite adsorbs Pb and MO dye better than biochar. The Fe_2O_3-BC nano-composite could be a good adsorbent for other cations and anions. More work need to be done in order to investigate the adsorption potential of other cations and anions using Fe_2O_3-BC nano-composite

Keywords: Biochar, adsorption, adsorbate, pyrolysis, heavy metal, biosorption

1. INTRODUCTION

Wastewaters are produced in many industrial processes, mostly from mining, steel mills, tanning plants, production of chemical fertilizers and pesticides, fabric dyeing plants, electroplating plants, motor and power engineering plants, and battery and accumulator production plants [1,8]. Heavy metals flow into the ecosystem due to civilization and industrial development [2]. The creation of undefined mineral and organometallic linkages in aqueous and land environments can be attributed to heavy metals. In the environment, heavy metals show high mobility. Plant roots take up heavy metals which end up in the digestive systems of humans and animals [6]. Heavy metals pose serious threats to living organisms due to toxic effects on certain elements of the environment and bioaccumulation in the food chain [9]. The methods commonly used for metal ions removal are chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction from aqueous streams [31, 40]. New technologies for removal of toxic metals from wastewaters have focused attention to biosorption, because biological materials have strong metal binding capacities. Adsorption technologies are of the most effective methods for dye removal due to its high efficiency, low cost, and easy to perform [36, 37,38].

Several single solution experiments have been carried out on heavy metal removal [3,13,19], [28] used solid olive solid residues, [18,26,30] used activated sludge, biosorbents and aquatic macrophytes respectively for zinc removal from aqueous solutions. However, it is important to note that wastewaters contain various heavy metals in solution [14,27,33]. It is prudent to carry out experimental work where one or more heavy metal is under study.

Biochar (BC) is prepared by pyrolysis (300^{o}C and above) of a biomaterial in the absence of air until all the organic compounds except carbon are volatilised [12,22]. It has been used for tertiary treatment of municipal and industrial wastewaters [15]. Biochar adsorbs soluble organics namely nitrogen, sulphides and heavy metals in wastewater following biological or physical–chemical treatment [15]. Biochar though effective in adsorption, is limited to wastes with low organic concentrations (less than 5%), low inorganic concentrations (less than 1%) and unable to remove highly soluble organics, or those with low molecular weights [23,25].To counter BC deficiencies in adsorption, there is need to activate it and enhance it with an oxide. Iron oxide has been used as an adsorbent in several studies in aqueous solutions [2,21,34,39]. However, to increase the number of adsorption sites, activated BC is among the adsorbents available for such studies [4,41,35].

The synthesis of activated biochar using microwaves is an area that needs more investigation because biochar generation from paper and pulp sludge has not received much research attention to date. Some researchers have reported an increase in surface area and porosity on microwave generated biochar, which was accompanied by an increase in the adsorption capacity of the adsorbent [11]. In addition, the smaller the particle size the greater the surface area for adsorption, so the activated BC ground to nano scale is expected to adsorb more [24]

Biochar adsorption studies have received a lot of attention from different angles. In agriculture, biochar has been employed in the remediation of soils from various forms of pollution [42]. Biochar has been found to be beneficial in reduction of soil atmospheric damage by soil wastes, removal of soil pollutants and improvement of soil quality. The adsorption capacities of biochar as an adsorbent on phosphorus and nitrogen have been investigated in agriculture [43]. It has been established that, the physicochemical properties of biochars are greatly influenced by feedstock material and the pyrolysis temperatures used [29,43].

In most cases the biosorption studies focused mainly on single solutions, few on binary solutions and very few on ternary solutions. An activated metal oxide biochar nano-composite represents an emerging group of adsorbents for removal of neutral and ionic contaminants in aqueous solutions [36]. This study focused on preparation of an activated metal oxide biochar nano-composite, characterisation and application in single solutions.

Activated BC has lower adsorption towards anions in solutions and it has been mainly applied to single solutions [4]. It needs modification for efficient removal of anions in single, binary and ternary solutions. A metal oxide biochar nano composite represent an emerging group of adsorbents for removal of neutral and ionic contaminants in aqueous solutions [36]. The main benefits of biosorption over conventional treatment methods are low cost and high efficiency. It also minimise chemical or biological sludge and the biosorbent can be regenerated [5,20]. The biosorption method has been proposed as an effective decolourization method for dye contaminated wastewaters [10, 17, 30, 41]. Chemical methods for heavy metals removal are expensive. Engineered biochar (activated) has got unique properties potentially competent of heavy metal removal and decolourization ability in wastewater, therefore capable of removing dyes [30,39].

2. MATERIALS AND METHODS

2.1 Chemicals and Materials

The chemicals and materials which were used in this study includes Paper and Pulp Sludge (PPS), KOH analytical grade, HCL, iron chloride ($FeCl_3$), deionised water, pH meter (Mettler Toledo), Shaker (Merck) and microwave (Samsung).

2.2 Preparation of Biochar (BC) and Fe_2O_3-BC

The BC and Fe_2O_3-BC were prepared according to the procedure mentioned by [7,11]. Briefly, 500 g of Paper and Pulp Sludge (PPS) obtained from Kadoma Paper Mills was dried at 105^{o}C for 24hrs. The PPS was pre-ashed to remove volatiles in an oven at 200^{o}C for 2hrs in an air tight container. The carbonization of the pre-ashed PPS was carried out in a muffle furnace at 500^{o}C and 700^{o}C separately for 2hrs. Potassium hydroxide (5 grams) was used to impregnate the biochar (1:2). Deionised water (100 mL) was added to dissolve all the KOH pellets, and the mixture left for 24 hrs at room temperature. Further activation of the impregnated BC was carried out using a microwave (800 watts) for 6 minutes. The sample was then cooled at room temperature and washed with hot distilled water. 12 grams of BC were thoroughly mixed with 4 grams of $FeCl_3$ solution. The mixtures were put in a muffle furnace at 500^{o}C and 700^{o}C separately for 2hrs each. The BC and Fe_2O_3-BC samples were ground, sieved through 250µm and stored in a closed container for use.

The percentage conversion of PPS to BC was calculated as:

$$\%BC = \frac{m1}{m2} * 100$$

Where *m1* is the starting mass of PPS and *m2* is the mass of BC produced. The percentage conversion was 24% at 700^{o}C

2.3 Characterisation of Biochar and Fe_2O_3-BC

The BC and Fe_2O_3-BC samples were characterised using Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) for surface area analysis.

2.3.1 Fourier-transform infrared spectroscopy (FTIR)

Infrared red spectroscopy (FTIR 3000, WQF-520, attenuated) was used to identify the functional groups present in the synthesized samples of biochar before and after adsorption. The FT-IR studies were carried out in the 4000 to 400 cm^{-1} wavenumber range. Background correction was done first and the dried solids were pressed with FTIR grade KBr and the pellets scanned 32 times using transmission mode with a resolution of 4 cm^{-1}.

2.4 Adsorption Studies

The adsorption properties of the synthesised Fe_2O_3-BC and BC were determined by application in aqueous solutions of known heavy metal (Pb) and dye (Methyl Orange) concentrations. A UV/VIS Spectrophotometer (Lasany Double Beam LI-2802) and FAAS (AA-6701F) were used for the measurement of Methyl Orange and Lead concentrations. Three replicates of different concentrations were prepared one for lead removal and the other for methyl orange removal. 1000 ppm stock solutions each of Lead and Methyl orange were prepared in 1 litre distilled water. Afterwards, solutions were diluted to different concentrations. The pH values of solutions were adjusted by addition of HCl and NaOH. Effects of pH, contact time, adsorbent dosage and adsorbate concentration on the adsorption of Pb and Methyl Orange (MO) was investigated through a series of experiments.

2.4.1 Effect of pH

The effects of pH on adsorption of Pb were investigated at pH 2, 4, 10 and 12 using a 50 ml solution of 5 mg/L Pb, with 50 mg of Fe_2O_3-BC and BC. For MO dye the effect of pH on adsorption were investigated at pH 2, 4, 8, 10 and 12 using a 20 ml of 50 mg/L MO solutions and 50 mg of Fe_2O_3-BC and BC.

2.4.2 Effect of contact time

The effect of contact time on Pb adsorption was studied by shaking 50 mg of (Fe_2O_3-BC and BC) for 15, 30, 60 and 90 minutes in a 50ml solution of 5 mg/L Pb. For MO, the effect of contact time was studied by shaking 50 mg of Fe_2O_3-BC and BC for 15, 30, 60, and 90 minutes in a 20ml solution of 50 ppm MO solution.

2.4.3 Effect of adsorbate concentration

The effects of initial Pb concentration were studied using 5, 10, 15, and 20 mg/L of Pb solutions, for each adsorbent in and BC. The effect of initial dye concentration was studied using 50,100, 150, 200 and 250 mg/L MO solutions. The adsorbents for Pb and MO were 50 ml solution of 50 mg Fe_2O_3-BC and 20ml solution of 50 mg Fe_2O_3-BC respectively

2.4.4 Effect of adsorbent dosage

For Pb, the effect of adsorbent dosage was investigated by separately shaking a 50 ml solution of 5 mg/L of Pb with 50, 100, 150 and 200 mg Fe_2O_3-BC for 30 minutes. The of adsorbent dosage on MO dye adsorption was investigated by separately shaking 50 mg/L solutions of MO dosage with 50, 100, 150, 200 and 250 mg Fe_2O_3-BC for 30 minutes.

The initial and equilibrium concentrations of Pb^{2+} ions and MO in solutions were recorded and the amount adsorbed was calculated using the equations:

$$Qe = \frac{V(Ci - Ce)}{m}$$

$$\%\, removal = \frac{Ci - Ce}{Ci} * 100$$

Where *Ci* and *Ce* are the initial and equilibrium concentrations of Pb^{2+} ions and MO in ppm,

Qe is the amount of Pb^{2+} ions and MO adsorbed at equilibrium in mg/g, *V* is the volume of Pb^{2+} and MO solutions (L) and *m* is the mass of BC and Fe_2O_3-BC in grams[11,38].

The Langmuir and Temkin equations were used to describe the equilibrium between the adsorbate and adsorbent represented as:

$$\frac{Ce}{Qe} = \frac{Ce}{Qmax} + \frac{1}{Qmax * kl} \quad ,$$

$$Qe = \frac{RT}{b} lnaCe$$

Where $Q_{max,}$and *kl* are the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively. Plotting Ce/Qe versus Ce, gives a straight line with Q_{max} and *kl* determined from the intercept and the slope of the graph respectively. Also a plot of *Qe* versus ln*Ce* gives a straight line [32].

3. RESULTS AND DISCUSSION

3.1 FTIR Characterisation

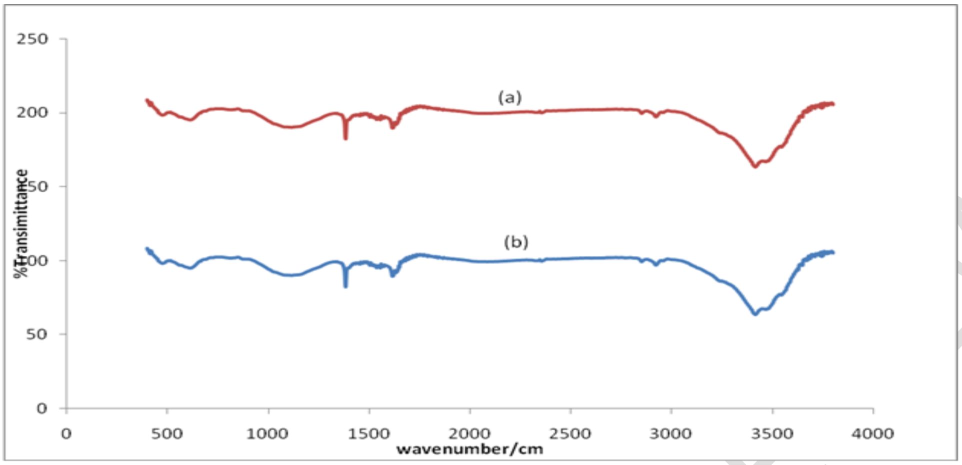


Figure 1: Fe_2O_3-BC FTIR Spectra (a) after adsorption and (b) before adsorption

Figure 1 shows –OH stretching as can be depicted from the pronounced peaks in the range of 3300-3500cm^{-1}. Also present were -CH_x stretching bands, 1600cm^{-1} related to the aromatic structure, 1390 cm^{-1}phenolics -OH, 830 cm^{-1} alkene CH band, 600cm^{-1} due Fe-O bond and 490cm^{-1} regions with Fe_2O_3-BC. The 490 cm^{-1} region with Fe_2O_3-BC show the presence of Iron oxide. This is in agreement with literature [11]. The major differences between the peaks before adsorption and after adsorptions were where the 1100cm^{-1} peak broadened to stretch from 9750- 1275cm^{-1} corresponding to the MO fingerprint region [16]. This indicates the effect of heavy metal and dye addition.

3.2 SEM Characterisation results

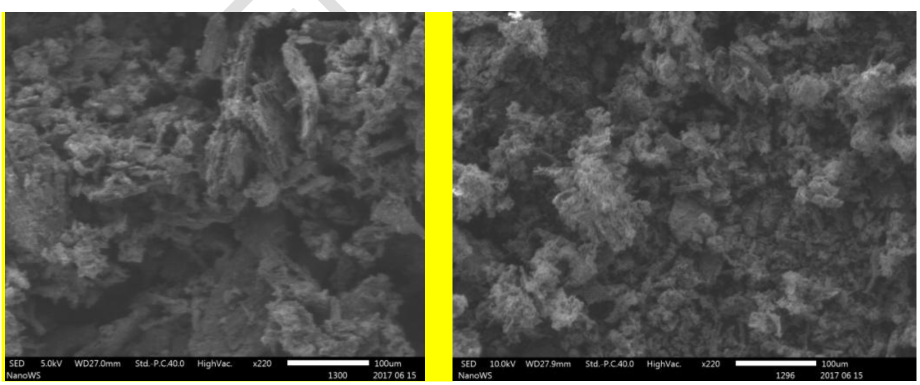


Figure 2: SEM Images for the Biochars

The scanning electron microscopy (SEM) images above are showing the surface structures of the adsorbent materials. The surface area of both adsorbents was very large before adsorption experiments. After adsorption both biochars had reduced surface area.

3.3 Adsorption Experiment Results

3.3.1 Effect of pH

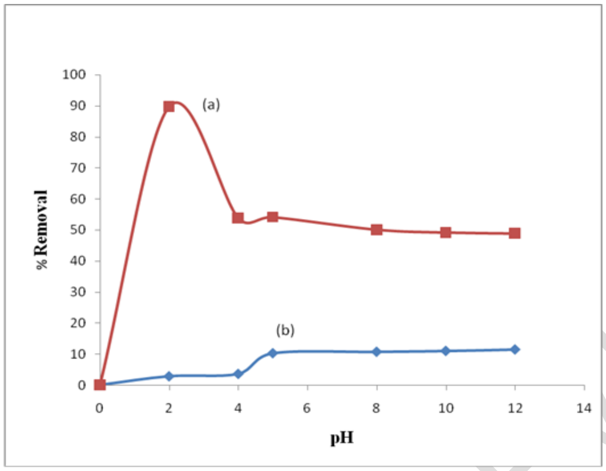


Figure 3: Effect of pH on MO removal, (a) using Fe_2O_3-BC and (b) using BC

Figure 3 shows that Fe_2O_3-BC had a highest percentage MO removal of 89.81% at pH 2, while BC had 11.53% at pH 12.This may prove that at pH 2; Fe^{3+} is more effective in acidic conditions for the removal of MO. Fe^{3+} ions with the combination of H^+ ions present at low pH provided the much needed cationic binding sites for anion MO. Generally Fe2O3-BC showed higher adsorption capacity for methyl orange at all pH values as compared to BC. The BC low adsorption may be attributed to the fact that it is a weak adsorbent towards anions. The trend depicts that Fe2O3-BC is a better adsorbent for MO under any given pH conditions as compared to BC.

3.3.2 Effect of Contact Time

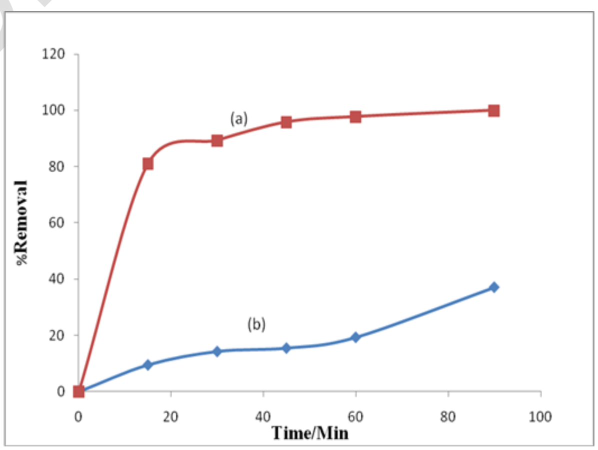


Figure 4: Effect of Contact Time on MO removal, (a) using Fe_2O_3-BC and (b) using BC

In Figure 4, the high rate of MO removal (90%) was witnessed in the first 15 minutes. Less than 50% of MO was removed by BC after 90mins. The rapid MO adsorption is attributed to the presence of large number of surface sites initially and steadies thereafter [7]. The results clearly showed that Fe_2O_3-BC is a better adsorbent for methyl orange at any given contact time as compared to BC. This could be attributed to differences surface features and available surface areas among the adsorbents. It is also important to vary the particle size of the adsorbent to observe the trends in adsorption with various times.
Figure 5 below shows the effect of contact time on the adsorption of Pb^{2+}.

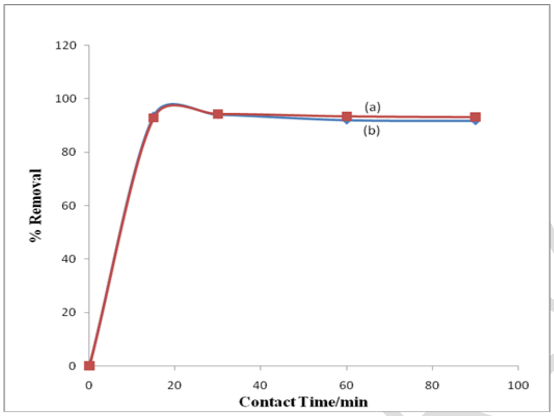


Figure 5: Effect of Contact time on Pb^{2+} removal (a) using Fe_2O_3-BC and (b) using BC

Figure 5 shows that both adsorbents BC and Fe_2O_3-BC had 97% Pb removal in the first 15 minutes. The adsorptions were rapid for the first 15 minutes and gradually approached equilibrium between 30 and 90 minutes. This trend ascertains that BC performs well with cations in adsorption studies. However, the adsorption performance of BC was found to be comparable to that of Fe_2O_3-BC on Pb^{2+} adsorption. The trend depicts that Fe_2O_3-BC performs well with both cations and non cations like methyl orange in adsorption.

3.3.3 Effect of Adsorbate concentration

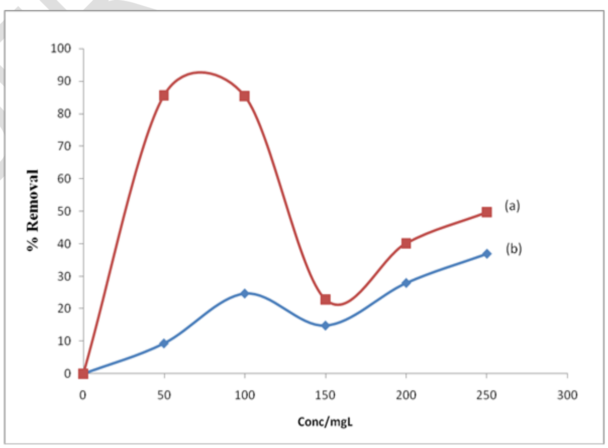


Figure 6: Effect of Adsorbate concentration on MO removal (a) using Fe_2O_3-BC and (b) using BC

In figure 6, 91% MO removal was achieved after the addition of 70 mg/L adsorbate concentration for Fe_2O_3-BC. There were fluctuations in MO percentage removal as the concentration was increased. The BC adsorbent gave a maximum of 37% after the addition of 200 mg/L MO. The general decrease in percentage removal after addition of 75 mg/L adsorbate in both adsorbents could be because the active binding sites were all occupied as the MO concentration is increased. The graphs partially rise and levels off at very high adsorbate concentrations. Levelling off is attributed to saturation point, since only little or no adsorptions are possible after saturation point.

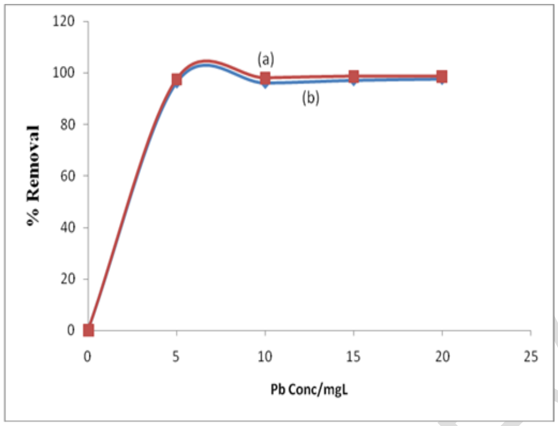


Figure 7: Effect of Adsorbate concentration on Pb^{2+} removal (a) using Fe_2O_3-BC and (b) using BC

Figure 7 shows the optimum Pb^{2+} concentration of 6.5 mg/L for both adsorbents with 100% Pb^{2+} removal. The removal increased from 0 - 6.5 ppm. Both adsorbents show good sharp Pb^{2+} adsorptive properties at concentrations below 6.5mg/L. There was little effect of concentration after 6.5 mg/L most probably due to saturation. Both adsorbents performed in almost a similar way, giving a maximum adsorption of 100%. There were no major differences in adsorption capacities of both adsorbents.

3.3.4 Effect of Adsorbent dosage

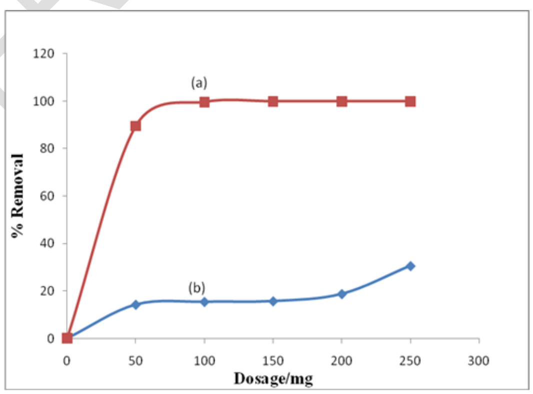


Figure 8: Effect of Adsorbent dosage on MO removal (a) using Fe_2O_3-BC and (b) using BC

In figure 8, 100mg of Fe_2O_3-BC adsorbent had a 100% removal of MO. The BC adsorbent after addition of 250 mg had a maximum removal of 30.61% though there was a sharp increase between 200 and 250 mg. This is in agreement with literature that at low pH, BC has few H^+ ions and at high pH more anions are predominantly present thereby hindering binding of MO onto the BC surface [30]. The Fe_2O_3-BC at low pH contained both Fe^{3+} and H^+ ions which were available to adsorb the entire available MO in solution.

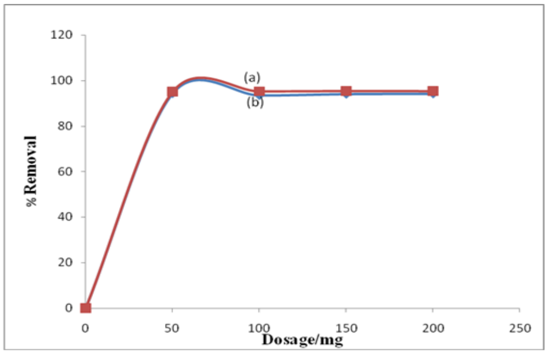
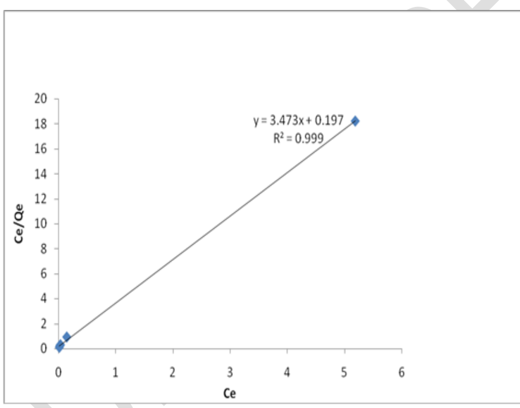


Figure 9: Effect of Adsorbent dosage on Pb^{2+} removal (a) using Fe_2O_3-BC and (b) using BC

Figure 9 shows that 100% of Pb^{2+}ions removal was achieved on addition of 65mg of both adsorbents. There was rapid removal of Pb^{2+} ions from 0-65 mg, followed by a sharp decline towards 100 mg and 200 mg. There were no major differences in adsorption capacities of both the adsorbents. Adsorption diminishes as the active sites are used up.

3.4 Adsorption Isotherms

3.4.1 Langmuir Plots



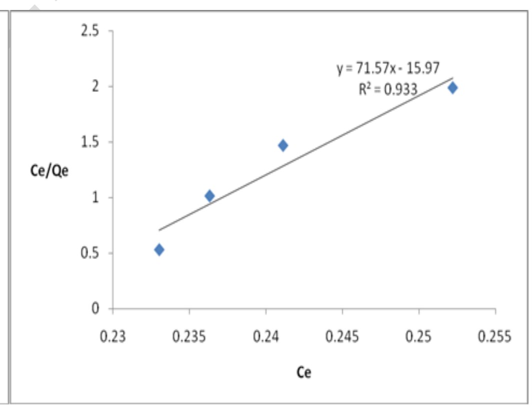
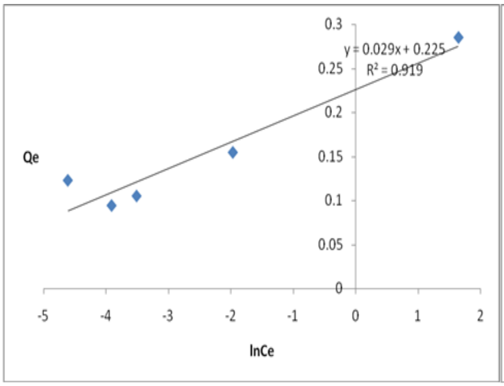


Figure 10: Langmuir Plot for MO results

Figure 11: Langmuir Plot for Pb^{2+} results

Figure 10 shows that the Langmuir isotherm and describes the adsorption of MO dye onto Fe_2O_3-BC with R^2 value of 0.999. The closeness of R^2 value to 1 indicates that the data obtained fits Langmuir Isotherm model of monolayer adsorption kinetics. The Fe_2O_3-BC nano-composite used can be said to have a series of distinct homogeneous sites available for binding the MO anions in solution. Figure 11 describes the sorption of Pb^{2+} ions on the Fe_2O_3-BC with R^2 value of 0.933 also fits the Langmuir Isotherm well.

3.4.2 Temkin Plots



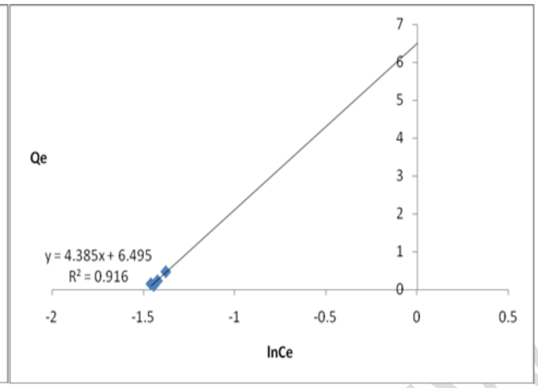


Figure 12: Temkin Plot MO results

Figure 13: Temkin Plot Pb^{2+} results

Figures 12 and 13 show the Temkin plot with R^2 values of 0.919 and 0.916 for the sorption of MO onto Fe_2O_3-BC and Pb^{2+} ions on the Fe_2O_3-BC respectively, fitting in the model that the heat of adsorption of all the molecules in the layer would decrease linearly rather than logarithmic with coverage.

4. CONCLUSION

Fe_2O_3-BC had highest percentage removal of 89.81% at pH 2 while BC had a highest of 11.55% at pH 12 of MO in solution. The dosage of 100 mg of Fe_2O_3-BC had 100% removal of MO and 250 mg BC achieved 30.61% removal in 30 minutes. The maximum concentrations were 70 ppm and 55 ppm respectively for Fe_2O_3-BC and BC adsorbents. In the removal of Pb^{2+}ions in solutions both Fe_2O_3-BC and BC performances were almost similar with maximum removal of 97% in 30 minutes. 65 mg for both Fe_2O_3-BC and BC adsorbents had 100% removal. The adsorption performance of Fe_2O_3-BC is far much better than that of biochar in single aqueous solutions. Fe_2O_3-BC is an effective alternative adsorbent for Pb^{2+}ions and methyl orange dye in aqueous solutions. There is need to perform further studies in order to find out the adsorption performance of Fe_2O_3-BC in binary and ternary solutions. The adsorption performance of Fe_2O_3-BC also needs to be evaluated on other common heavy metals and organic pollutants.

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