Journal of Basic and Environmental Sciences 2 (2015) 1 – 8 **ISSN 2356-6388**

Removal of Zn(II), Fe(II) and Mn(II) from Industrial Wastewater by using Active Carbon Prepared from mango seed as Adsorbent.

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* Abstracted from his M. Sc. thesis

Article Information

Received; 2 September. 2014
In Revised form; 12 December 2014
Accepted; 12 December 2014

Keywords:
Mango seed
Fe (II)
Mn (II)
Zn (II)

Abstract

Activated carbon derived from mango seed was prepared and tested as a potential raw material for local activated carbon production. Chemical activation by impregnation using 65% phosphoric acid was followed by thermal treatment at 550°C. The activated carbon was investigated to find the suitability of its application for removal of heavy metal such as Fe (II), Mn (II) and Zn (II) from the synthetic wastewater. The effects of various parameters such as adsorbent dose, solution pH, contact time, and initial metal ion concentration on adsorption efficiency were studied during batch experiment. The adsorption mechanism was studied in terms of Friendlish and Langumier isotherm.

1. Introduction

Activated carbon is a microcrystalline form of carbon with very high porosity and surface area. It may be visualized as foam solid that has a large surface within a rigid granule or particle structure of relatively small volume. Its chemical structure allows it to preferentially adsorb organic materials and other non-polar compounds from gas or liquid streams [1]. Activated carbons (AC) are an effective adsorbent for many pollutant compounds (organic, inorganic, and biological) of concern in water and wastewater treatment [2-7]. The major use of activated carbon is in solution purification and for the removal of taste, color, odors and other objectionable impurities from liquids, water supplies and vegetable and animal oils.

Any carbonaceous material (natural or synthetic) with high carbon content can be used as raw material for preparation of AC. The most common raw materials are agricultural byproducts such as wood, sawdust, rice husk, nut shells, fruit pits, charcoal, brown and bituminous coals, lignite, peat, bone, paper mill waste (lignin), and synthetic polymers like PVC, are used for manufacturing of activated carbon. In fact, any carbonaceous low-cost materials (of animal, plant, or mineral origin) with high carbon and low ash content can simply be changed into activated carbon under the proper thermal decomposition process.

The present study is undertaken with a view to assess the feasibility of raw mango seed converted to activated carbon as an adsorbent and investigated it for the removal of Fe (II), Mn (II) and Zn (II). The effects of various parameters such as adsorbent dose, pH, contact time and initial metal concentration on the adsorption process have been studied. Adsorption studies will also be carried out to evaluate the adsorptive capacity of the adsorbent.[8-10]

2. Experimental

2.1. Preparation of Activated Carbon:

Mango seeds were collected from night market in Egypt. They was cut and cleaned from its grass, washed several times with distilled water to remove all foreign materials, mud and kept in an oven maintained at 70°C for a period of 24 hours. Then the material was ground and sieved to get desired particle size (1 mm). Part of the produced materials was used as it as sorbent while the other were soaked in 65% phosphoric acid and left overnight at room temperature, after that the samples were put in crucible in the closed muffle furnace Selecta- HORN (Model -S. No 0483272) and heating started by adjusting the furnace temperature to the desired value (550^{o}C) [11-15].

The end product was repeatedly washed using hot water until the washings showed pH > 6.5; after that by DDW about 10 ml the washed sample was then dried again at 110°C to facilitate crushing and grinding. The final sample (local activated carbon) was kept in air-tight bottles [16].

2.2. Characterization of the Activated Carbon:

pH measurements: For measuring pH values of aqueous suspensions of the carbon samples, 0.1 g portions of finally powdered active carbon were mixed with 20 ml CO_2 -free distilled water in 50 ml capacity stopper Pyrex bottles. The suspensions were shaken mechanically for 2 hours at 25°C then the pH values were measured using pH cyber scan 1000---S.N,69400 -pH meter.

Ash content was measured by burning the produced activated carbon in a muffle furnace at 650°C. One gram of dry carbon was transferred into a crucible and then placed in the furnace for four hours. The difference between the original and final weight of the carbon represents the ash content per gram.

Moisture content was also obtained by weighing 10 grams of the activated carbon at 105°C for three hours. Then the carbon was cooled in the absence of humidity and reweighed again. The difference between the initial and final mass of the carbon represents the water content in the sample.

Adsorption of metal ions:

For the preparation of synthetic wastewater, all the chemicals used were of analytical reagent grade. Stock Fe^{3+}, Mn^{2+} and Zn^{2+} solutions (1000 mg/l) were prepared by dissolving 4.978 g $FeSO_4.7H_2O$, 3.123 $MnSO_4.7H_2O$ and 4.396 $ZnSO_4.7H_2O$ in 1000 ml double-distilled water. All working solutions of different concentrations were prepared by diluting the stock solution with distilled water.

The pH of the test solutions was adjusted using reagent grade dilute hydrochloric acid and sodium hydroxide (0.1M). pH cyber scan 1000-S.N,69400 -pH meter was used to measure the pH of solutions, and shaker 3108 GFL (Type 3018) was used. After agitation, the adsorbate and adsorbent were separated using a 0.45 µm membrane filter (Schleicher & according to Standard Methods for the examination of water and wastewater [17].

The metal ion concentrations were measured by atomic absorption model TRACE 1300, chemistry administration Lap., Cairo, Egypt.

The adsorption studies ware carried out by batch technique. For this investigation, a series of flask containing equal volume (50 ml in each case) of adsorbate solutions of varying concentration were employed, at desired pH, temperature and contact time. After agitation, the solutions were filtered and the concentrations of metal ion in the solution were analyzed

2.3. Investigated parameters:

Effect of contact time on the removal efficiency of metal ion: adsorption process was processed for different shaking time of 5, 10, 20, 45, 90, 360, 1080, and1440min, at constant pH, initial concentration, and temperature.

Effect of adsorbent dosage on the removal efficiency: adsorption process was processed for adsorbent dosage of 0.05, 0.1, 0.15, 0.2 and 0.25 g/l, at constant pH, initial concentration, and temperature.

Effect of pH on the removal efficiency: adsorption process was processed for different pH values of 2.15, 4.32, 5.3, 6.28, 7.54 and, 8.29 at constant contact time, initial concentration, and temperature.

Effect of initial concentrations of metal ion on the removal efficiency: adsorption process was processed for different initial concentrations of 50, 75, 125, and150, mg/l at constant pH values, constant contact time and temperature.

Effect of Temperature on the removal efficiency: adsorption process was processed for different temperature values of 35,45, and,55 at constant contact time, initial concentration, and dose.

3. Results and discussions

The effect of activation conditions on the percentage of yield, pH value, moisture and ash contents are shown in Table (1). The yield of activated carbons was calculated from the sample weight after activation to its initial weight. As the temperature increases, the AC yields decreases since more volatiles components might be released, leaving only small quantities.

Moisture contents measured from the loss of water over initial weight of raw materials. The average moisture content of the activated samples was in the range of 6.86% – 8.01 %. The moisture content detected was from the contact with the moisture in the atmosphere after activation.

Ash content is the measurement of the amount of mineral matter (e.g. Ca, Mg, Si, and Fe) in activated carbon. Thus, low ash content is preferable for activated carbon. Further chemical acid treatment is required for high ash content activated carbons. The high ash content of the activated carbon would be explained by their high specific mineral content in the raw materials [18]. As temperature increased, the volatile content of activated carbons decreased while ash content increased. This is expected because increased devolatilization during activation resulted in the char that was being predominantly carbon [19].

The ash contents of the solid products depend on the chemical composition of the raw materials and the degree of carbonization. Materials, which have undergone deep carbonization, accompanied by removal of large amounts of volatile organic compounds, are converted into solid residues with low contents of organic material and high content of ash.

Table (1)

No	Code Sample	Moisture %	Ash Content	Yield %	pH
1	Cm	6.86	8.00	68.8	3.59
2	Cp	8.01	9.00	65.6	2.06

3.1. Factors influencing the adsorption of metal ions

The influence of several operational parameters such as dose of adsorbent, initial pH, temperature, initial metal ion concentration contact time was investigated. The results are expressed as the removal efficiency (E) of the adsorbent on, defined as:

$$E\ (\%) = [(C_o - C_1) / C_o] \times 100, \qquad (1)$$

Where C_o and C_1 are the initial and equilibrium concentration of metal ion solution (mg/l), respectively [20].

3.1.1. Effect of pH

Study on the effect of PH on the % removal of Fe^{2+},Mn^{2+},Zn^{+2}(Fig. 1) shows that both Fe^{2+},and Zn^{+2} exhibit no variation with PH change .on the other hard the % removal of Mn^{2+} increases from 46.952% at PH=2.15 to 99.943% at PH=5.3 .The maximum value of percent removal is found at PH=5.3 this value was kept for further studies . On using activated carbon as sorbent .very similar observation was obtained the maximum percent was obtained at PH=5.3 this value was kept for further studies.

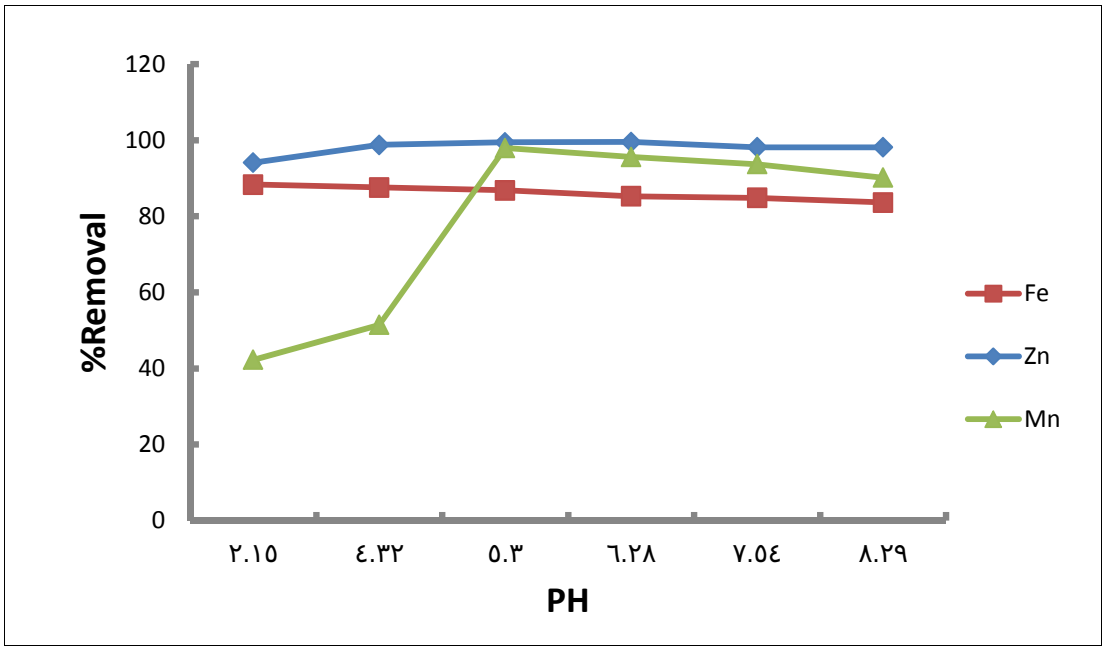

Fig1: Effect of pH on adsorption of Fe^{2+}, Mn^{2+} and Zn^{2+}

3.1.2. Effect of dose:

Study on the effect of dose of the removal% of Fe^{2+}, Mn^{2+}, Zn^{+2} (Figure. 2) shows that both Fe^{2+}, Mn^{+2} and there are differences and increases with the change in the dose of Fe^{3+} in the amount of 50.4915% to 0.05gm in the amount of 99.443 0.25gm Mn^{2+} of 61.232% in the amount of 91.436 % to 0.05gm in the amount of 0.25gm and a simple change in the Zn^{2+} .The maximum value of a percent have been found to remove the amount of 0.25 g This value was kept for further studies. Obtained very similar observation was obtained maximum 0.25gm percent in dose this value was kept for further studies.

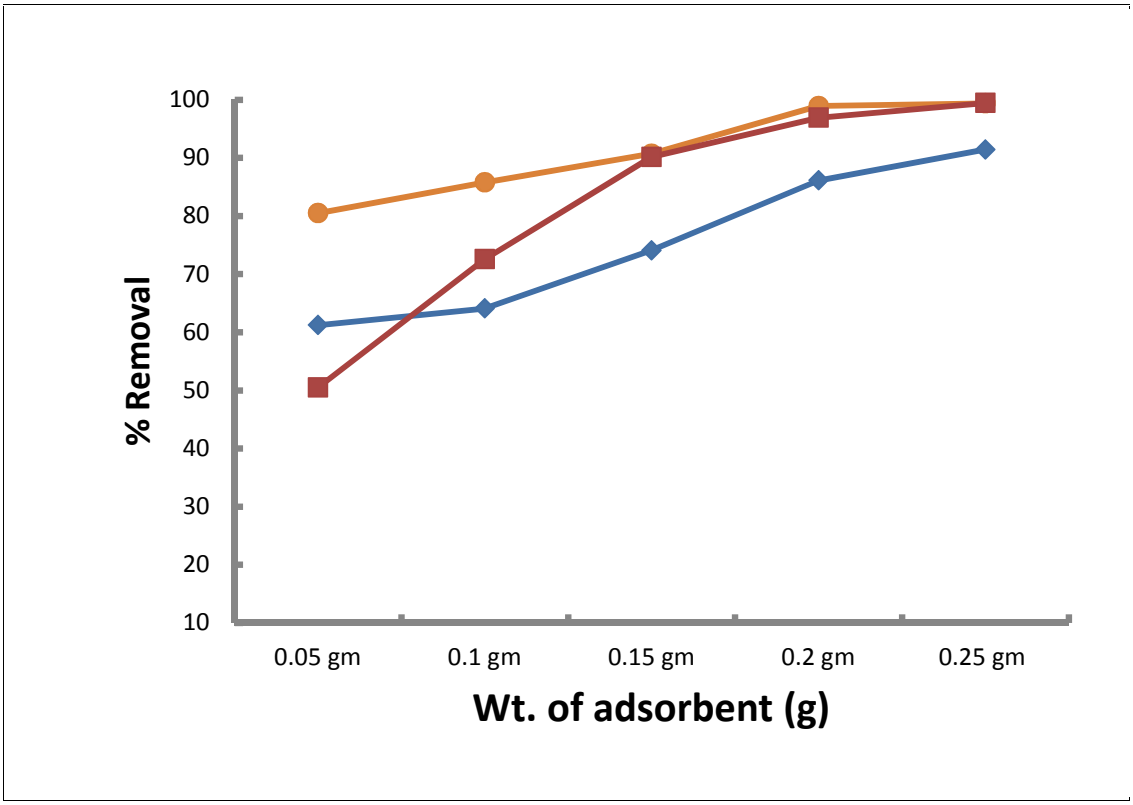

Fig 2: Effect of adsorbent dose on adsorption of Fe^{2+}, Mn^{2+} and Zn^{2+}

3.1.3. Effect of initial concentration:

The effect of initial Fe(I1) Mn(II) and Zn(11) ions concentrations ranging (50 – 150 mg/l) on the removal by activated carbons was studied. The results are illustrated graphically in figure (3.)

A study on the effect of ion concentration in the material removed from both Fe^{2+}, Mn^{2+}, Zn^{2+} Figure (3.) shows that both Fe^{2+} and Zn^{2+} Mn^{2+}. And the highest removal initially at 50 ppm gave remove the amount of 62.432 % and there was a decrease in the amount of removal greater the concentration until it reached 28.311 % at a concentration of 150 ppm, as well as an element Mn highest removal % 77.707 at 50 ppm until it reached a concentration of 69.053% at150ppm

If the maximum value of 50 % to remove ppm kept this value for further studies. On the use of activated carbon as an absorbent. Been getting maximum surveillance is very similar 50 ppm per cent in the ion concentration of material kept this value for further studies.

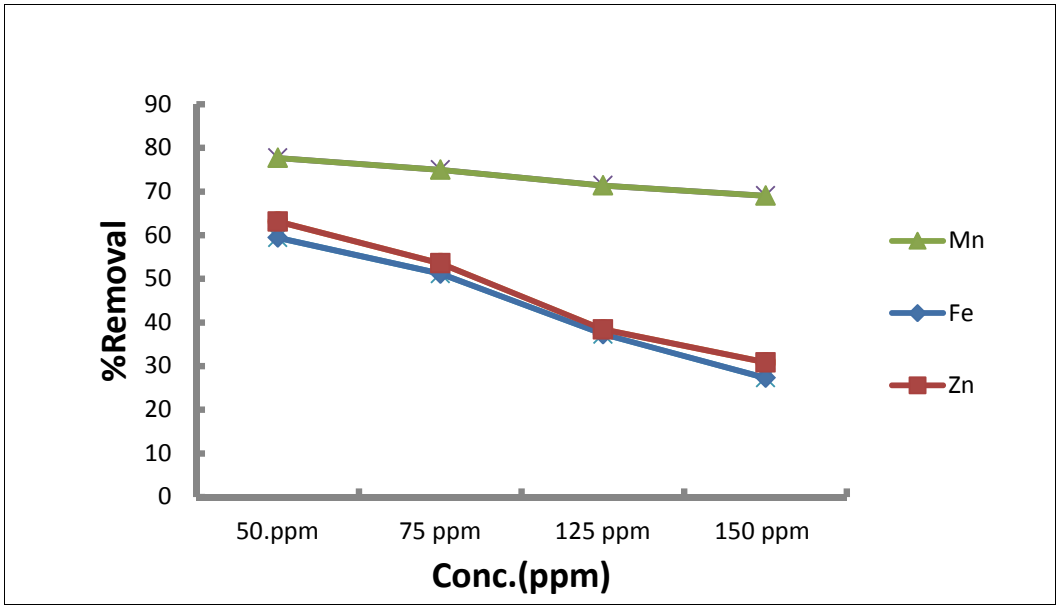

Fig 3: Effect of contact time on adsorption of Fe^{2+}, Mn^{2+} and Zn^{2+}

3.1.4 Effect of contact time:

Study the effect of time on the removal% of Fe^{2+}, Zn^{2+} and Mn^{2+}. as in figure (4.) found that Fe^{2+} and Mn^{2+}Event remove weak in the beginning when 5 minutes was the removal 50.865% in $Fe^{2+}$and 43.987% in Mn^{2+}, reaching the maximum value for them at the time of 18 hours was the removal 87.916% Fe2+ and 74.823% Mn2+ and Zn^{2+}did not happen was a big change slightly has been found to remove 87.916% at 18 hours this value was kept for further studies. Obtained very similar observation has been to get the most percent in 87.916% at 18 hours this value was kept for further studies.

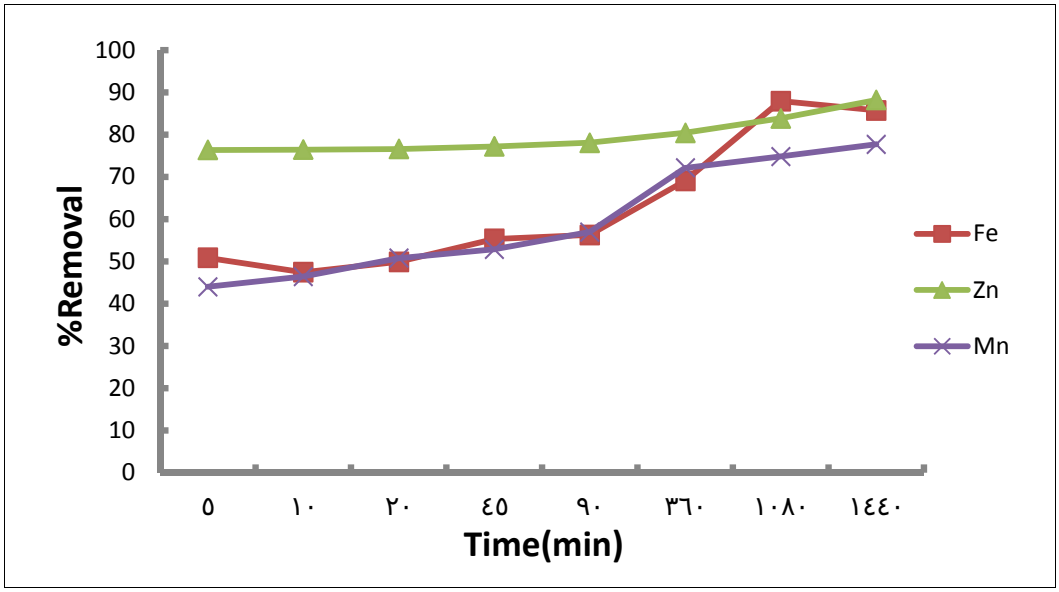

Fig 4: Effect of contact time on adsorption of Fe^{2+}, Mn^{2+} and Zn^{2}

3.1.5. Effect of temperature

In the case of temperature with a fixed quantity and time was found to be the highest and best results Adsorbents for the removal of the three elements are* Remove In the case of activated carbon nuclei mango seeds were the removal of the elements as follows of 8.1666% at 35c to 95.2432% at 55c -35.405%at 35c to 90.799%at 55c (Fe – Zn) and a simple change in the Mn. The maximum value of a percent has been found to remove the amount of 55c. This value was kept for

further studies. On the use of activated carbon as absorbent. Obtained very similar observation was obtained maximum 55c percent in dose this value was kept for further studies. figure (5)

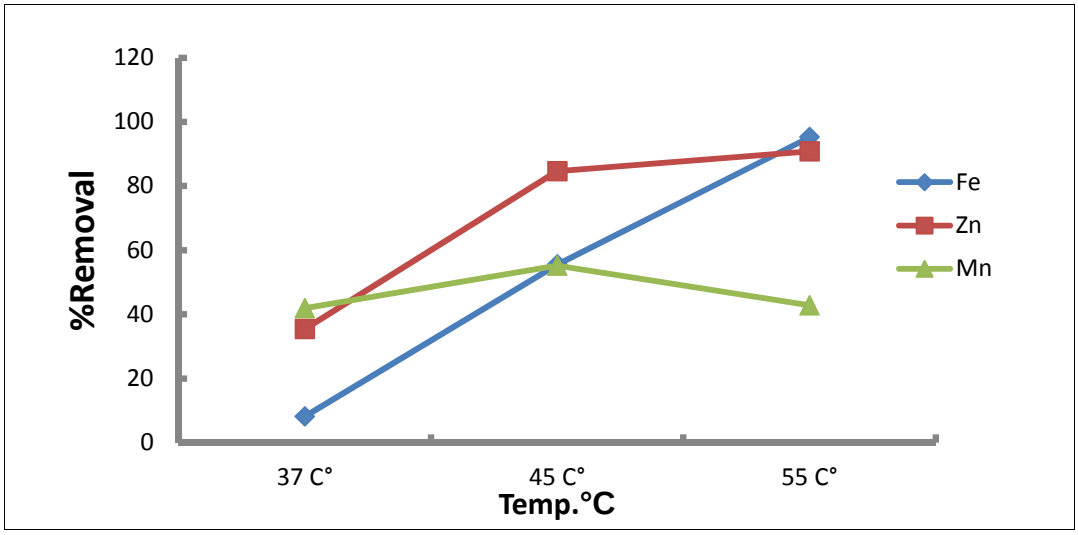

Fig 5: Effect of temperature on adsorption of Fe^{2+}, Mn^{2+} and Zn^{2+}

3.1.6. Freundlich adsorption isotherm:

The Freundlich isotherm assumes that the adsorption occurs on heterogeneous surface at sites with different energy of adsorption and with non-identical adsorption sites that are not always available.

At equilibrium conditions, adsorbed amount qe can be predicted by using Freundlich equation

$$\log q_e = \frac{1}{n}\log C_e + \log k_f \qquad (2)$$

Where,

q_e = metal ion concentration in solid at equilibrium (mg/g).

C_e = metal ion concentration in solution at equilibrium, (mg/L).

k_f = measure of adsorption capacity.

n = adsorption intensity.

A plot of log qe versus log C_e gives a slope of $\frac{1}{n}$ and intercept of log kf. Freundlich plot for the adsorption of Fe^{+3} ,$Zn^{+2}$and Mn^{+2}ions on four activated carbons is given in the Figure (5abc) and the results of Freundlich plot are given in Table (2). The results showed that the coefficient of correlation was high (R^2 values between 0.9905 and 0.959) indicating a good linearity. The results show that the values of n are greater that unity (n between 1.88 and 1.59) indicating that all metal ions are favorably adsorbed on activated carbons.

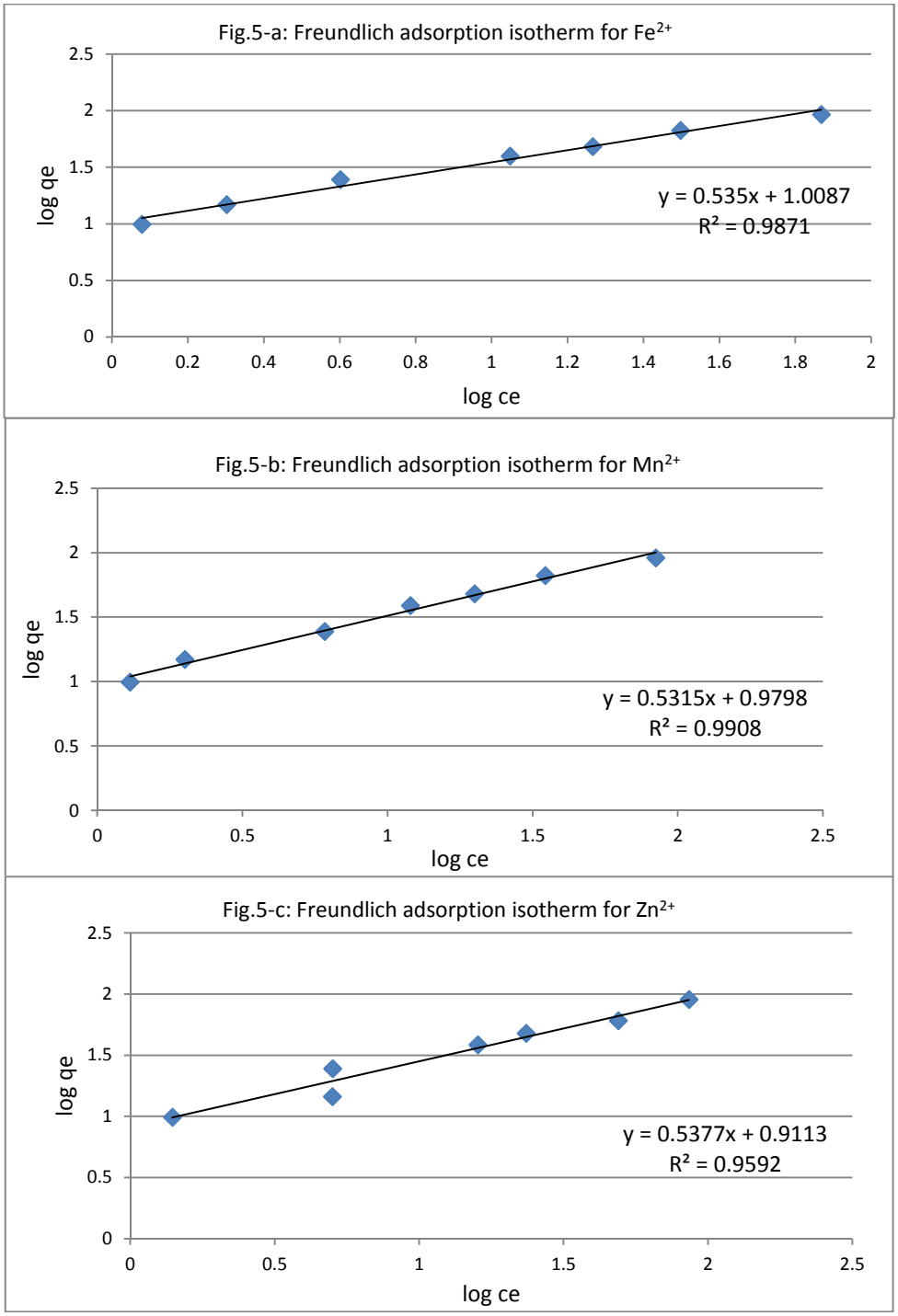

Fig $5_{a\text{-}c}$: Freundlich adsorption isotherm for the removal of Fe^{2+}, Mn^{2+} and Zn^{2+} ions.

Table 2: Values of Freundlich adsorption isotherm for the removal of Fe^{2+}, Mn^{2+} and Zn^{2+} ions.

Metal ion	Kf	N	R^2
Fe^{2+}	9.33	1.77	0.9871
Mn^{2+}	9.89	1.65	0.9909
Zn^{2+}	10.08	1.44	0.9592

4. Conclusions:

Production of activated carbon derived mangoseed had been demonstrated to be feasible. High surface area activated carbon was obtained by chemical activation of mangoseed with H_3PO_4 and one step activation which was carried out in an inert gas atmosphere. The optimum conditions for removal of Fe^{2+}, Mn^{2+} and Zn^{2+} ions were as follows temperature 45c,dose of active carbon 0.2 gram, initial concentration 125 ppm, pH 5.30 and time 1440minet.

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