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## Removal of Some Heavy Metals Contaminants from Aqueous Solutions By Applying Biomass-Based Modified Activated Carbon

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### Abstract

Activated carbon (AC) has been prepared from rice husk (RH) as an agricultural by-product. Different analytical instruments characterized the prepared activated carbon. $Fe^{3+}$ and $Mn^{2+}$ were extracted from the aqueous solution. The effects of many different variables namely, pH effect, reaction time, adsorbent amount, starting concentration of metal ions, interfering ions and temperature on the adsorption of ions were evaluated. The optimal adsorption of $Fe^{3+}$ and $Mn^{2+}$ was 3 and 6, respectively. The optimal contact time was determined to be 2 hours for both $Fe^{3+}$ and $Mn^{2+}$ ions. The kinetic and thermodynamic of adsorption process was found to be a pseudo-second order for both $Fe^{3+}$ and $Mn^{2+}$ ions. The equilibrium data was applicable to Langmuir, and Freundlich isotherm. The correlation coefficient ($R^2$) of both isotherms were 0.99 & 0.89 for $Fe^{3+}$, respectively and 0.99 & 0.77 for $Mn^{2+}$, respectively. The obtained data predicted also that; the endothermic system governs the adsorption process. Furthermore, the maximum adsorption capacities for $Fe^{3+}$ and $Mn^{2+}$ were 72.2 & 49.6 mg/g, respectively and the removal of metal ions were 90.12 & 83.42 %, respectively. Finally, the results revealed that the adsorption process of the two metal ions is consistent with the pseudo-second-order kinetics.

**Keywords:** Activated carbon, Aagricultural by-product, Rice husk, Heavy metals, $Fe^{3+}$ & $Mn^{2+}$ ions.

### INTRODUCTION

Via natural causes and human activities, heavy metals (HMs) are released into the atmosphere, resulting in environmental pollution [1]. Duan saied that Heavy metal has been regarded as extremely dangerous environmental pollution, which are toxic to human beings even at low concentrations level [2]. In recent years, HMs have been a significant threat to humanity because they are non-biodegradable and there responsible for bio-accumulating trends, increased toxicity, different disorders as well as diseases [3]. In groundwater sources utilized by various water systems, iron and manganese are commonly present. No damage to human bodies is caused by the presence of iron as well as manganese in potable water. Higher concentration, however, triggers issues of discoloration, staining, turbidity and bad taste. As well, it contains accumulations of iron and manganese dioxides in the pipes [4]. The accumulation of iron as well as manganese in the distribution systems will cause the pipe diameter to be reduced and the pipe will eventually be blocked [5]. Iron and manganese bacteria are another concern that

is associated with the presence of iron as well as manganese in water. These bacteria pose no health hazard, but in toilet tanks they can cause red brown (iron) as well as black brown (manganese) slime and can cause water systems to become clogged. In light or dark conditions, iron as well as bacteria grow on iron and manganese contained in water [6]. Investigation of technologies of water treatment, such as oxidation/reduction, coagulation/ flocculation, biological treatment, membrane separation, ion exchange, and adsorption, has become the world preoccupation. Adsorption has evolved as the most efficient heavy metal removal techniques due to the adsorption process provides design and operation flexibility [7]. Of the mentioned methods, adsorption is considered to be the most effective physicochemical technique for heavy metal removal due to the simplicity of operation, cost-effectiveness, and regenerative nature of the adsorbents Adsorbents investigated for the treatment of heavy metals include cellulose nanofibers, biochar, zeolites, carbon nanotubes, agro-industrial waste materials,

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granular/powdered activatedcarbon , and modified activated carbon [8].

Agricultural waste which are renewable, highly efficient, and of low cost, have been used as precursors for synthesis of activated carbon [9] Activated carbon is the material commonly used in water treatment, among various adsorbents such as zeolites, silica gels, aluminas and resins, due to the following advantages: the ability to eliminate a wide range of pollutants, chemical inertness and thermal stability [10]. AC is a plant-based carbon material, which is a porous, amorphous solid carbon [11]. It has been applied as an adsorbent by researchers to eliminate HMs from aqueous media and industrial waste water [1]. Carbon has a large number of pores of different sizes, all of which allow access from the aqueous medium to different forms of contaminants. Coal, the petroleum products used to prepare industrial activated carbon, adds to the high cost of wastewater treatment [12]. Rice husk (RH) is an abundant as well as cheap material which can be converted into AC for various applications. Various pollutants such as textile dyes, organic contaminants, inorganic anions, pesticides, and heavy metals can be effectively removed by RH-derived AC [13]. Rice husk accounts for approximately 1/5th. of the world's total rice. It includes cellulose, hemicellulose and lignin that promote heavy metal adsorption. It has been effective in removing coloured metal ions from the water portion. By modifying its texture by chemical and/or thermal treatments, the adsorption ability of RH can be improved. It is used in abundance for the removal of contaminants because of its granular form, solubility in water, availability as well as chemical stability [3]. Low-cost methods for extracting iron and manganese from ground water using activated carbon based on rice husk have been developed (RHAC) [4].

For elimination of Mn2+ from aqueous solution and industrial waste water, grafted banana peels (GBPs) can be applied as an effective adsorbent. Mn2+ adsorption on GBPs was reported to be 94% [1]. The removal of Fe3+ and Mn2+ ions from El-Umum drain water, Alexandria coast, Egypt, was successfully applied to activated carbon and rice husk [14].

In this work, AC was produced from agricultural waste generated from rice production which obtained from the local farms in Egypt. It was used to remove dissolved Fe3+ and Mn2+ ions from aqueous solutions. The optimum conditions to achieve removal efficiency adsorbance using such materials were investigated. Consuming part of biomass in such application saves the environment from another type of pollution which results from discarding biomassread these instructions carefully and print them.

## MATERIALS AND METHODS

RH is an agricultural solid waste derived from the cultivation of rice which acquired from local farms in Egypt. The impregnating agent was phosphoric acid, sodium hydroxide, and acetic acid for the chemical activation of RH. Manganese chloride and iron chloride were used for preparation of aqueous solutions of $Mn^{2+}$ and $Fe^{3+}$, respectively.

## Instruments and Measurements

The pH values of different solutions were measured by using Digital pH metres (Thermo Scientific, USA instruments). Atomic Absorption Spectrophotometer (AAS), (Varian AA240FS, Austria) was used for measuring the concentration of metal ions. The different samples were shacked with an orbital shaker, (Thermo Science, UK). The surface area and pore characteristics of various samples were performed via nitrogen adsorption/desorption isotherms that were measured at 77 °K on an automatic adsorption instrument (Quantachrome Instruments, Model Nova 1000 e series, USA). Elemental analysis was carried out by Energy Dispersive X-ray (EDX) (JMS-PLASMA-X2- with Resolving Power 1200). Fourier Transform-Infrared Spectroscopy (FTIR) were recorded using a Mattson 5000 FTIR spectrometer. Scanning Electron Microscopy (SEM) of selected materials were carried out using JSM T 20 JOEL, JAPAN in the secondary–electron image mode, at an accelerated voltage of 20 Kev. The data was calculated using NOVA Win 2.0 software.

## Preparation of activated carbon

The rice husk sample was collected and washed with tap water followed by deionized water to remove particulate material from their surface. The sample was dryed in an oven at 100±2°C for 120 minutes. Approximately 40 g of RH was mixed and stirred with 100 ml of 1 M NaOH for 90 minutes then heated at 100°C. The sample was calcinated in an electric furnace at 500°C for 90 minutes (heating rate; 50°C/10 min). The sample was cooled and grinded to create powdered activated carbon at room temperature, followed by washing with hot de-ionized water for 20 minutes. The washing process was repeated four times, followed by drying in the oven at 110°C for 120 minutes. Finally, it was cooled at room temperature and the sample weight was determined. The same procedure was followed with acetic as well as phosphoric acid to activate RH. The prepared sample was recorded in **Table 1**.

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**Table1:** The various types of the prepared activated carbon, calcined at 500°C for 90 min.

| Symbols | Methods |
|---------|---------|
| P | Carbonization |
| P-1 | Activation by $H_3PO_4$(0.5M) |
| P-2 | Activation by $H_3PO_4$(1M) |
| P-3 | Activation by $H_3PO_4$(3M) |
| P-4 | Activation by $CH_3COOH$(1M) |
| P-5 | Activation by   NaOH(1M) |

### Batch Sorption Experiments

The adsorption experiments were conducted using the technique of batch balance. The pH effect on metal adsorption has been studied. In this respect, 25 ml (50 ppm) of $Fe^{3+}$ or $Mn^{2+}$ ions were added to 0.05 g of prepared activated carbon at 25°C for 120 minutes. 0.1N NaOH or 0.1N HCl were used to get  pH range from 1 to 6. These suspensions were shaken until equilibrium, then the mixture was filtered with Whatman filter paper. The residual concentration of each substance was measured by using atomic absorption.

Different doses of adsorbents (0.025-0.5 g) were applied to various bottles containing 25 ml of metal ion solution  at pH 3 for $Fe^{3+}$ and pH 6 for $Mn^{2+}$ and agitated on a shaker (100 rpm) at 25°C for 2 hours. Then filtered and analyzed the content of each flask.

Adsorbent (activated carbon, 0.05 g) was applied to the various conical flasks containing 25 ml of each metal ion at temperature of 25°C, and pH 3 for $Fe^{3+}$ and pH 6 for $Mn^{2+}$.  The influence of different contact time (5, 15, 30, 60, 120 &180 minutes and 24 hours), temperature (25, 35, 50 and 65°C), and $Fe^{3+}$ and $Mn^{2+}$ ions concentrations (10 to 400 ppm) on the removal of metal ions were also studied.

The effect of some interfering ions, such as anions (e.g., chlorides, sulphates as well as nitrates), or cations (e.g., $Na^+$, $Mg^{2+}$ as well as $K^+$) on the efficacy of adsorption or the percentage of Fe(III) and Mn(II) uptake was also investigated. In this regard, 10 ml of the initial $Fe^{3+}$ or $Mn^{2+}$ solution containing the same interfering ion concentration was shaken under optimum removal conditions with 0.03 g of adsorbent. The uptake of $Fe^{3+}$ & $Mn^{2+}$ ions was measured.

Adsorption uptake and the removal percentage were calculated using Equations (1-2) [1]:

$$q_e = (C_o - C_e) (V/m) \qquad (1)$$
$$\text{Removal, } \% = (C_o - C_e) (100/C_o) \qquad (2)$$

Where

$q_e$ : uptake of adsorbate per unit mass of adsorbent (mg/g).

$C_o$: startingl concentration of $Fe^{3+}$ or $Mn^{2+}$ in the aqueous solution (mg/l).

$C_e$: the final equilibrium concentration of test solution (mg/l).

m: adsorbent mass (g). V: sample volume(l).

### Characterization of Activated Carbon

### Density

In terms of apparent mass, packaged density, elemental analysis and carbon yield, the physical properties of different prepared activated carbon samples under investigation have been studied **.** Density is an integral property of all matter [15]. There are two kinds of density, called apparent and packed density, correlated with activated carbon. The apparent prepared carbon density is defined as the mass of the unit volume, including the pores and spaces between the particles, using the known sample mass in the graduated cylinder. Packed density was calculated by determining the volume of a known sample in a graduated cylinder after tamping, showing no further volume change and calculating the packed density as equation (3) [16].

Packed density (g/ml) = [wt. of material (g) / vol. of packed dry material (ml)   (3)

Carbon yield is the remaining sum of the original precursor after activation and can be determined by Equation (4) [15].

Yield, % = [final wt (g)/ original wt]x100      (4)

### RESULTS AND DISCUSSION
### Preliminary Sorption Investigation

The main tasks of this section were to investigate and to select the suitable adsorbents to be used for removal of $Fe^{3+}$ or $Mn^{2+}$ from aqueous solution. In this concern, four different adsorbent samples prepared as mentioned before were tried to examine their relative capability for adsorption $Fe^{3+}$ and $M^{2+}$ ions as illustrated in **Table 2**.

Table 2: **Preliminary test for selection of adsorbent samples ($C_o$ of $Fe^{3+}$ & $Mn^{2+}$ ions = 50 mg/l, pH= 1.5, 3 & 6 for each batches respectively, Time = 2h, Wt = 0.05g, agitation speed =100 rpm and Temp. 25 °C)**

| Type of Adsorbent | pH = 1.5 | | pH = 3 | | pH = 6 |
|---|---|---|---|---|---|
| | Fe (III) | Mn (II) | Fe (III) | Mn (II) | Mn (II) |
| | Removal,% | | | | |
| P | 20.4 | 69.1 | 17.8 | 36.68 | 77.9 |
| P-2 | 9.9 | 60.1 | 90.12 | 48.48 | 83.42 |
| P-4 | 9.7 | 64.1 | 10.86 | 39.13 | 75.0 |
| P-5 | 18.8 | 72 | 18.3 | 34.52 | 78.41 |

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From Table 2, the results showed that the capacity of the four -adsorbent to adsorb $Fe^{3+}$ or $Mn^{2+}$ from aqueous solution was significantly different. Several interaction mechanisms between the adsorbent surface and the metal containing species present in the aqueous solution are demonstrated by the observed wide difference in the adsorption of both metal ions. P-2 was found to be superior in $Fe^{3+}$ and $Mn^{2+}$ percent elimination, respectively. P-2 was, therefore, chosen for further study. The phosphoric acid impregnation factor was studied at varying concentrations. In this regard, the results are shown in **Table 3**.

Table 3: **Preliminary test for selection of adsorbent samples ($C_o$ of $Fe^{3+}$ & $Mn^{2+}$ ions = 50 mg/l, (pH= 3 for Fe(III) & 6 for Mn(II)) respectively, Time = 2h., Wt = 0.05g, agitation speed =100 rpm and Temp. 25 ºC)**

| Adsorbent | Removal,% of Fe | Removal,% of Mn |
|-----------|-----------------|-----------------|
| P-1 | 11.26 | 34.92 |
| P-2 | 90.12 | 83.42 |
| P-3 | 85.77 | 46.23 |

For this form of activated carbon, we also established physical and chemical characterization. In the following portion, the adsorption of $Fe^{3+}$ and $Mn^{2+}$ to activated P-2 carbons in aqueous solution, respectively, by optimizing different parameters, e.g. pH, balance time, initial concentration, adsorbent dose and temperature, will be addressed. The collection of parameters where maximum adsorption occurred was the criterion for optimization.

**Characterization of Prepared Activated Carbon**

**Physical properties**

The Physical properties of various prepared activated carbon samples under investigation were studied in terms of apparent density, packed density, elemental analysis and carbon yield (**Error! Not a valid bookmark self-reference.**).

**Table 4:** The physical properties of the selected prepared activated carbon sample

| sample | Apparent density(g/ cm$^3$) | Packed density(g/ cm$^3$) | Yield, % | Surface area (m$^2$/g) |
|--------|------------------------------|----------------------------|----------|-------------------------|
| AC(P-2) | 0.606 | 0.088 | 38.5 | 16.7341 |

**Elemental analysis by EDX**

Energy Dispersive X-ray (EDX) of the AC(P-2) before metal ions adsorption was performed. The results (Fig. 1) confirmed the presence of carbon (53.98), oxygen (14.09), silicon (12.59), and copper (5.97), aluminium (5.52), zinc (3.76), as well as potassium (2.80) wt.,% along with the traces of chloride and calcium as shown. in **Error! Reference source not found.**. The results indicated that, activated carbon has high content of carbon.
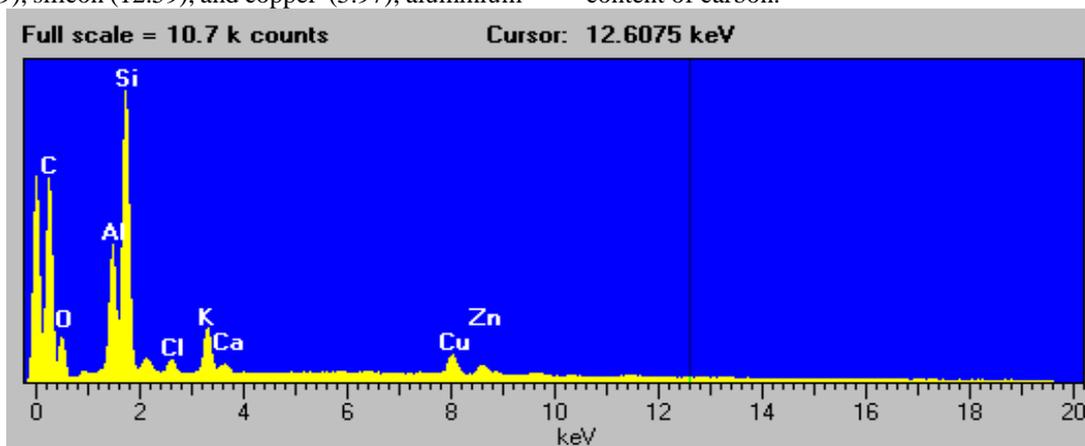


Fig. 1: Elemental analysis by EDX spectrum of AC(P-2)

**Table 5:** Elemental analysis of the selected prepared activated carbon, %

| Adsorbent | C | O | Si | Cu | Al | Zn | K | Cl | Ca |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| AC(P-2) | 53.98 | 14.09 | 12.59 | 5.97 | 5.52 | 3.76 | 2.80 | 0.85 | 0.44 |

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### Chemical properties

#### (FTIR analysis)

Agricultural wastes contain cellulose, lignin and hemicellulose in their composition as main chemical constituents. Cellulose as one of the main constituents is a polysaccharide formed from glucose units. The main function groups in these units are the expected hydroxyl groups which appears usually around 3400 $cm^{-1}$, C-H aliphatic which appears usually around 2900 $cm^{-1}$ and C-O band which appears around 1100 $cm^{-1}$ [17]. Hemicellulose is showing similar peaks as it has a similar structure of cellulose with a difference that it contains other sugars than glucose [18]. Lignin has no proved structure until now but it is the only part
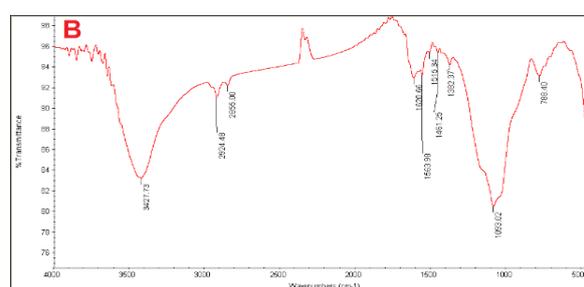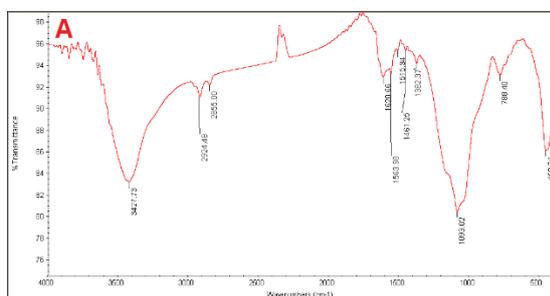
in the waste contains aromatic species [19].These aromatic parts can give peaks in the region from 1400-1600 $cm^{-1}$. In addition it may contains carbonyl group which gives peak in the region form 1600-1800 $cm^{-1}$ [20].

It can be seen the appearance of the expected peaks in **Fig. 2(A)**. The expected hydroxyl group, aliphatic C-H as well as C-O peaks are appeared at 3424, 2921 and 1093 $cm^{-1}$, respectively. The C=C & C-C usual for the benzene ring appear at 1563&1511 $cm^{-1}$ for C=C and 1454&1380 $cm^{-1}$ for C-C and ortho di-substituded group cyanate $C \equiv N$ at 2278 $cm^{-1}$.

After interaction with metal ions [$Fe^{3+}$ & $Mn^{2+}$] in the **Fig. 2(B)** Similarly, the intensity level of the peaks is still low but with a slight shift in position.



Fig. 2: FTIR spectrum of of AC(P-2) before and after adsorption of $Fe^{3+}$ & $Mn^{2+}$ ions A) & (B), respectively

### Scanning Electron Microscopy (SEM)

To observe the changes in the morphology of adsorbents following adsorption, scanning electron microscopy (SEM) was performed. In secondary-electron picture mode, the SEM images of AC were carried out using JSM T 20 JOEL, JAPAN at an

accelerated voltage of 20 Kev. Before adsorption, the near view of AC(P-2) in **(Fig. 3A)**, is showing a porous surface with wide channels on a regular basis. After metal ion adsorption, the adsorbent surface morphology covered with $Fe^{3+}$ as well as $Mn^{2+}$ ions and surface irregularities **(Fig. 3B)**.
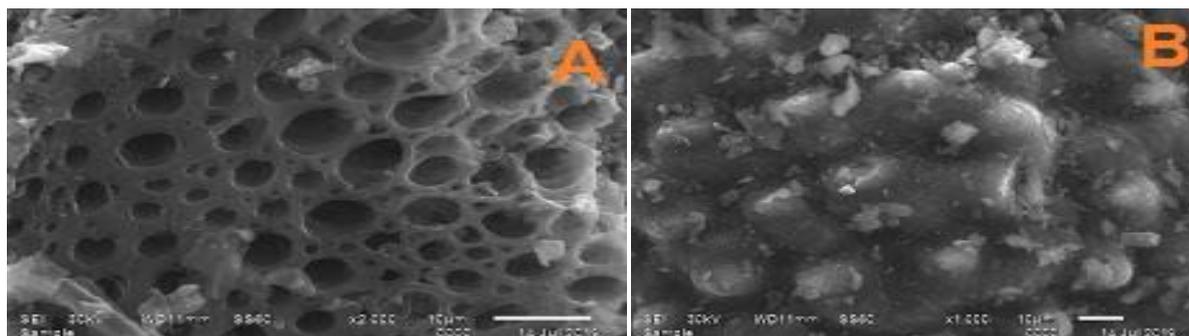


Fig. 3: (SEM) analysis of of AC(P-2); (A) before adsorption of $Fe^{3+}$ & $Mn^{2+}$ ions, (B) after adsorption Fe(III)& Mn(II)

### pH Effect

pH of the initial solution is the most important factor affecting the sorption of heavy metal ions or organic compounds from aqueous solution on sorbents due to the dissociation and ionization of adsorbate and surface functional groups on the adsorbent [21-22-23]. Adsorption of metal ions increases with increasing the

pH value (blow the precipitate limits) [24-25-26]. for $Mn^{2+}$, The solution pH was varied from 1.5 to 6. $Mn^{2+}$ interact with negatively charged adsorbent. The adsorption of $Mn^{2+}$ at lower pH was low due to the development of positive charge on the active sites of adsorbent. At low pH the H+ ions concentration is high

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so there is competition between H+ ions and Mn2+ ions in the bulk of solution to bind with the negatively charged surface of adsorbent . The adsorption of $Mn^{2+}$ increased with increasing the solution pH up to 6. The adsorption of $Mn^{2+}$ decreases at pH >6, due to hydroxide ions $Mn^{2+}$ precipitated and forming manganese hydroxide precipitate [1]. For $Fe^{3+}$ The solution pH was varied from 1 to 3. The use of very acid solutions was claimed to be ineffective,because the strong affinity of protons for the surface sites would hinder the adsorption of $Fe^{3+}$.Nevertheless, it was found here that increasing of pH1 to 3 significantly increased the amount of adsorbed iron on the AC. but at higher pH, (pH >3) oxy-hydroxides may exist; such solid forms of iron are not expected to diffuse easily into the inner porosity of ACs, and precipitate in the macropores and to coat the outer surface of the carbon particles [27]. The results showed that the maximum adsorption rate was recorded for $Fe^{3+}$ and $Mn^{2+}$ (90.12, 83.42%) at pH 3 and 6, respectively, in **Fig. 4**.

## Contact Time Effect

Effect of contact time on adsorption of $Fe^{3+}$ and $Mn^{2+}$ was achieved, the adsorbed amount of $Fe^{3+}$ and $Mn^{2+}$ ions by the substrate showed that the rate of adsorption significantly increased to 20.04 and 18.73 mg/g, respectively for the metal ions present for 120 min of contact time (Fig. 5). The Increase in rate of removal of metal ions with increasing adsorption time could be due to greater contact between the surface of the adsorbent and metal ions. Also, the existence of a large number of active surface sites on active carbon and the rapid diffusion of metal ions from the bulk of the solution to the adsorbent surface [28]. The adsorption was very rapid initially and large amount of $Fe^{3+}$ as well as $Mn^{2+}$ removed in first 50 min. However, there is no major improvement in the removal of metal ions by further increases in contact time (up to 120 min), this is simply due to saturation of the active site and does not enable further adsorption.
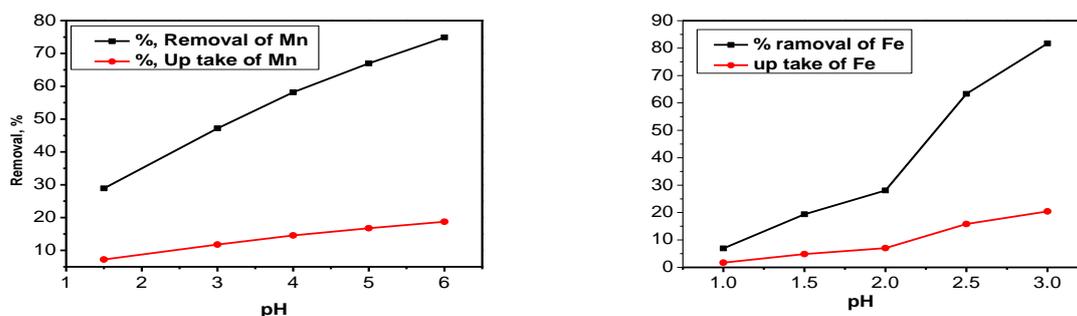


Fig. 4: The influence of pH on the absorption and removal by AC(P-2) of $Fe^{3+}$ & $Mn^{2+}$ ions from aqueous solutions (Conc. = 50 mg/L, Time = 2h, Wt = 0.05gm, agitation velocity = 100 rpm and Temp. 25 °C) by percentage
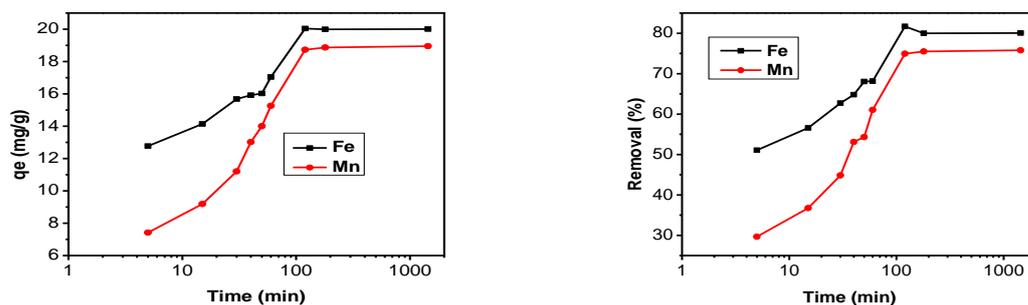


Fig. 5: Effect of contact time on the uptake as well as removal, % by aqueous solutions of $Fe^{3+}$ & $Mn^{2+}$ ions by AC(P-2) (Conc. = 50 mg/l, Time = 2h, Wt = 0.05gm, pH = 3 and 6 for $Fe^{3+}$ & $Mn^{2+}$ ions respectively, Agitation velocity = 100 rpm and Temp = 25 °C).

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## Adsorbent Dose Effect

In adsorption studies, the dose of the adsorbent is an important parameter since it specifies the potential of the adsorbent for a given initial metal solution concentration. Fig. 6 shows the effect of the adsorbent dose on absorption (mg/g) as well as the removal percentage of $Fe^{3+}$ and $Mn^{2+}$ elimination. Adsorption potential (mg of metal adsorbed/g of adsorbent) was also increased with increasing adsorbent dosage. Initially, the percentage of removal increased rapidly with the increase in adsorbent dose, increases of $Fe^{3+}$ as well as $Mn^{2+}$ adsorption percentage is due to
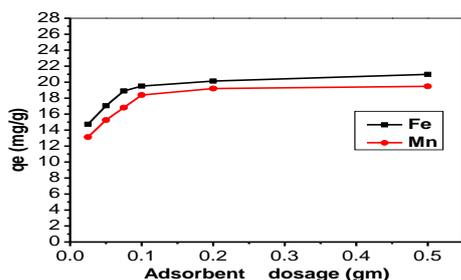
increasing the amount of activated carbon, the percentage of $Fe^{3+}$ and $Mn^{2+}$ adsorption elimination increased from 14.74 to 20.13 (mg/g) and from 13.13 to 19.21 (mg/g), respectively with an increase in the adsorbent dose from 0.025 to 0.2 g. Increased adsorption of metal ions with rising concentrations of activated carbon may be attributable to the availability of more active metal ion absorption sites at higher adsorbent dose levels [29]. Metal adsorption was not affected by further rises in adsorbent quantity because the adsorbent is already adsorbing the available metal ions [1].
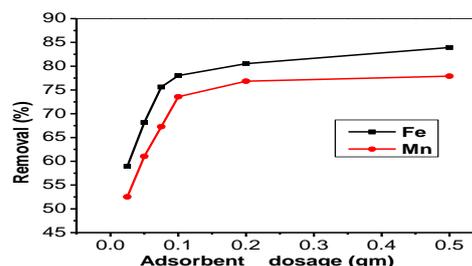


Fig. 6: Effect of the adsorbent dosage on $Fe^{3+}$ & $Mn^{2+}$ ions uptake as well as percentage removal by AC(P-2) (Conc. = 50 mg/l, Time = 2h, pH = 3 & 6 respectively for of $Fe^{3+}$ & $Mn^{2+}$ ions, Agitation velocity = 100 rpm and Temp = 25 ºC).

## Initial Metal Ions Concentration Effect

The initial of metal ion concentration effect was studied in different ranges such as, 10, 25, 50, 100, 200 and 400 ppm for $Fe^{3+}$ as well as $Mn^{2+}$. The pH value was fixed at 3 and 6 for $Fe^{3+}$ and $Mn^{2+}$, respectively. The uptake of $Fe^{3+}$ as well as $Mn^{2+}$ ions has increased from 4.75 to 69.9 and from 4.25 to 47.65 (mg/g) for $Fe^{3+}$ as well as $Mn^{2+}$, respectively by increasing the concentration of the metal ion at 25 °C, Error! Reference source not found.. It is clear that the equilibrium uptake $q_e$ increased as the initial concentration increased till saturation. As the number

of available sites is much larger than that of metal ions species, the adsorption process appears to proceed rapidly and can be adsorbed more favorable sites became involved first. Also, when the metal concentration increases, the high-affinity sites begin to reach saturation, as well as energetically less favorable ones (low affinity surface sits) become involved in the adsorption process causing elimination of uptake [30]. It is evident from Error! Reference source not found. that the amount adsorbed on the solid phase at lower initial concentrations of adsorbate was smaller than the corresponding amount when higher initial concentration were used.
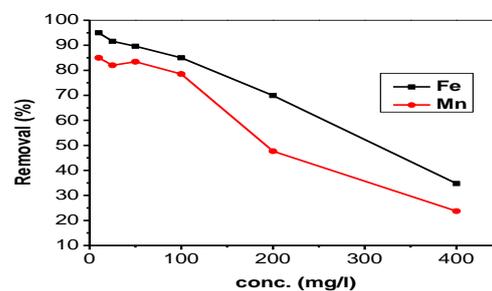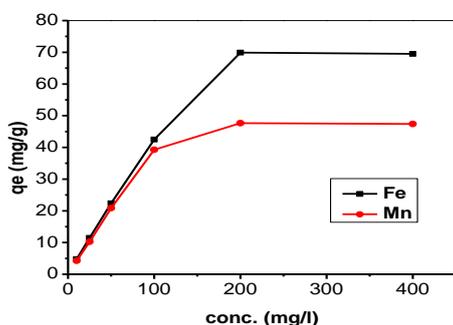


Fig. 7: Effect of the initial concentration of metal ions on $Fe^{3+}$ & $Mn^{2+}$ ions uptake and percentage removal by AC(P-2) (Time = 2h, Wt = 0.05 gm, pH = 3 and 6 for $Fe^{3+}$ & $Mn^{2+}$ ions, Agitation velocity = 100 rpm, Temp = 25 ºC).

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## Temperature effect

The effect of temperature on the uptake and adsorption of Fe (III) as well as Mn (II) was studied in different ranges as 25, 35, 50 and 65 ºC. The experimental results given in (**Error! Reference source not found.**) indicate that the magnitude of adsorption is direct proportional to the solution temperature in adsorption of $Fe^{3+}$ and $Mn^{2+}$. The uptake of $Fe^{3+}$ as well as $Mn^{2+}$ ions has increased from 12.29 to 17.04 and from 11.04 to 15.26 (mg/g), respectively, when the temperature increased from 25 to 65°C. The high temperature improved the mobility of metal cations and favored intraparticle transmission as well as endothermic chemisorption process. In addition, the biomass components at high temperature might contribute to the increase of biosorption capacity [31]. Moreover, an increase in temperature may lead to a swelling effect on the internal structure of the biomass, enlarging the pores in the active carbon resulting in an increase in the surface area available for bio-absorption, diffusion, penetration of mineral cations within the pores and the subsequent increase in both the bio-absorption capacity as well as the bio-absorption rate [32].
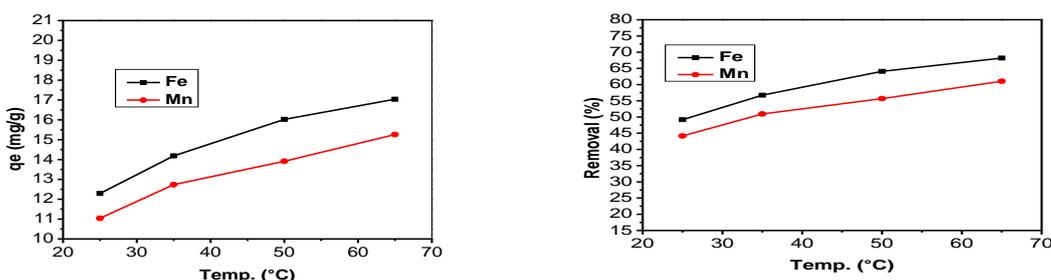


Fig. 8: Effect of temperature on $Fe^{3+}$ & $Mn^{2+}$ ions uptake and percentage removal by AC(P-2) at 25, 35, 50 and 65 ºC (Conc. = 50 mg/l, Wt = 0.1 gm., pH = 3 and 6 for $Fe^{3+}$ & $Mn^{2+}$ ions, velocity of agitation = 100 rpm).

## Effect of interfering ions (cations and anions)

In addition to some anions such as $Cl^-$, $SO_4^{2-}$ as well as $NO_3^-$ (manganese and ferric salts) on the absorption of $Fe^{3+}$ and $Mn^{2+}$, the effect of some cations such as $Na^+$, $Mg^{2+}$ and $K^+$ (chloride form) has also been studied under optimal conditions. **Table 6**, showed that the percentage of $Fe^{3+}$ removal was reduced by 24.72 % in the presence of $Na^+$, $Mg^{2+}$ and $K^+$ cations, while the percentage of $Fe^{3+}$ removal was reduced by 35.12 % in the case of anions $Cl^-$, $SO_4^{2-}$ and $NO_3^-$. In the other side, the percentage of $Mn^{2+}$ removal was reduced by 12.01 % in the presence of the same cations, while in the case of anions $Cl^-$ the removal was reduced by 25.025% . This means that, the presence of anions or cations reduces the potentials of AC (P-2) for uptake and elimination of $Fe^{3+}$ and $Mn^{2+}$, respectively. The decrease in sorption potential in the presence of cations may be due to the presence of other ions in the solution which may compete for the adsorption sites with the metal ion of interest. Therefore, it reduces the binding of this metal ion. The amount of inhibition depends on the frequency of biomass binding to the respective ions [33]. The decrease in the absorption potential in the presence of anions can be attributed to the formation of metal ions complexes with a high affinity for the solution compared to the free metal ions, i.e., inhibition of the absorption of metal ions [34].

**Table 6:** Effect of interfering ions on $Fe^{3+}$ & $Mn^{2+}$ ions percent removal as well as uptake on AC(P-2) (from solutions) (Contact time 2h., pH=3 for $Fe^{3+}$ ions & pH= 6 for $Mn^{2+}$ ions, conc. =50 mg/l).

| Adsorbent | Metal ions | Removal of metal only, % | Up take mg/g | Types of ions | | Removal in Presence of interfering ions, % | Up take mg/g |
|---|---|---|---|---|---|---|---|
| AC(P-2) | $Fe^{3+}$ | 90.12 | 22.53 | Cations in presence of $Fe^{3+}$ | $Fe^{3+}$ | 65.4 | 16.35 |
| | | | | | $Na^+$ | 37.8 | 9.45 |
| | | | | | $Mg^{2+}$ | 16.4 | 4.1 |
| | | | | | $K^+$ | 18.8 | 4.7 |
| | | | | Anions in presence of $Fe^{3+}$ | $Fe^{3+}$ | 55 | 13.75 |
| | | | | | $Cl^-$ | 23.8 | 5.95 |
| | | | | | $(SO_4)^{2-}$ | 35.2 | 8.8 |
| | | | | | $(NO_3)^-$ | 28.8 | 7.2 |

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| | $Mn^{2+}$ | | | Cations in presence of $Mn^{2+}$ | $Mn^{2+}$ | 71.4 | 17.85 |
| | | | | | $Na^+$ | 34.4 | 8.6 |
| | | 83.42 | 20.86 | | $Mg^{2+}$ | 20.6 | 5.15 |
| | | | | | $K^+$ | 15 | 3.75 |
| | | | | Anions in presence of $Mn^{2+}$ | $Mn^{2+}$ | 58.4 | 14.6 |
| | | | | | $Cl^-$ | 21 | 5.25 |
| | | | | | $(SO_4)^{2-}$ | 31.8 | 7.95 |
| | | | | | $(NO_3)^-$ | 23 | 5.75 |

## Adsorption Isotherms

The adsorption isotherm displays the amount of adsorption absorbed at a constant temperature by the unit mass of the absorbent from the liquid phase. The study of adsorption equilibrium data is very important to improve the design of the adsorption device. The correlation between metal ions adsorbed on the adsorbent and their concentration in solution is the adsorption isotherm. For the analysis of adsorption data, various isothermal models have been widely used. In this paper the interaction of $Mn^{2+}$ and $Fe^{3+}$ ions with adsorbents was studied using Freundlich and Langmuir adsorption models.

## Langmuir isotherm

The Langmuir model assumes that the adsorption (uptake) of metal ions is a monolayer adsorption on a homogeneous surface without any interaction between the ions adsorbed. The linear form of the Langmuir equation is given by the equation (5) [37].

$$C_e/q_e = (1/q_m b) + (C_e/q_m) \qquad (5)$$

$$R_L = 1/(1+ bCo) \qquad (6)$$

Where $q_e$ is the equilibrium concentration of the adsorbent (mg/g), $q_m$ is the adsorbent monolayer power (mg/g), b is the adsorbent constant (L/mg) and $C_e$ is the equilibrium concentration of the solution (mg/L). A plot of $C_e/q_e$ versus $C_e$ should be a straight line with a slope of $1/q_m$ and an intercept of $(1/q_m b)$, as shown in Fig. 9, according to Equation 5. The graphical representation of $(C_e/q_e)$ versus $C_e$ provides a straight line for the $Fe^{3+}$ and $Mn^{2+}$ ions adsorbed into AC (P-2) respectively. The numerical value of the $q_{max}$ and b constants was determined from the plot slope and intercept. The value of the adsorption power of $q_{max}$ of the monolayer corresponds to the coverage of the monolayer and determines the total capacity of the adsorbent for a particular metal ion.
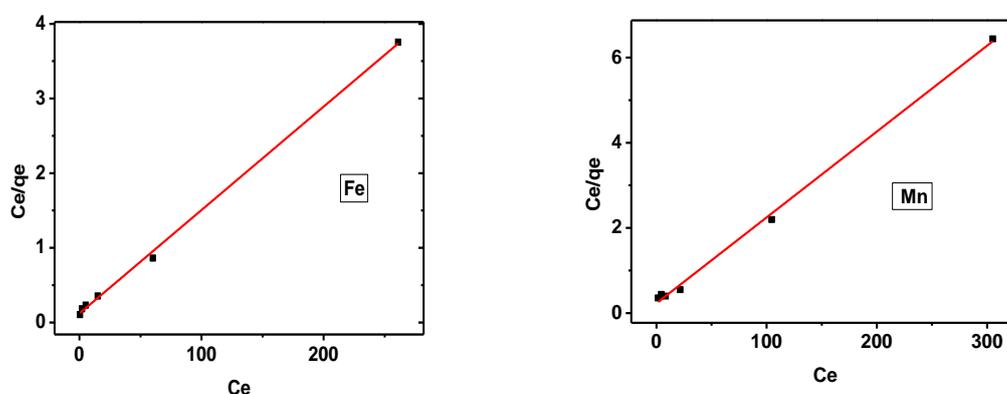


Fig. 9: Langmuir isotherm plots for the adsorption of $Fe^{3+}$ & $Mn^{2+}$ ions using AC(P-2).

The adsorption potential $q_{max}$ calculated by the Langmuir model from **Table 7** was 72.2 and 49.67 (mg/g) for $Fe^{3+}$ and $Mn^{2+}$, respectively.

The characteristics of the Langmuir isotherm can be represented in terms of dimensionless equilibrium parameters ($R_L$). In the present investigation, the values of $R_L$ were 0.042 and 0.054, confirming the beneficial adsorption of $Fe^{3+}$ and $Mn^{2+}$, respectively.

Table 7: **Parameters of Langmuir and Freundlich for $Fe^{3+}$ & $Mn^{2+}$ ions adsorption using AC(P-2), respectively**

| Adsorbent | Metal Ions | Langmuir isotherm | | | | Freundlich isotherm | | |
|---|---|---|---|---|---|---|---|---|
| | | $q_{max}$ (calculated) (mg/g) | qmax (experimental) (mg/g) | b | $R^2$ | n | $K_f$ (mg/g) | $R^2$ |
| AC(P-2) | Fe(III) | 72.20 | 70.25 | 0.087 | 0.99 | 2.24 | 5.65 | 0.89 |
| | Mn(II) | 49.6 | 47.65 | 0.11 | 0.99 | 2.21 | 8.72 | 0.77 |

**Freundlich Isotherm**

The classical Freundlich isotherm [36] can be written as in Equation (7) and can be written in logarithmic form as in equation (8).

$$q_e = K_F C_e^{1/n} \qquad (7)$$
$$\log q_e = \log K_F + (1/n) \log C_e \qquad (8)$$

Where, respectively, $K_F$ (mg/g) and n are the adsorption power adsorption strength constants. The $K_F$ values can be used to express the relative potential of adsorption, and n indicates that adsorption is adverse to adsorption (n<1) [37] or preferential adsorption (n>1).

By plotting log $q_e$ versus log $C_e$, Fig. 10, the applicability of the Freundlich sorption isotherm was analysed. The $K_F$ as well as 1/n values are estimated from the intercept and slope of the linear regressions in **Table 7**, respectively.

The results in Table 7, by comparing the calculated correlation coefficients, $R^2$, for each model it can be concluded that the experimental data fit the Langmuir model better than the Freundlich model and from the Langmuir

isotherm parameters, the maximum capacity $q_{max}$ of Fe and Mn were found to be was 72.2 and 49.67 (mg/g) respectively, for of $Fe^{3+}$ as well as $Mn^{2+}$ by the adsorbent
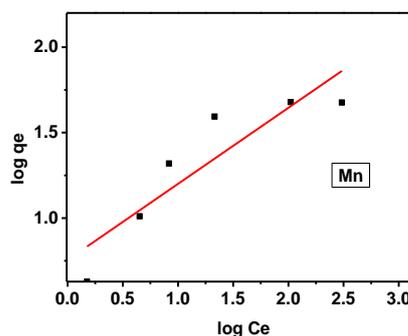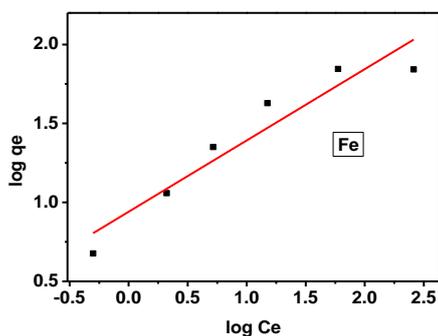


**Fig. 10:** Freundlich isothermal plots using AC(P-2), respectively, for the adsorption of $Fe^{3+}$ & $Mn^{2+}$ ions

**Adsorption Kinetic Studies**

**First -order kinetic model**

For the analysis of adsorption kinetics, pseudo-kinetic models of the first as well as second order were applied to the experimental data [38&39]. The Lagergren's 1st. rank rate equation is one of the most widely used liquid equations.
Adsorption studies and is expressed by Equation (9).
Log $(q_e - q_t) = \log q_e - K_f t/2.303$ (9)

Where the quantities of adsorbed solute (mg/g) are $q_e$ and $q_t$, respectively, at equilibrium and at time t (min). $K_f$ is the pseudo first-order rate constant (min⁻¹). It is possible to produce the value of $q_e$ (mg/g) from the intercept and the value of $K_f$ (min⁻¹) from the slope by plotting the log $(q_e - q_t)$ versus (t) which gives the straight line shown in Fig. 11, **Table 8**.

**Table 8: Kinetic parameters for adsorption of Fe$^{3+}$ & Mn$^{2+}$ ions using AC(P-2), respectively**

| Adsorbent | Metal Ion | q$_e$ exp (mg/g) | Pseudo-First order | | | Pseudo-Second order | | |
|---|---|---|---|---|---|---|---|---|
| | | | K$_f$ (min$^{-1}$) | q$_e$ calc. (mg/g) | R$^2$ | Ks (g mg$^{-1}$. h$^{-1}$) | q$_e$ calc. (mg/g) | R$^2$ |
| **P-2** | **Fe$^{3+}$** | 20.04 | 0.014 | 9.33 | 0.93371 | 0.00505 | 21.20 | 0.98 |
| | **Mn$^{2+}$** | 18.73 | 0.017 | 10.33 | 0.5841 | 0.00284 | 20.74 | 0.97 |
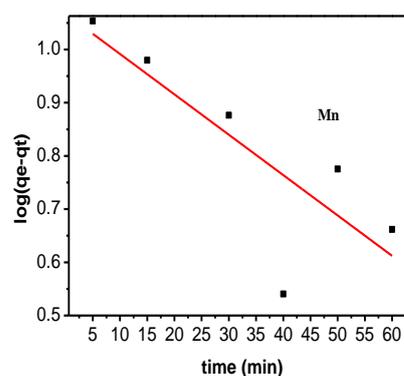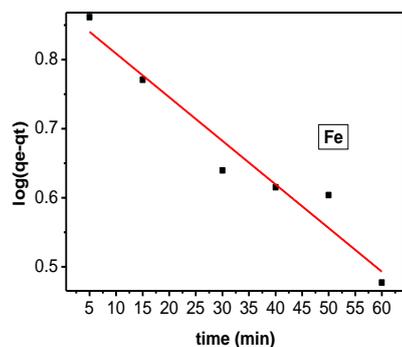


Fig. 11: Pseudo-first -kinetic order on AC(P-2) for Fe$^{3+}$ & Mn$^{2+}$ ions respectively (Conc. = 50 mg/l, t = 120 min, shaker = 100 rpm as well as pH= 3 for Fe$^{3+}$, and 6 for Mn$^{2+}$ at 25 °C).

**Second-order kinetic model**

Although Equation (10) expresses the linear form of the pseudo-second-order equation.

$$t/ q_t = 1/ k_s q_e^2 + t/ q_e \qquad (10)$$

Where the quantities of solute adsorbed (mg/g) are q$_e$ and q$_t$, respectively, at equilibrium and at time t (min).

K$_s$ is the equilibrium constant of the pseudo-second order rate (g/mg.min). It is possible to determine the value of K$_s$ from the intercept and the value of q$_e$ (mg/g) from the slope by plotting t/q$_t$ versus (t), which gives a straight line shown in Fig. 12, **Table 8**.
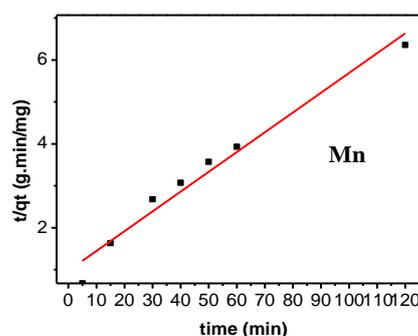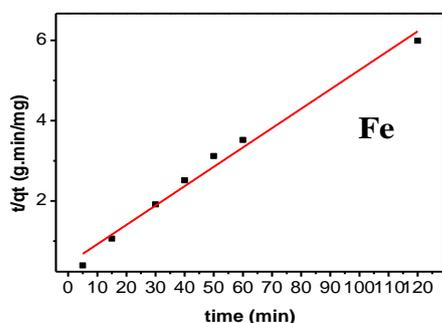


Fig. 12: Pseudo-second-Kinetic order for AC(P-2) for Fe$^{3+}$ & Mn$^{2+}$ ions. (Conc. = 50 mg/L, t = 120 min, shaker = 100 rpm as well as pH= 3 for Fe$^{3+}$, and 6 for Mn$^{2+}$ at 25 °C).

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**Table 8** showed that the $q_e$ values were very similar to the experimental values and the correlation coefficient of the second-order pseudo-kinetic model was higher than that of the pseudo-first-order kinetic for P-2 ($R^2$ = 0.98 & 0.97 for $Fe^{3+}$ and $Mn^{2+}$, respectively). The high value of the correlation coefficient is an indication of the accuracy of the pseudo-second equation of the experimental data compared to the pseudo-first equations $Fe^{3+}$ and $Mn^{2+}$. This may allow us to conclude that the adsorption process is chemisorption in nature. This suggests that the adsorption perfectly complies with the reaction of pseudo-second order and the chemisorption mechanism seemed to regulate the adsorption of $Fe^{3+}$ as well as $Mn^{2+}$.

**Thermodynamic parameters**

The thermodynamic parameters represent the feasibility as well as spontaneity of the bio-sorption process's. Ingeneral, the free energy, changes in enthalpy, and entropy of Gibbs are used to determine whether or not the bio-sorption mechanism occurs spontaneously or not. The normal changes of Gibbs free energy ($\Delta G^o$), enthalpy ($\Delta H^o$), and entropy ($\Delta S^o$) adsorption can be evaluated from Van't Hoff Equation 11[40]

$$\ln K_d = \Delta S^o /R - \Delta H^o /RT \quad (11)$$

The values of $\Delta H^o$ and $\Delta S^o$ were obtained from the slope and intercept of the linear plot of ln $K_d$ versus 1/T and the results which shown The determination of thermodynamic parameters are obtained in **Table 9 and Fig. 13**.

**Table 9: Thermodynamic parameters for adsorption of** $Fe^{3+}$ **&** $Mn^{2+}$ ions **using** AC(P-2), **respectively**

| Adsorbent | Metal ion | R-Square | $\Delta H^o$ ( K J /mol) | $\Delta S^o$ (J /mol.K) | $\Delta G^o$( K J /mol) | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | 25 °C | 35 °C | 50 °C | 65°C |
| **P-2** | **$Fe^{3+}$** | 0.99134 | 18.5563 | 113.85 | -15.37 | -16.51 | -18.21 | -19.92 |
| | **$Mn^{2+}$** | 0.9736 | 5.2915 | 109.52 | -17.34 | -18.44 | -20.08 | -21.72 |

Negative values of $\Delta G^o$ at different temperatures (Table 9) indicated that the adsorption of $Fe^{3+}$ as well as $Mn^{2+}$ on the AC(P-2) bio-sorption was spontaneous and the affinity for AC(P-2)was higher at a higher temperature. The positive value of $\Delta H^o$ for $Fe^{3+}$ and $Mn^{2+}$ (18.56, 5.29 kJ/mol) indicates the endothermic nature of this bio-sorption process. Moreover, the

positive value of $\Delta S^o$ indicated that the entropy increased at the solid/solution interface. The decrease in free energy ($\Delta G^o$) with increasing temperature indicates that this bio-sorption process was endothermic.
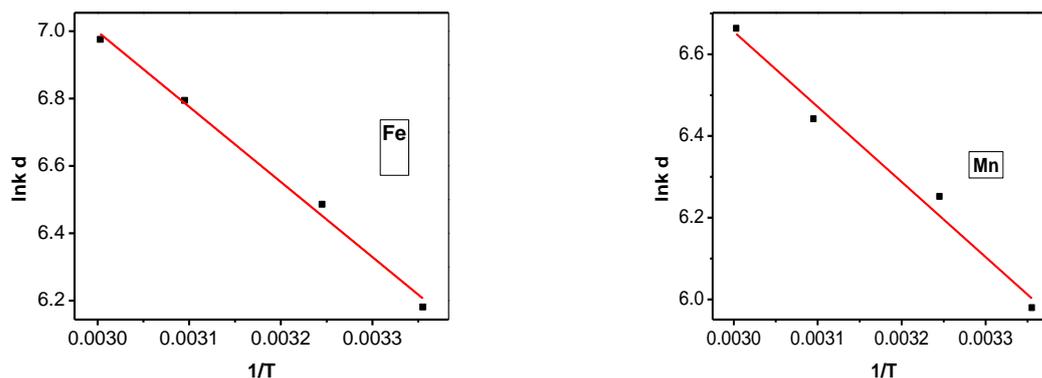


Fig. 13: Plot of ln $K_d$ vs. 1/T for adsorption of  $Fe^{3+}$ & $Mn^{2+}$ ions onto AC(P-2).

**Comparison with other adsorbents**

To explain the validity of AC(P-2) as an effective adsorbent of $Fe^{3+}$ and $Mn^{2+}$, respectively, it is important to compare its adsorption capacity with

other registered adsorbents. The $q_{max}$ values for $Fe^{3+}$ as well as $Mn^{2+}$ on different adsorbents are contrasted with our adsorbent values and are summarized in **Table 10.**

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**Table 10:** Comparison of maximum adsorption capacities of $Fe^{3+}$ & $Mn^{2+}$ ions on different adsorbent

| Adsorbent | Adsorption capacity (mg g$^{-1}$) | | Reference |
|---|---|---|---|
| | $Fe^{3+}$ | $Mn^{2+}$ | |
| Chemically modified banana peels | - | 5.7306 | [1] |
| Physically modified bagasse peels | 74.18 | - | [41] |
| chemically modified bagasse pulp | - | 28.13 | [41] |
| GAC | - | 6.94 | [42] |
| MAC | - | 14.49 | [42] |
| Activated carbon based urea formaldehyde resin | 12.8 | - | [43] |
| Sawdust | - | 4.72 | [44] |
| Untreated volcanic ash | - | 30 | [45] |
| Hazelnut hull | 13.59 | - | [46] |
| Birbira(Militia Ferruginea) Leaves | - | 3,41 | [47] |
| Ricinus Communis seed shell | 48,54 | - | [48] |
| Activated carbon from coconut shells | - | 75,65 | [49] |
| Saponified Apple Waste | 144,9 | - | [50] |
| Pecan nutshell | - | 98 | [51] |
| Bombax malabaricum | - | 8,2 | [52] |
| Pithecellobium dulce | - | 7 | [53] |
| Ipomea batatas | - | 6 | [54] |
| Peltophorum ferrugineum | - | 5,5 | [54] |
| Pithecellobium dulce carbon | - | 7 | [54] |
| Husk of cicer arientinum | 72,16 | | [54] |
| Chemically activated rice husk AC(P-2) | 72.2 | 49.6 | **This work** |

## Application study

The use of AC(P-2) as an adsorbent for groundwater treatment was investigated. It can be seen from **Table 11** that AC(P-2) showed a successful ability to deal with $Fe^{3+}$ and $Mn^{2+}$ in groundwater. Usually the capacity of AC(P-2) to extract $Mn^{2+}$ ions is greater than that of $Fe^{3+}$ ions. In addition, the results showed that the percentage of extracted $Fe^{3+}$ and $Mn^{2+}$ ions was 63.9 as well as 48.9% respectively, and AC(P-2) also showed good ability to treat groundwater $Fe^{3+}$ and $Mn^{2+}$ ions.

Table 11: **Treatment of $Fe^{3+}$ & $Mn^{2+}$ ions in Dahmasha's ground water Plant by using AC(P-2) adsorbent**

| Parameters | Tested parameters | Sample before adding AC | Sample after adding AC |
|---|---|---|---|
| **Physical** | **Colour** | Colourless | Colourless |
| | **Taste** | Accp. | Accp. |
| | **Odour** | Odourless | Odourless |
| | **conductivity** | 986 | 915 |
| | **TDS** | 631 | 549 |
| | **Turbidity** | 2.96 | 0.48 |
| | **pH** | 7.23 | 7.49 |
| **Chemical** | **T. hardness as CaCO₃** | 407 | 395 |
| | **Ca. hardness as CaCO₃** | 249 | 240 |
| | **Mg. hardness** | 158 | 155 |
| | **Chloride** | 151 | 147 |
| | **Sulfate** | 90 | 87 |
| | **T. alkalinity** | 246 | 236 |
| | $Fe^{3+}$ | 0.97 | 0.35 |
| | $Mn^{2+}$ | 0.47 | 0.24 |
| | **Residual Aluminum** | N.D | N.D |
| | **Cupper** | N.D | N.D |
| | **Zinc** | N.D | N.D |

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| | | | |
|---|---|---|---|
| **Nitrite** | | N.D | N.D |
| **Floride** | | N.D | N.D |
| **Total P.** | | N.D | N.D |
| **Free. chlorine** | | 1.3 | 1.1 |

## Conclusions

The present study addressed the preparation of new activate carbon from rice husk to remove heavy metals from the aqueous solution, by activating phosphoric acid (1N). The results show that rice husk is a successful precursor to the development of high-performance active activated carbon for use in removing $Fe^{3+}$ and $Mn^{2+}$ from aqueous solutions. The significant parameters were optimized with a full factor experimental design through response surface methodology. At pH 3 and 6, respectively, the maximum absorption of $Fe^{3+}$ and $Mn^{2+}$ was observed.

By increasing the primary ions concentration and the dose of adsorbent, the absorption of $Fe^{3+}$ and $Mn^{2+}$ on this substance was improved. For both $Fe^{3+}$ and $Mn^{2+}$. The optimal connection time was 2 hours. The data also predict that an endothermic system controls the adsorption process. Moreover, the maximum adsorption capacities of $Fe^{3+}$ as well as $Mn^{2+}$ were 72.2 and 49.67 (mg/g), and metal ion removal were 90.12 and 83.42%, respectively. RH can be effectively used to manufacture inexpensive local water treatment $Fe^{3+}$ and $Mn^{2+}$ absorbents because the feed stocks are available at low cost domestically and in abundance.

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