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Removal of Some Heavy Metal Ions from an Aqueous Systems as Mn(II) and Fe(III) Using Egg Shell

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ABSTRACT : ***The adsorption technique for the process of extracting or separating heavy metal contaminants from solutions was more effective. Egg shell (ES) was identified by FT-IR spectroscopy, (SEM) and X-ray fluorescence which used to separate manganese(II) and iron(III) from an aqueous systems. pH, sorbent weights, contact time, initial concentration and temperature of manganese (II) and iron(III) were studied to obtain the most favorable conditions for removal of these ions. The results were clear that the removal of metal ions raised with increasing of contact time and sorbent weight. Also, the removal percentage decreased as the initial concentration of the two metals increased. The overall adsorption capacities of ES for manganese(II) was 35.62 mg/L and for iron(III) was 35.12 mg/L. The results showed that the removal of manganese(II) and iron(III) was enhanced under the following optimal conditions: pH 5, contact time 35 minutes, sorbent weight 0.4 g, and temperature 50 °C. The sorbent material could be effectively regenerated by using distilled water for more than five cycles. Adsorption kinetics followed the pseudo-first-order model, and Langmuir isotherm provided a good fit to the experimental data.***

KEYWORDS: Adsorption, heavy metals, aqueous systems, egg shell.

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I. INTRODUCTION

The levels of heavy metal contamination in water systems are increasing due to industrialization, climate change, and urbanization. Various sources contribute to this pollution, including mining residue, leachates from landfills, wastewater from both municipal and industrial sources, runoff from urban areas, as well as natural events like volcanic eruptions, weathering, and rock erosion. Over the past few years, the pollution of rivers and groundwater due to insecticides has become a prominent environmental concern with wide-ranging implications. The extensive application of agrochemicals in diverse agricultural activities, such as orchards has resulted in the widespread occurrence of insecticides in water fountains. This contamination arises from various corridors, filtered into the soil, wind erosion, aerial spraying, industrial effluents, and other sources. Consequently, pesticides are found in water across different countries globally **[1].** Toxic materials typically consist of heavy metals pollutants, which have the potential to cause significant harm to water systems and soil. The ongoing problem of heavy metals pollution in water systems poses a serious threat to both human health and the environment **[2].** Several strategies were developed for removing heavy metals from aqueous systems **[3].** The current therapy methods for heavy metal removal from polluted aqueous systems are often expensive and can sometimes result in the generation of additional toxic substances **[4].** The requirement for environmentally friendly, cost-effective, and non-toxic waste-generating processes and separation techniques is evident. In this context, the adsorption process emerges as a promising solution. It is characterized by its low cost, simple, selectivity, and the potential for recovering the adsorbed substances **[5].** The adsorption method is highly suitable for removing heavy metals, both in low and high concentrations. It offers advantages such as easy separation under favourable conditions, the use of renewable adsorbents, a high adsorption load for heavy metals, and the production of zero sludge. These factors contribute to the effectiveness and efficiency of the adsorption process in heavy metal removal **[6-8].** According to the definition provided by the (IUPAC), ES is characterized by a highly porous surface and possesses various superficial jobs **[9].** The significant porosity of ES allows for a vast surface area, which in turn facilitates effective adsorption. Additionally, the chemical properties of its surfaces contribute to enhancing the efficiency of adsorption processes **[10,11].** Aim of the work, ES sample was collected to adsorb some heavy metal ions from aqueous systems such as Mn(II) and

Fe(III). Physical and chemical characteristics of the gained adsorbed materials were investigated by FT-IR, X-ray fluorescence and SEM.

II. EXPERIMENTAL

2.1. Treatment of ES adsorbent

ES adsorbent material is collected from local market the ES samples (poultry ES) used in this study were obtained, the samples were collected, washed with water and dried for 2 h in an oven at 125 °C, cool to room temperature, crushed, sieved to 63 µm, used in the experiments [12].

2.2. Preparation of Mn(II) and Fe(III) adsorbate

Stock solutions (1000 mg/L) of Mn(II) and Fe(III) dissolve 4.18 g of $MnCl2.6H2O$ (M.Wt. 233.94 g/mol) and 4.84 g of $FeCl3.6\ H2O$ (M.Wt. 270.30 g/mol). The solutions were stored in a one litre measuring flask, diluted with bidistilled water to different concentrations as required.

2.3. Method of determination of Mn(II) and Fe(III) in solutions

Mn(II) and Fe(III) were determined by dissolving known amount metals into quick-fit glass bottle containing ES sorbent in 50 mL. The experiments run out after controlling the pH range from 2 to 8. The kind of two metal ions on range of pH is documented [13]. The amount of two metal ions adsorbed percentage removal by sorbent was calculated by using equations 1 and 2 [14].

$$\mathrm{Qe} = \frac{\mathrm{V(Ci-Ce)}}{\mathrm{W}} \times 100\ \% \qquad (1)$$

$$\%\text{Removal Efficiency} = \frac{(\mathrm{Ci}-\mathrm{Ce})}{\mathrm{Ci}} \times 100 \qquad (2)$$

Qe (mg/L) is the quantity of metal ions, V is the volume (L), W is the material dose (g), Ci (mg/L) is the metal concentration and Ce (mg/L) is the balance metal concentration in solution.

2.4. Isotherm studies

The adsorption process on ES sorbent was determined using Langmuir isotherm and Freundlich isotherm models. The mathematical expression of the linearized pattern of the two models can be stated by equations 3 and 4 [15].

$$\frac{1}{Q_e} = \left(\frac{1}{K_L.Q_m}\right)\frac{1}{C_e} + \frac{1}{Q_m} \qquad (3)$$

$$\mathrm{Log}\ Q_m = \log K_f + \left(\frac{1}{n}\right)\log C_e \qquad (4)$$

Ce is the balance concentration (mg/L), Qe (mg/L) and Qm (mg/L) are the adsorption capacity at balance and the maximum load of adsorption, respectively, KL is the constant (L/mg), while Kf (mg/g) and 1/n is the capacity of adsorption at unit.

2.5. Adsorption kinetics

The adsorption kinetics were studied by using psedo-first-order (Lagergren equation 5) [16] and psedo-second-order (equation 6) [17] to clarify the adsorption action of Mn(II) and Fe(III) ions on ES adsorbent to fit the experimental information

$$\ln(\mathrm{Qe}-\mathrm{Qt}) = \ln \mathrm{Qe} - \mathrm{K1t} \qquad (5)$$

Qt (mg /L) is the amounts of metal ions adsorbed per liter of the adsorbent at time t (min.) and Qe (mg /L) is the adsorption capacity at equilibrium, and K1 (1/min.) is the rate constant of the sorption process.

The equation of psedo-2nd-order kinetic model is:

$$\frac{t}{Q_t} = \left(\frac{1}{K_2 . Q_e^2}\right) + \left(\frac{1}{Q_e}\right) t \qquad (6)$$

Where K2 [g/ (mg min.)] is the rate constant

III. RESULTS AND DISCUSSION

3.1 FT-IR spectra of ES

The mass arrangement and some cavities on the external surface of ES Figure 2a, [18-20]. This states that adsorption occurs through the transfer of metals ions from an aqueous solution to a solid's surface. Functional group analysis of raw ES and after adsorption are determined by Fourier transform infrared (FT-IR) spectrometry. Based on the results from Figure 1, Infrared bands at 1407 cm-1 and 872 cm-1 shows the C – O stretching and bending of CaCO3, mean, while the sharp band at 712 cm-1 represents a Ca–O bond [21-23]. The existence of OH in Ca(OH)2 in the peak of around 3622 cm-1, 2325 and 2312 cm-1. It was formed during adsorption of water by CaO [22]. Band at 690 cm-1 can be attributed to Ca–O band [24]. Bands at 1407 cm-1, 1398 cm-1 and 712 cm-1 represent the stretching vibration of the CO32- group present in the ES [25, 26].

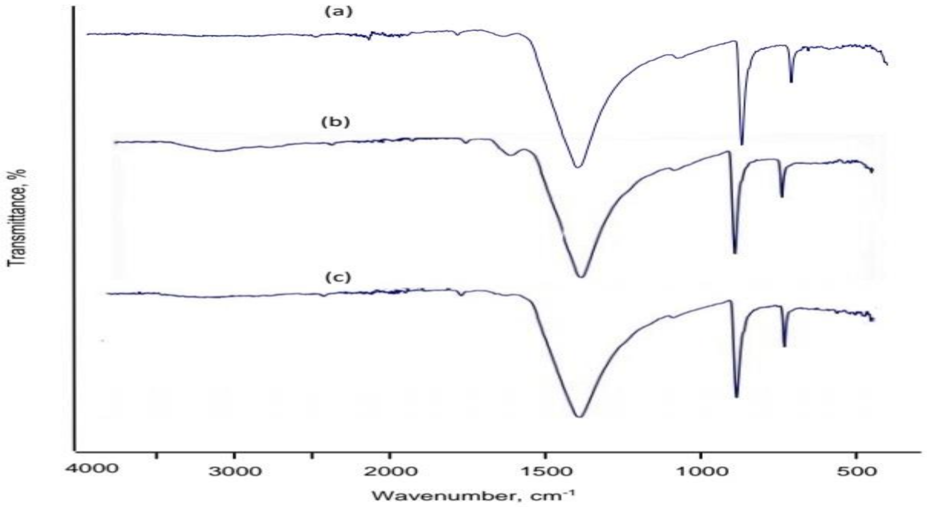


Figure 1 Infrared spectra for (a) row Egg-shell, (b) after adsorption of Fe(III) and (c) after adsorption of Mn(II)

3.2. SEM of ES

The scanning electron microscope was used for characterization of ES before and after adsorption of Mn(II) and Fe(III) ions (Figure 2).The adsorption action involves mass group and presence of porous on the outermost layer or boundary of the adsorbent material. The surface of the ES adsorbent plays a vital role in increasing their overall surface area[27-29].

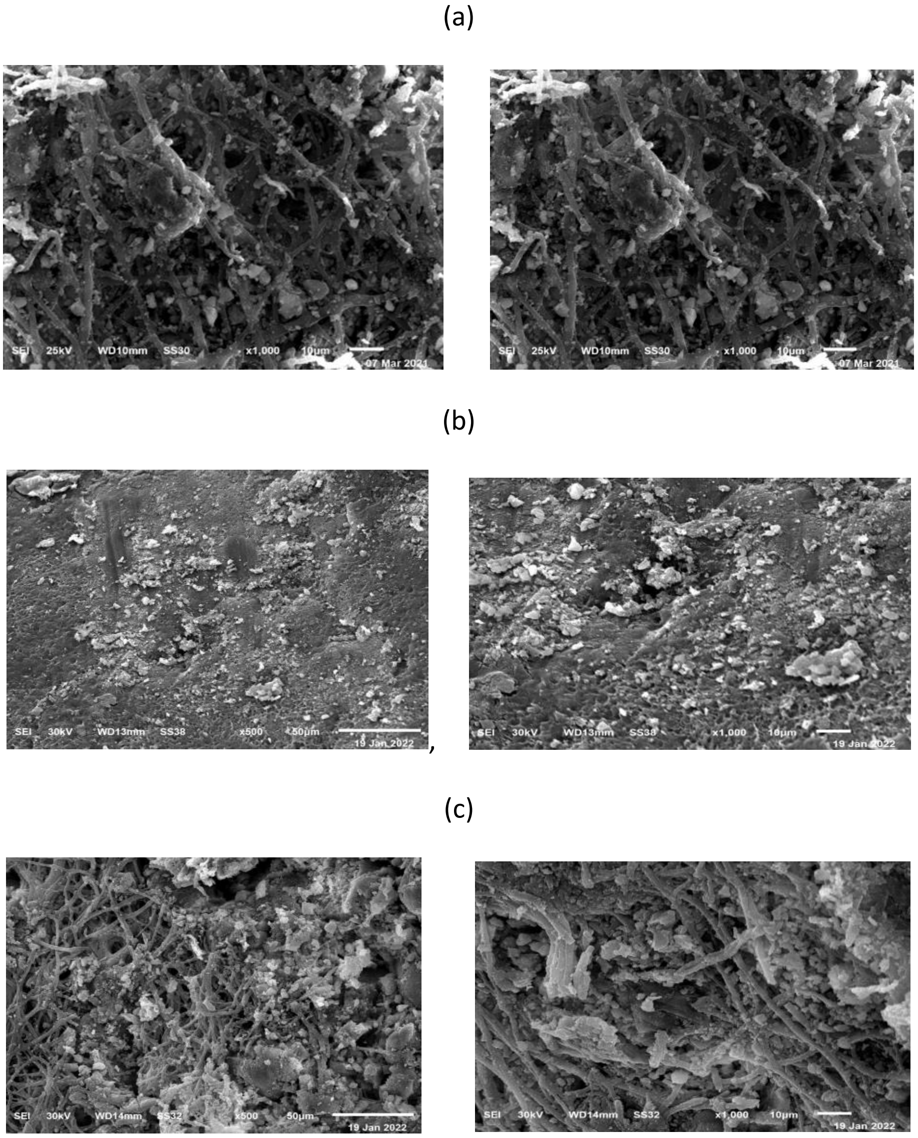


Figure 2 Scanning electron microscope for (a) row Egg shell, (b) after adsorption of Fe(III) and (c) after adsorption of Mn(II)

Table 1: X-ray fluorescence.

Compounds	SiO_3	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	SO_3	Ignition loss
Egg shell %	0.03	0.02	≤0.01	≤0.01	≤0.01	≤0.01	54.10	≤0.01	≤0.01	0.26	≤0.01	0.37	45.11

3.3. X-ray fluorescence

X-ray fluorescence data Table 1 for ES supported represents of SiO_3 0.03%, TiO_2 0.02%, CaO 54.1%, P_2O_5 0.26%, SO_3 0.37% and Loss on ignition (Loi) 45.11%.

3.4. Factors affecting on removal of Mn(II) & Fe(III) from aqueous solutions

3.4.1. Effect of pH

The process was carried out with standard solutions at pH values 2, 3, 5 and 8. The results were showed in Figure 3 the removal percentages for Mn(II), Fe(III) increased by increasing of pH value of the solution until pH 5 (98.5%, 97%) **[30,31].**

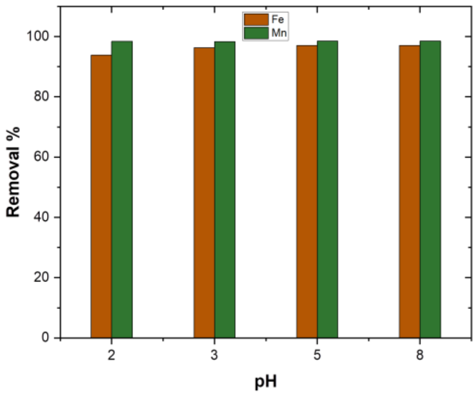


Figure 3 Effect of pH

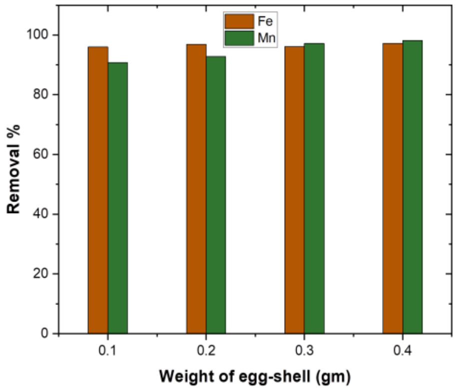


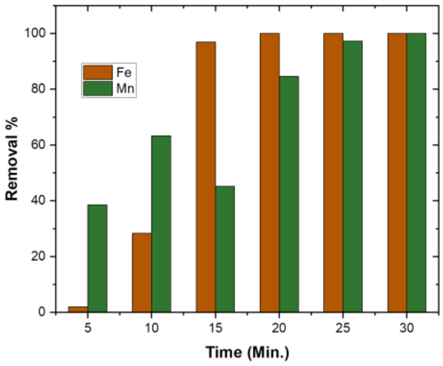
Figure 4 Effect of weight of egg shell

3.4.2. Effect of weight of sorbents

50 mL from standard solutions from Mn(II) and Fe(III) ions, the pH of solutions was 5. Different weights from sorbents (0.1, 0.2, 0.3 and 0.4 g) were added to the standard solutions. The mixture was shacked. The removal percentages for Fe(III), which is nearly equal to 96 %, 96.9%, 96.16% and at (0.4 g) equal to 97.23 %. For Mn(II), the removal percentage increased by increasing the weight of sorbent,90.76%, 92.76% 97.14% and maximum of removal 98.2% at sorbent weight (0.4 gm) Figure 4**.**

3.4.3. Effect of contact time

50 mL from standard solutions metal ions and 0.4 g ES. The pH 5 used for extracting of metal ions. The optimum time at constant other conditions observed at 35 minutes for metal ions with extracting percentages (2%, 28.3%, 96.92%,100%,100% and 100%) for Fe(III) and (38.54%, 63.32%, 45.24%, 84.6%,79.2% and 100%) for Mn(II) Figure 5 **[32].**



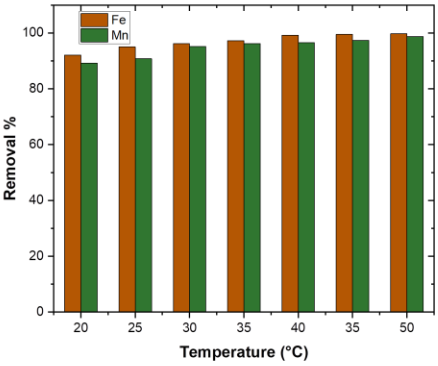


Figure 5 Effect of contact time

Figure 6 Effect of temperature

3.4.4. Effect of temperature

50 mL from standard solutions from metal ions. At temperature 20, 25, 30, 35, 40, 45, and 50 °C. The temperature at constant other conditions observed at 50 °C with removal percentage of Fe(III) was (99.7%) and for Mn(II) the removal percentages observed (98.7%) Figure 6 **[33].**

3.4.5. Effect of concentration of metal ions

A series of standard solutions were prepared with various concentrations of metal ions at 20, 30, 40, 50, 60,70, 80 and 90 mg/L. Each experimental was done for each concentration of metal ions at constant conditions (contact time 35 minutes, pH 5, temperature 50 °C and weight 0.4 g). Maximum removal of Fe(III) ions for at 30 mg/L equal 94.10%,. Maximum removal of Mn(II) ion at 30 mg/L equal 93.30%,. Figure 7 **[34].**

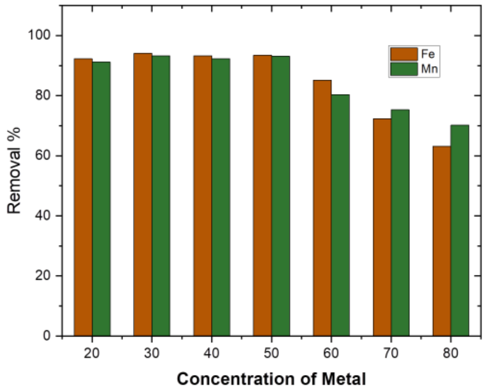


Figure 7 Effect of intial concentration of metal ion

3.5. Adsorption isotherm study

. In Freundlich model, the different values of reactivity of active sites (n) indicate different types of adsorption behaviour The graphs (Fig. 8 (a) and (b)) **[35].** For values of 1/n greater than 1, the adsorption is held by chemical bonds, and for values of 1/n less than 1, the adsorption is favourable physical adsorption. For data in Table 2, it was observed that the 1/n values for the adsorption of Mn(II) and Fe(III) on ES was less than unity. This suggests that physical adsorption is favourable for the adsorption of these ions on these particular adsorbents. To compare the maximum adsorption load of ES and as with other statement adsorbents for the removal of Mn(II) and Fe(III) ions, the data were recorded in Table 3 **[36-39].**

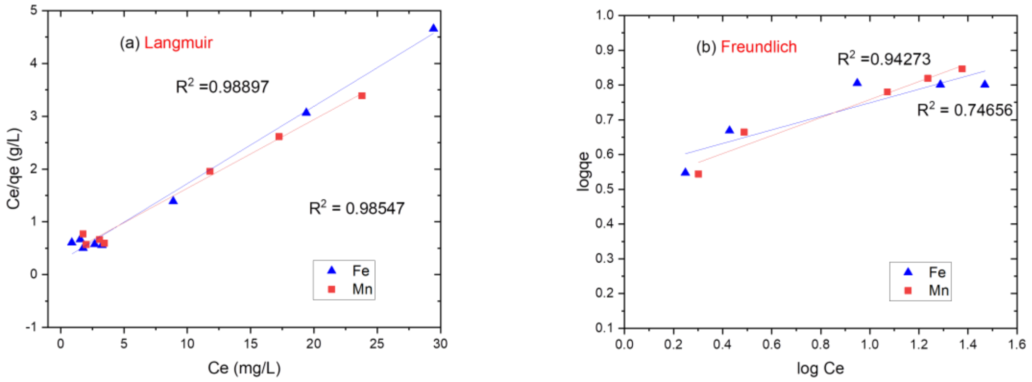


Figure 8 **Adsorption isotherm (a)Langmuir (b) Freundlich**

Table 2: Isotherm parameters for the removal Mn(II) and Fe(III) by egg shell and adsorption capacity of prepared sorbents for as uptake

Isotherm parameters			
Types of isotherm	parameters	Egg shell	
		Fe(III)	Mn(II)
Langmauir	q_{max}(mg/L)	3.8	2.98
	K_L(L/mg)	1.78	2.57
	R^2	0.98897	0.98547
Feundlish	K_f	1.749	3.1568
	$1/n$	0.70629	0.30694
	R^2	0.74656	0.94273

Table 3: Comparison of Egg shell and some other species.

Material	Metal ions	Factors	Q or %	References
Maringa Seedpods	Fe(II) Mn(II)	contact time 60 min., pH8, conc.20mg/l dosage 1g.	80.90 100	**[36]**
Olive Pomace	Fe(II) Mn(II)	contact time 120 min., pH5, Conc.50mg/L dosage 10 g/L.	10.40 10.46	**[37]**
Activated Carbon from Coconut Shells	Fe(II) Mn(II)	contact time 90 min., pH5, Conc.20 – 100 mg/L Dosage 0.1 g.	81.89 75.65	**[38]**
Tea leaves-derived Char (TLC), Rice straw-derived Char (RSC),and Nanosilica (NS)	Fe(III) Mn(II)	the maximum contact time was 720 min, the adsorbent dose was 0.1 g and temperature was 30 °C	98.05% , 97.92%,	**[39]**
Egg Shell	Fe(III) Mn(II)	Contact time 35 min., pH5. Conc. 30 mg/L, Dosage 0.4 g.	99.68 98.70	**This study**

3.6. Adsorption kinetics

Fig. 9 (a and b) depict the kinetics models for the adsorption of metal ions onto ES. By plotting the logarithm of the difference between balance adsorption load (Qe) and the adsorption load at time t (Qt) against time (t), the rate fixed (K_1) and balance adsorption load (Qe) measured by the slope and intercept of the plot. In Table 4, (R^2) ES obtained using the 1st-order kinetic model, were greater compared to those obtained using the pseudo-2nd-order kinetic model. Additionally, the studied balance adsorption loads (Qe) from the pseudo-1st-order kinetic model closely match with the process data for ES. In summary, the results suggest that the adsorption kinetics of Fe(III) and Mn(II) onto ES follow the pseudo-1st-order kinetic model. Respective models exhibit good agreement with the experimental data for ES.

Table 4: Kinetic Parameters

Adsorbent	Metal ion	Psedo-first-order model			Psedo-second-order model			
		Q_e(cal) (mg/L)	K_1(min^{-1})	R^2	Q_e(cal) (mg/L)	K_2(g mg^{-1} min^{-1})	R^2	Q_e (exp.) (mg/L)
Egg shell								
	Fe(III)	35.12	6.3×10^{-5}	0.74656	8.8	0.0312	0.0797	35.28
	Mn(II)	35.62	3.7×10^{-5}	0.94273	5.8	0.0054	0.292	34.98

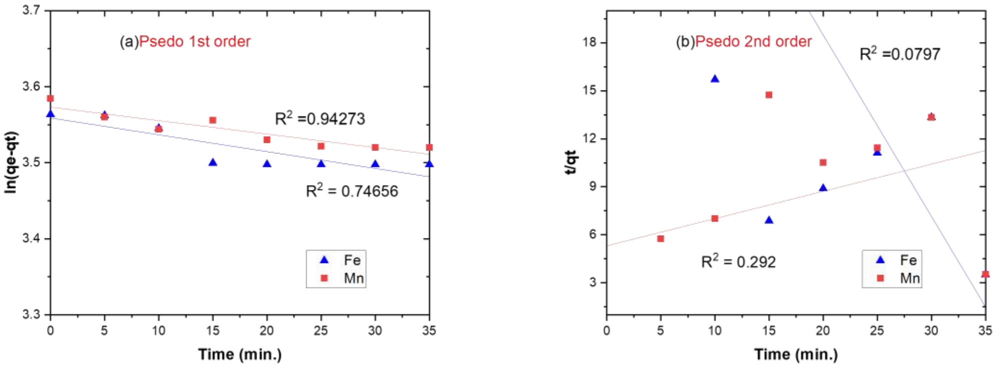


Figure 9 Adsorption Kinetics (a) Psedo 1st order (b) Psedo 2nd order

3.7. Reactivation study

After conducting multiple cycles of adsorption and desorption, washing by distilled water, The removal percentage of Fe(III) on ES as shown in (Fig.10 a) decreases by approximately 6 %, hereafter five experiments. Similarly, the percentage removal of Mn(II) on ES (Fig.10 b) decreases by 5 %, after five cycles. In case of washing by 1N HCl, the removal percentage of Fe(III) on ES as shown in (Fig.10 a) decreases by approximately 20.00%, hereafter five experiments. Similarly, the percentage removal of Mn(II) on ES (Fig. 10 b) decreases by 17.00%, after five cycles. In case of washing by 1N NaOH, The removal percentage of Fe(III) on ES as shown in (Fig.10 a) decreases by approximately 16.00%, hereafter five experiments. Similarly, the percentage removal of Mn(II) on ES (Fig.10 b) decreases by 15.00%, after five cycles. Adsorption tests were carried out washing and without washing, by distilled water, 1N HCl, and 1 N NaOH. The results, sketched in Fig.10 (a,b), The information provided suggests that washing the adsorbents with distilled water was sufficient to make them usable. The primary mechanism for the adsorption approach appeared to be ion sharing. washing the metals from the adsorbents with distilled water was not show significant possible for adsorption. The decrease in adsorption capacity observed after each adsorption step was rated to the loss of binding sites on the adsorbent subjects. Nevertheless, Results score that the used adsorbents can still be effectively reused for adsorption purposes, even after undergoing five experiments of adsorption, with only a slight reduction in their adsorption load. It is important to note that the provided information was based on the given statement or hypothetical scenario, and specific experimental details, data, and analysis techniques were not provided. Therefore, the interpretation and conclusions are limited to the information presented in the statement **[40].**

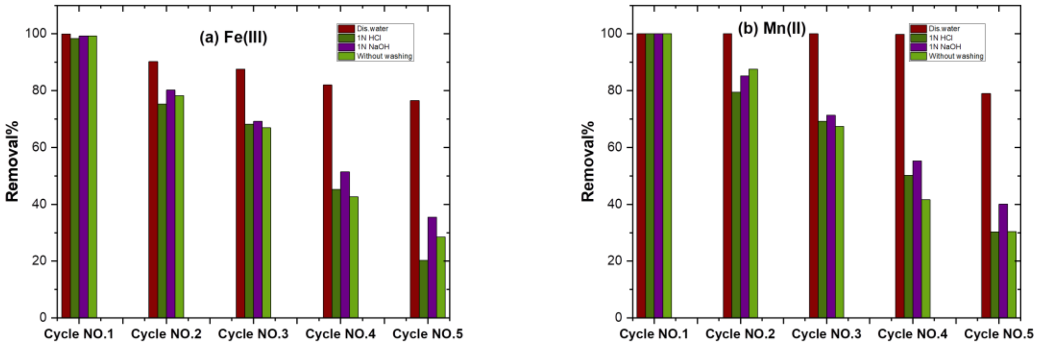


Figure 10 Regeneration study washing by distilled water,washing by 1N HCl,washing by 1N NaOH, without washing (a) Fe(III) (b) Mn(II)

IV. APPLICATION

The study examined the use of adsorbent material ES for the adsorption of metal ions from sub-river (A) and underground well (B) samples collected from different areas (Zagazig and Borg Alarab). The water samples were processed with 0.4 grams of the adsorbent materials at pH 5, with a contact time 35 minutes, temperature 50 °C. The concentrations were measured before and after the removal process, (Table 5).The results indicate that ES was perfect in removing 98% of both Fe(III) and Mn(II) from the water samples. In summary, adsorbent material ES was found to be highly effective at removing Fe(III) and Mn(II) ions from the surface water and underground water samples, with removal percentages ranging from 97% to 98%.

Table 5: Using Egg shell in the removing of Fe(III) and Mn(II) ions

Samples	sorbent	conc. before mg/L		conc. after mg/L	
		Fe(III)	Mn(II)	Fe(II)	Mn(II)
A	Egg shell	8.38	1.23	0.129 (98.4%)	0.031 (97.48%)
B	Egg shell	5.68	1.03	0.098 (98.27%)	0.024 (97.67%)

V.CONCLUSION

In light of these results , we can be concluded that materials ES can be used efficiently in the removal of Mn(II) and Fe(III) from aqueous solutions. The results indicated this process dependent on pH value, weight of sorbents, contact time, temperature and initial concentration of the separated metal ions. The experimental data showed the final optimum conditions as the follows: contact time 35 minutes, pH 5, temperature 50 °C, initial concentration of metals 30 mg/L and weight of, and were 0.4 gm. The order of the removal of the two heavy metal ions from aqueous solutions at the optimum conditions found as Mn (II) < Fe (III). The metal ions showed different behaviors by raising of the concentration of the metal ions towards adsorption on ES. The experimental studies showed that, can be used as inexpensive and effective substance for removing a large amount of toxic metals from aqueous solution.

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