Removal of manganese (Mn$^{+2}$) from aqueous solution by low-cost adsorbents and study the adsorption thermodynamics and kinetics

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Abstract. In this research a simple method was used to treat water contaminated by heavy elements containing ions using chicken eggshell powder and to study its adsorption capacity in many laboratory conditions in terms of (time, acidity, heavy metal concentration, weight of the adsorbent material, and temperature) and the diagnosis of the adsorbed substance using Devices for identifying the effective groups on the adsorbent surface used IR ray and its ability to removal the manganese ion as well as studying the thermodynamic adsorption for it ($\Delta H$, $\Delta G$, $\Delta S$). And through studying the thermodynamic adsorption process, it is possibility to know the type of exothermic or endothermic, automatic or non-automatic and random or regular, through the data can be controlled by the efficiency and speed of adsorption, The kinetics of the reaction were also studied, the interaction constant was calculated, and the degree of interaction was determined from the first or second order. The best adsorption operators that were used laboratory (time =60 min, pH = 6, Ce = 100 ppm, weight = 0.5 g, temperate =25 C), IR spectroscopy appear Functional groups (S-H, C-O, O-H, C=C, C=O, N-H, C-N and O=C-O salt Ca) was (2515.18, 1259.52, 3300 broad, 1635.64 , 1799.59 , 3300.20 , 1419.61 and two strong bond (1600 – 1400)) respectively.

1. Introduction

Contamination of the earth with poisonous metals has been broad and frequently includes enormous volumes of wastewater [1]. Squander water tainting is regularly expanding issue which the entire world is presently confronting. Squander water includes fluid waste released by residential, mechanical waste, rural action and business properties. Mechanical waste establishes the significant wellspring of metal contamination in characteristic water [2]. Numerous heavy metal ions such as chromium, cadmium, manganese, mercury, lead and copper, among others, are known to be significantly toxic to human health and environment even at low concentrations [3] Manganese plays a critical role in human life, the integrity of the digestive system, as an anti-oxidant food, body growth and relief of paralysis and muscle tension hypermanganese-semia, have been reported in patients with Mn poisoning.[4]. Metallic particle adsorption may result in implantation of mineral connections or coordination with beneficial function groups found in characteristic proteins, fats, and carbohydrates placed on cell walls, a procedure mediated by connecting minerals to living or dead biomass[5].

Several studies have been conducted based on the interest of vital sorbents containing calcium carbonate such as dead limestone skeleton, seashells, bone charcoal, clams, oysters, crabs, shrimp prawns; Fish scales, coral reefs that some of these vital absorbents can use to remove heavy metals up to 200 mg/l [6]. Plus, there are likewise numerous family unit and mechanical waste which have been broadly adsorption as organic spongy materials, for example, elastic, Hevea brasiliensis leaf powder, banana strip, pumpkin strip, eggshell, tea squander and so forth. These materials
indicated great evacuation of substantial metals, be that as it may, eggshells are picked in this paper, as this material is naturally widely available in large quantities of food scrap and industrial poultry animal waste [7]. In this way, alternative strategy utilizing minimal effort materials, for example, eggshell to removal substantial metals was endeavored use a basic adsorption process. Chicken eggshells can be utilized to retain substantial metals in wastewater due to their calcium carbonate content liable for the adsorption of minerals [8]. Adsorption is now recognized as an effective and economical method for treating wastewater contaminated with heavy metals. The adsorption process provides flexibility in design and operation and many cases will produce high-quality treatment waste. Additionally, because adsorption is sometimes reversible, adsorbents can be regenerated by the appropriate absorption process (9).

2. Materials and Methods

2.1. Preparation of Adsorbent
Chicken eggshell were collected and were washed with distilled water and dried at (80 °C) for 12 hours. It was cracking and crushing by using jaw crusher into small particles. Then milled with the domestic mill to obtain the powder, The material were sieved by sieve shaker to obtain particles in the range of 0.150mm size. The particles were washed with distilled water three times, then filtered and dried in it for two days, then dried at (70 °C) 24 hours. The dried materials were kept in airtight plastic bottles [10].

2.2. Prepare the Adsorbent Concentration
1- A 100 ppm solution of Mn+2 is prepared by dissolving 0.13742 grams of Manganese (+2) Sulfate (MnSO₄) in Deionized water and a solution made up to 500 ml, as calculated using:

\[
\text{M.Wt of MnSO}_4 = 150.999 \text{ g/mol}
\]

\[
\text{A.Wt of Mn} = 54.938 \text{ g/mol}
\]

\[
\frac{\text{W= PPM X AW}}{\text{MW}} = 100 \times \frac{150.999}{54.938} = 274.85347 \text{ mg/l} = 0.274853 \text{ g/l} = 0.137426 \text{ g/500ml}
\]

2- This solution is diluted as required to obtain standard solutions containing (5, 15, 30, 50, 100) mg/L of Manganese (+2), prepare 1- 0.2 N HCl solutions and 1 – 0.1 M NaOH are used to adjust the pH of the solutions, using the dilution law we have:

\[
N_1 X V_1 = N_2 X V_2 \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2)
\]

3- Volume 25 in a conical flask size 50 ml a specific weight of egg powder has been added to specific treatments or experimental conditions and then filtered with filter paper and the filtrate is taken for measurement.

4- Work is done using the bath method in the process of removing the manganese cation using an egg powder and consequently a certain weight of the powder to the conical flask mentioned previously with a known concentration and after changing the effect the value of the blank filter and we get the concentration of the unfiltered leachate on the surface [11].

2.3. Instruments
Working procedure and analytical methods: - electrical balance, PH instrument type professional bench top BP3001 (china), shaker thermal type JEIO TECH-BS-11 degetal Korea, Atomic absorption instrument type
phoenix-986AA-Co LTD.(UK), FT-IR apparatus type Shimadzu-japan (4000-400 cm⁻¹), glassware (beakers, conical flasks,) and filter paper (Whatman 40 mm).

2.4. **FT-IR Characterization of Chicken Eggs Shell**

The infrared spectrum in Figure 1 gave several clear packages that show that there are active groups with a negative charge on the surface of the chicken egg shell powder, and this shows the effectiveness of the adsorbed surface on the sniping or adsorption of manganese (Mn⁺²) cation, as shown in Table 1 these distinct packages of the surface [12].

![Figure 1. FT-IR of the chicken egg shell powder](image)

Table 1. Explains the effective groups

| Wavelength(cm⁻¹) | Structural and Functional group | Functional group            |
|-----------------|---------------------------------|-----------------------------|
| 2515.18         | S-H                             | Hydrogen Sulfide group      |
| 1259.52         | C-O                             | Carbon oxygen group         |
| 3300 broad      | O-H                             | Hydroxyl group              |
| 1799.59         | C=O                             | carboxylate groups          |
| 3300.20         | N-H                             | Nitrogen hydrogen bond      |
| 1419.61         | C-N’                            | Amines group                |
| 1635.64         | C=C                             | Alkeen group                |
| two strong bonds (1600 – 1400) | 0=C-O-salt | Carboxylate –salit groups |

2.5. **Sorption Experiments:**

Batch adsorption of the single-component system of Mn⁺² ions experiments have been carried out at temperature (70 °C) and shaker speed of 185 rpm to establish the optimal working parameters: pH, initial concentration, contact time, adsorbent dose and particles diameter. The procedure supposed to fill a 25mL flask were carried out at initial pH value ranging from 2 to 10; the concentration, contact time, adsorbent dose and particles diameter. The procedure supposed to fill a 20mL flask with 100 mL of each heavy metal...
ions solution Mn\(^{+2}\). Experiments were carried out at initial pH value ranging from 2 to 10; the initial concentration of heavy metal ions (5 – 100) mg/L, the contact time (15-180) min, adsorbent dose gram (0.5-2), L of each heavy metal ions solution Mn\(^{+2}\). Experiments particles diameter (150) micro mater and temperature effect (25°C - 65°C). After equilibrium, was established samples (25 mL) were taken from the flask. These samples were filtered and the concentration of heavy metal ions was measured by spectroscopy. The removal efficiency (R %) (Adsorption rate or percentage of adsorption) was calculated using the following equation:

\[
R\% = \left[\frac{(C_e-C_0)}{C_e}\right] \times 100 \quad \ldots\ldots\ldots\ldots(3)
\]

Where: Co and Ce are the initial and final concentration of the metal ions respectively (mg/L) [13]

Amount of adsorptionqe (mg/g) was calculated by:

\[
Q_e=\left[\frac{(C_0 - C_e)V}{w}\right] \quad \ldots\ldots\ldots\ldots(4)
\]

Where: V volume of solution, w weight of egg shell [14].

3. Result and Discussion

3.1. Effect of Contact Time

The contact time curves show the adsorption of cation Mn\(^{+2}\) of their aqueous solution onto the surface of the eggshell powder at a concentration (100 ppm). These curves indicated that the time needed to reach the equilibrium state is at (60 minutes) for the previously studied ion and its general form consists of two phases, the first is quick, starts with a slight decrease in the percentage of the adsorbed substance with increasing time and is done within the first 60 minutes from the start of adsorption This was most likely because of the foundation of other organic and inorganic or natural anions in solution (The result of partial and slight disintegration of the adsorbent surface with the aqueous solution, which gives the release of calcium ions and ions of amine albumin and other compounds that are part of the egg powder). and the second phase which it is followed by slow starts after min 60 to min 180 with an increase in the percentage of adsorption of adsorbed substance, as it attracts with the surface of the eggshell powder quickly so that it reaches the highest adsorbed amount, as the adsorption peak is clear by taking more adsorption and less contact time depending on the speed of ion transfer. Adsorbent from its aqueous solution to the adsorbent surface, as shown in the curve Figure 2 [15].

![Figure 2. Adsorbent from its aqueous solution to the adsorbent surface](image-url)
3.2. Effect of pH
It was observed in figure 3 when the direct increase of the acidic functions used in the experiment between the range (2 to 10) under constant conditions gave the results of the study somewhat exponential and the percentage of adsorption increases with it. Has been found by checking the curve shape mentioned in this research That is, in neutral and basic media, it is more concentrated than acidic media when the Mn$^{2+}$ cation competes on the surface of chicken eggshell powder[16], as it is greatly affected by the charge on which the adsorbed ion is in the aqueous medium of which (M = OH$^-$), and at low values from the acidic function, H$_3$O ions will compete with manganese cation on negative sites, and with the increase in the acidic function the OH ions will prevail, thereby reducing the competition of manganese cation to favor adsorption in neutral and basic media [17].

![Figure 3. Effect of pH on adsorption of Mn$^{2+}$ (weight = 0.5 g), (cons = 100 ppm), (temp = 25 °c), (time = 60min), (size The particles = 0.150 mm)](image)

3.3. Effect of Initial Concentration of Mn$^{2+}$
Study of the effect of adsorbed ion concentration on ion adsorption (Mn$^{2+}$) On the surface of the chicken eggshell powder and within the ranges ((5 - 15 - 30 - 50 – 100) ppm) when an acidic function, temperature, weight of adsorbent substance and time equal to (PH = 6), (25oc), (0.5 g) (60min) on respectively. It has been observed that the adsorption of Mn$^{2+}$ cation on the surface of the chicken egg shell powder increases to increase the concentration of the adsorbed cation, as the best concentration was at 100 ppm (90.79%).[18] Since the surface of the biological lime type, its adsorption will be of the electrostatic type. On other words, the increased concentration or number of adsorbed ions in relation to the volume of the solvent in the solution. This increases the possibility of ions separating from the solvent and thus increasing the adsorption amount. Note that the adsorption strength of the adsorbent substance increases as the adsorbed substance has little solubility in the solvent and as shown in the diagram in figure 4 [19].
3.4. Effect of Adsorbent Weight

It has been studied removal cation Mn$^{+2}$, By chicken eggshell powder using a fixed concentration of studied ions solution, four different weights of adsorbents at a constant temperature (25 °C). The adsorption ratios at the weights in the following grams (0.5, 1, 1.5, 2) are (90.80, 90.92, 91.29, 91.41) Respectively, the increase in the weight of the adsorbent material leads to an increase in the number of active sites and the number of pores on the surface that are prepared Adsorption of ions, i.e. increased surface efficacy and hence increased adsorption capacity and percentage of adsorption As in figure 5 [20].

3.5. Effect of Temperature on the Adsorption Rate

The patterns showed in Figure 6 in which the percentage of removal of ions Mn$^{+2}$ increases with increasing temperature at a certain range and then decreases. The highest adsorption rate for manganese was at (90.27%) within the range (25 - 45 °C) since its adsorption process is endothermic [21], but the percentage of removal will gradually decrease beyond 45°C as it begins to decrease when the temperature increases above (45°C). To become (90.1%), this is due to the increase in the temperature of the solution leading to an increase in the kinetic energy of the adsorbed Mn$^{+2}$ ions on the adsorbent surface and thus leads to its separation from the adsorbent surface and its return to the solution [22, 23].
3.6. Isotherms

Biosorption isotherms can be produced dependent on various hypothetical models where Langmuir and Freundlich and Temkin models are regularly used to fit empirical information when solute take-up happens by a monolayer biosorption. Langmuir isotherms accept monolayer biosorption, and are described by following equation:

$$Q_e = \frac{x}{m} = \frac{K_L C_e}{1+a C_e} \quad \text{(5)}$$

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a}{K_L} C_e \quad \text{(6)}$$

The Freundlich isotherm is explained by condition:

$$Q_e = K_f C_e^{1/n} \quad \text{(7)}$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad \text{(8)}$$

Where $Q_e$ and $Q_{max}$ are the balance and most extreme sorption limits (mg/g biosorbent), $C_e$ is harmony focus (mg/l arrangement), $b$ is the balance steady, $K_f$ and $n$ are Freundlich constants normal for the framework. While, Temkin model warmth of adsorption and the adsorbate–adsorbate connection on adsorption isotherms were concentrated by Temkin, who recommended that on account of these associations the vitality of adsorption of the considerable number of atoms diminishes directly with inclusion. Temkin isotherm is explained by the accompanying condition[24]:

$$Q_e = B_1 \ln K_t + B_1 \ln C_e \quad \text{(9)}$$

Where: $B_1 = RT/b \quad \text{(10)}$

The ions franchise data studied on the surface of chicken eggshells powder was treated according to the Langmuir equation, the Freundlich equation and the Tempkin equation. When drawing the graphical values of these equations, the constants and values have been obtained, as shown in Table (2). It was found that the higher value corresponds to the adsorption isotherm of this experiment. From the value of $R^2$, it was found that the higher value is that the adsorption isotherm application of this experiment and this is what was
observed in the isotherm line-up equation Langmuir is more identical to the interpretation of this type of adsorption the value of \( R^2 = 0.9324 \), as in the following diagrams in Figures 7-9 [25].

| Table 2. Isotherm constant |
|---------------------------|
| equation | Const1 | Const2 | Const3 |
| Langmuir | K | Qo | 0.9324 |
| 34.602 | 10.705 |
| Freundlich | n | kf | 0.8359 |
| 0.4218 | 10.688 |
| Tempkin | b | Kf | 0.4129 |
| 5.085 | 0.0089 |

**Figure 7.** Freundlich model isotherms.

**Figure 8.** Langmuir model Isotherms.
3.7. Thermodynamic

Thermodynamic factors have been studied in cation adsorption on the surface of chicken eggshell powder at different absolute temperatures ((298, 308, 318, 328 and 338 K)) and at a fixed concentration of the adsorbent material (100 ppm) using a weight (0.5 gm) of the adsorbent substance in volume Granule (0.150 mm) at contact time (60 min), acidic function (pH = 7) Using the following equations:

\[ \Delta G^\circ = -RT \ln K_c \] ………………………………………………………..(11)
\[ K_c = \frac{(C_0 - C_e)}{C_e} \] ………………………………………..(12)
\[ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \text{ or } \Delta G^\circ = -\Delta S (T) + \Delta H^\circ \] ……… (13)

As \( K \) is the equilibrium constant, \( T \) is the absolute temperature, \( R \) is the gas constant [26]. It was found that the direct increase of the adsorbed cation with increasing temperatures indicates that the adsorption is endothermic As the cations gain the necessary energy which increases their Its preference on the adsorbent surface, but when the temperature reaches 328, it will be a reverse reaction and the desorption process will occur (a decrease in the percentage of adsorption with increasing temperatures). This causes the binary manganese to escape from the adsorbent surface and return it to the aqueous solution. As in the following Table 3 and diagram 10 [27].

| T(K) | \( \Delta G \) (kJ) | \( \Delta H \) (kJ/mol) | \( \Delta S *1000 \) (kJ) |
|------|---------------------|---------------------------|-------------------------|
| 298  | -22.516             |                           |                         |
| 308  | -23.5758            |                           |                         |
| 318  | -24.5548            | 1.3186                    | 0.0806                  |
| 328  | -25.0704            |                           |                         |
| 338  | -25.7973            |                           |                         |
3.8. Kinetics

The kinetic adsorption study of metal particle removal is imperative to give understanding into the adsorption rate, give data on the contact time required for significant adsorption to occur and the components influencing or controlling the adsorption rate. To explore the method of Mn\(^{2+}\) adsorption by powder eggshells and controlling stages one of the most generally utilized motor model, the second-order hand was utilized to assess the adsorption of Mn\(^{2+}\). The condition for the pseudo-first request motor model can be diagram (11)

The linear type of conditions for the pseudo-first-order and pseudo-second-order motor models can be spoken to by (6) and (7), respectively:

\[
\frac{q_e - q_t}{q_e} = \frac{K_1}{2.303} t \quad \ldots \quad (14)
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \ldots \quad (15)
\]

Where \(q_t\) is the adsorption limit at time \(t\) (mg/g), \(k_1\) is the principal request-response rate steady (L/min), for first request models. An examination of the response rate constants and \(R^2\) values evaluated. It was found that the adsorption of second-order to match the values in the curve where \(R^2\); the value was (1) as depicted in Table 4 and Figure 11 and 12 [28, 29].

| Table 4. Kinetics |   |   |
|-------------------|---|---|
|                   | K1  | \(R^2\)  |
| PSEUDO-FIRST-ORDER | 2.7636 \(10^{-3}\) | 0.0418  |
| PSEUDO-SECOND-ORDER | K2  | \(R^2\)  |
|                   | 0.342 \(10^{-6}\) | 1       |
4. Conclusions
Adsorption considered that the adsorption energy of Mn$^{2+}$ on the eggshell of the chicken egg followed the dynamic second-order model flawlessly, and concluded the opportunity of chemical absorption. Dynamic adsorption is endothermic under normal conditions. The adsorption model is well equipped with Langmuir isothermal. Upon reviewing a set of researches, I recommend applying several equations that explain other aspects of the adsorption nature of what is happening in concession to obtain other points for this experiment including the BET equation and Dubinin-Radushkevich, etc. The reusability study revealed that adsorbents can be reused very well multiple times under fewer experimental conditions. These discoveries recommended that chicken egg shell has higher adsorption limits and more rapid removal of Mn$^{2+}$. Unlike horticultural waste and other forest deposits as biological absorbers, it is a type of new strategy for treating large mineral wastewater in applications.
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