



# Heavy Metals Removal Using Surface Modified Glauconite Mineral

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**Abstract:** The objective of this paper is to enhance the adsorbing performance of the natural Egyptian phyllosilicate mineral, glauconite (greensand), through surface modification to obtain a particular combination of physical and chemical properties. It was found that Zn removal increased from 84% to 94%, while Pb removal varied from 96.67% to 99% by using from 10-25g/l modified glauconite in a solution having 50 mg/l  $Zn^{2+}$  and 30 mg/l  $Pb^{2+}$  ions. Adsorption data were investigated using Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms. Linear regression methods are used to determine adsorption capacities and optimum adsorption isotherms.  $R^2$  value of Langmuir isotherm model for  $Pb^{2+}$  is higher than other models. The maximum monolayer coverage ( $Q_0$ ) from Langmuir isotherm model was calculated to be 15.363 and 21.654 mg/g and the separation factor indicating a favorable sorption experiment is 0.0324 and 0.13207 for  $Zn^{2+}$  and  $Pb^{2+}$  respectively. Also from Freundlich isotherm model, the intensities of adsorption ( $n$ ) that indicated favorable sorption are 1.3036 and 1.364 for  $Zn^{2+}$  and  $Pb^{2+}$  respectively. The heat of sorption process was calculated from Temkin isotherm model to be 6.44101 and 4.1353 J/mol for  $Zn^{2+}$  and  $Pb^{2+}$  respectively, that indicated to the physisorption process which  $B < 20$  kJ/mol so, Temkin isotherm is not fitted with experimental adsorption but the mean free energy was calculated from DRK isotherm which are 24.693 and 47.093 KJ/mol, where  $E_D > 8$  proved that the adsorption experiment followed a chemisorption process. So the relative adsorption capacity for metals was in the order  $Pb > Zn$ .

**Keywords:** Adsorption, Heavy Metals, Surface Modification, Glauconite, Equilibrium Isotherms

## 1. Introduction

Water contamination due to increased population and industrial activities is one of the most challenging issues to the researchers, because it is continuously increasing threats to both human health and the environment. This pollution mainly caused by waste water drain from different industries e.g. metal plating, mining processes, fertilizer industries, tanneries, batteries, paper industries and pesticides, etc. [1-2]. This waste water contains mainly heavy metals which their concentrations increase especially in developing countries. Heavy metals are well known as non-biodegradable unlike the organic contaminants. These toxic heavy metals can accumulate in living organisms cause severe illness such as hyper tension, anemia, cancer, renal kidney disease, nervous system damage and mental disorder [3-4]. Zinc and lead are

the most hazardous heavy metals which take intensive attention as popular containments of industrial wastewaters. In more details contaminated water with zinc in a level of 3–5 mg/l may appear clear forming a plating film on boiling. Owing to the standard limits of water, it generates a strong demand to improve the efficiency of existing methods for removing Pb and Zn from the water. Many techniques are used for the effective removal of toxic heavy metals from aqueous solutions such as adsorption, flocculation, coagulation, membrane filtration, electrochemical process, solvent extraction, bio-sorption, chemical precipitation, ion-exchange, as well as various other processes [5-6]. However, most of these techniques have several disadvantages such as production of secondary pollution, high cost, high levels of energy and chemicals needed, and weak treatment operation at low metal concentrations. [7-8]. Adsorption method is an effective and economic way for heavy metal wastewater

treatment. The adsorption process show design and operation flexibility and usually produce high-quality treated effluent. In addition, adsorbents can be regenerated by desorption process due to reversibility of adsorption in some cases. Many natural and artificial materials are used for adsorption process. Therefore, researchers are now interested on using new natural adsorbents with low cost and local availability such as olive stone waste, phosphate rock, clay minerals, oil shale ash, chitosan, zeolite, fly ash, and biosorbents. Glauconite is a group of dioctahedral, potassium, iron rich, compositionally heterogeneous, phyllosilicate minerals and it has been recognized as useful in water treatment [9]. Manganese oxides are usually used in different applications such as, energy storage, electrochemical capacitors, and catalysis. Manganese oxides could be used for the adsorption and removal of different heavy metals from aquatic environment as reported in researches. For example, removal of copper (II) and lead (II) from aqueous solutions by manganese oxide-coated Zeolite [10], removal of lead (II) from aqueous solution by manganese oxide-coated carbon nanotubes [11-12], for the removal of the toxic hexavalent chromium by manganese oxide nanofibers [13] and removal of Cadmium by  $\text{MnO}_2$  loaded D301 resin [14]. The aim of this paper is to enhance the adsorbing performance of Egyptian glauconite (greensand) through surface modification by coating with  $\text{MnO}_2$  forming manganese greensand for removal of Zn and Pb from industrial waste water through filter model that could be used easily in the removal process. The adsorption equilibrium was fitted using Langmuir, Freundlich, Temkin and Dubinin-Raduskevich isotherm models

## 2. Materials and Methods

### 2.1. Materials

Glauconitic sandstone samples were collected from the Abu Tartur mine which is located 650 km southwest of Cairo, Egypt, in the Western Desert. Manganese sulfate and potassium permanganate from Aldrich were used in glauconite coating forming manganese greensand. Heavy metals solutions of Pb and Zn were prepared from analytical grade chemicals in double distilled water.

### 2.2. Methods

#### 2.2.1. Surface Modification of Glauconite

Glauconite sample was screened to the proper effective size ( $-850 +250 \mu\text{m}$ ), followed by water washing for clay removal from the surface. Due to the friability of glauconite mineral as most of the pellets appeared soft and can be crushed with the fingernail, the research team decided to use the chemical treatment for glauconite mineral instead of mechanical treatment which causes a lot of turbidity, 130000 NTU which affects the color of water after treatment. Manganese dioxide coating was applied to the media by soaking the washed glauconite grains in a plastic or a glass jar, (1: 3) solid /liquid ratio, in a solution of  $\text{MnSO}_4$  and

shacked gently from time to time. The coating was applied by going through a series of exhaustion and regeneration cycles. Each cycle deposited manganese dioxide that was held on the filter grain by ion exchange. After definite time and several cycles, enough manganese dioxide coated the filter grain to act as oxidizing catalyst to speed up the oxidation reduction reaction and make sure it is carried to completion in the filter, not after it. Perkin-Elmer Atomic Absorption "A Analyst 200" was used in measuring the initial and equilibrium concentrations of heavy metals [15].

#### 2.2.2. Characterization

A Philips PW 1730 powder X-ray diffractometer with Fe-filtered Co (K-alpha) run at 30 kV and 20 mA was used to determine the qualitative and the semi-quantitative mineralogical composition of glauconite. Infrared vibrational spectra were recorded on a Nicolet Magna 750 Fourier-transform spectrometer. For glauconite sample, 28 scans were accumulated over the  $4000\text{--}400 \text{ cm}^{-1}$  spectral range employing the transmittance mode and a resolution of  $4 \text{ cm}^{-1}$ . The pressed KBr disc employed for this purpose was prepared using 0.4 mg of sample and 200 mg of KBr. Samples were observed on fractured surface under a JSM-6400 scanning electron microscope (SEM) to examine the morphology of glauconite before and after treatment. A laser Zeta Meter 'Malvern Instruments Model Zeta Sizer2000' was used for zeta potential measurements. Surface area of the glauconite samples was measured using the Quantachrome NOVA Automated Gas Sorption [15].

#### 2.2.3. Separation Experiments

The separation experiment was carried out in greensand filter. First of all, a good filter medium should have some characteristics including low resistance to filter flow, resists chemical attack and have sufficient strength to withstand the filtration pressure and mechanical wear. According to the above recommendations, as seen in Fig. 1, greensand filter consists of 3-Liter polyacrylate filter column with dual media sand (0.1mm) for removal of precipitated iron and any other suspended materials in water and manganese greensand (0.03 – 0.1mm) of about 17 cm thickness and a diameter of about 5 cm. This filter was designed by the Research team and was manufactured in Egyptian National Research Center Workshop, NRC by local materials to be available and more economic. A flow direction from the top to the bottom of the filtration column, Fig. 2, is the favorable direction due to the gravity power but in the presence of clay-sized particles, it is preferred to water to be flowed from bottom to the top of filter unit to prevent these particles from transportation by fluid flow. The operating conditions are depending on the physical characteristics of the coated media and chemical composition of untreated water. It should be taken into consideration that high concentrations of heavy metal ions require lower flow rate for equivalent run lengths and low concentrations require high flow rate. The factors affect the process of separation as bed thickness, contact time and amount of modified minerals used to determine the optimum conditions for removal. Metal solutions with known and

different concentrations of Zn and Pb were prepared by dissolving their salts in double distilled water (Synthetic) and other sources of waste water from factory of batteries located in Cairo and the adsorption process was evaluated under different operating conditions as pH, heavy metal concentration, mixing speed and adsorbent dose. All the experiments of filtration were carried out at time of 20 min. at room temperature ( $25 \pm 3$ ) and the filtrate analyzed for metal ions concentration using Atomic absorption. The removal efficiency was determined by computing the percentage sorption using the formulae in Eq. (1)

$$\% \text{ Sorption} = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

Where,  $C_i$  and  $C_e$  are the initial and equilibrium concentrations of heavy metals (mg/L), respectively (18). The adsorption capacity,  $q_e$  (mg/g), was calculated according to the following equation:

$$Q_e = \frac{(C_o - C_e)v}{w} \quad (2)$$

Where,  $C_o$  and  $C_e$  are the initial and equilibrium solution concentrations respectively;  $V$  the volume of the solution (L);  $W$  the weight of the sample (manganese green sand) in grams [16]. The data was fitted into the following isotherms: Langmuir, Freundlich, Temkin and Dubinin-Raduskevich.

### 2.3. Adsorption Isotherms

The equilibrium data, commonly known as adsorption isotherms are basic parameters for the design of adsorption systems and these data provide information on the adsorbent capacity or the amount required to remove a pollutant mass under the system conditions. The Langmuir and Freundlich models equations are commonly used to describe the adsorption isotherms at constant temperature for application in the water and wastewater model treatment design. These two isotherms beside Temkin and Dubinin-Radushkevich

isotherm models were used to access the different isotherms and their ability to correlate experimental data [15].

#### 1. Langmuir Adsorption Isotherm

This isotherm describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent containing a finite number of identical sites, and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases [17], and it is well known that the Langmuir equation is intended for the homogenous surface. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Based upon these assumptions, Langmuir represented the following equation:

$$Q_e = Q_o K_L C_e / (1 + K_L C_e) \quad (3)$$

Langmuir adsorption parameters were determined by transforming the Langmuir equation (3) into linear form.

$$1/Q_e = 1/Q_o + 1/Q_o K_L C_e \quad (4)$$

Where:  $C_e$ : the equilibrium concentration of adsorbate ( $\text{mg/L}^{-1}$ ),  $q_e$ : the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g).  $Q_o$ : maximum monolayer coverage capacity (mg/g) and  $K_L$ : Langmuir isotherm constant (L/mg). The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter  $R_L$ , which is a dimensionless constant referred to as separation factor or equilibrium parameter [18].

$$R_L = 1 / (1 + K_L C_o) \quad (5)$$

Where:  $C_o$ : initial concentration and  $K_L$ : the constant related to the energy of adsorption (Langmuir Constant).  $R_L$  value indicates the adsorption nature to be either unfavorable if  $R_L > 1$ , linear if  $R_L = 1$ , favorable if  $0 < R_L < 1$  and irreversible if  $R_L = 0$ .

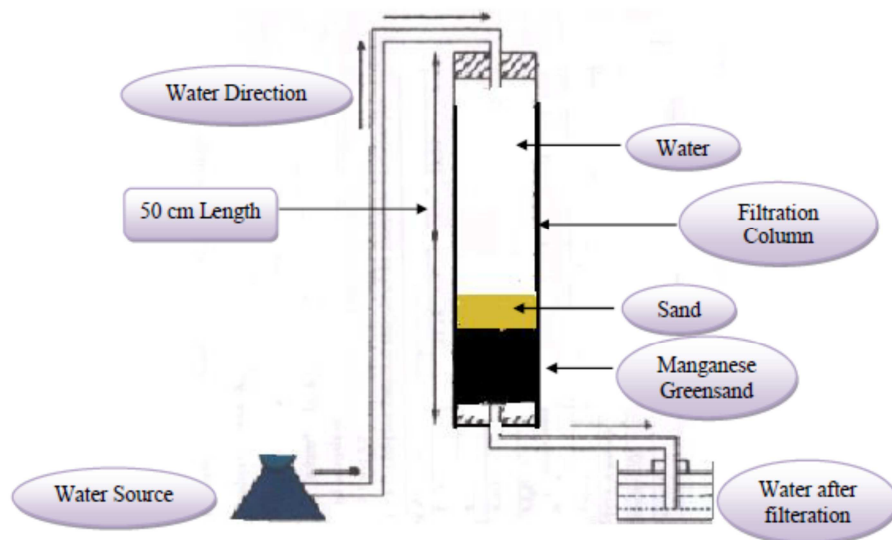


Fig. 1. Sketch of Green Sand Filter Unit.



**Fig. 2.** Designed Green Sand Filter Unit.

## II. Freundlich Adsorption Isotherm

This isotherm is commonly used to describe the adsorption characteristics for the heterogeneous surface as well as multilayer sorption [19]. These data often fit the empirical equation proposed by Freundlich:

$$Q_e = K_f C_e^{1/n} \quad (6)$$

Eq. (6) is linearized into logarithmic form for data fitting and parameter evaluation as follows:

$$\log Q_e = \log K_f + 1/n \log C_e \quad (7)$$

Where  $K_f$ : Freundlich isotherm constant (mg/g),  $n$ : adsorption intensity,  $C_e$ : the equilibrium concentration of adsorbate (mg/L),  $Q_e$ : the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g). The constant  $K_f$  is an approximate indicator of adsorption capacity, while  $1/n$  is a function of the strength of adsorption in the adsorption process, the smaller  $1/n$ , the greater the expected heterogeneity [20].

## III. Temkin Isotherm

The Temkin was tested for equilibrium description at room temperature. The model was respectively represented by equ.8, where  $B$ : the Temkin constant related to heat of sorption (J/mol),  $A$ : the Temkin isotherm constant (L/g),  $R$ : the gas constant (8.314 J/mol K),  $b$ : is Temkin isotherm constant and  $T$ : the temperature (K) [20-21].

$$q_e = B \ln (A + C_e) \quad (8)$$

Where,  $B = RT/b$

## IV. Dubinin–Radushkevich Isotherm Model

This isotherm model was chosen to estimate the characteristic porosity of the biomass and the apparent energy of adsorption applied. The model is represented by the equation

$$q_e = q_D \exp (- B_D [RT \ln (1 + 1/C_e)] \quad (9)$$

Where,  $B_D$  is related to the free energy of sorption per mole of the sorbate as it migrates to the surface of the biomass from infinite distance in the solution and  $q_D$  is the Dubinin-Radushkevich isotherm constant related to the degree of sorbate sorption by the sorbent surface [21-22]. The linear form of equation is given as;

$$\ln q_e = \ln q_D - 2B_D RT \ln (1 + 1/C_e) \quad (10)$$

The apparent energy ( $E_D$ ) of adsorption from Dubinin-Radushkevich isotherm model can be computed using the relation given as below [21].

$$ED = \sqrt{1/2B_D} \quad (11)$$

## 3. Results and Discussion

### 3.1. Mineral Characterization

Fig. 3 shows XRD pattern of Egyptian glauconitic material which indicates that it is composed mainly of 1M-glauconite poly-type associated with quartz, phosphosiderite, potassium iron silicate and iron-hydrogen phosphate. Chemical analyses indicate that the fresh glauconite is enriched in  $Fe_2O_3$  and  $K_2O$  compared to the surface samples. Fig. 4 shows the FTIR spectrum of glauconite which confirms the presence of stretching vibration band of -OH at  $3538 \text{ cm}^{-1}$  and the deformation band at  $801 \text{ cm}^{-1}$ . Also, the silicate network is characterized by stretching vibration bands at  $1060 \text{ cm}^{-1}$  for Si-O and  $998 \text{ cm}^{-1}$  for Si-O-Si and deformation band at  $488 \text{ cm}^{-1}$  for Si-O-Fe. [15].

The BET isotherm shows that the surface area is in the range between  $47.28 \text{ m}^2/\text{g}$  and  $62.42 \text{ m}^2/\text{g}$  and the porosity percentage is in the range between 11.93% and 19.47%. These results are confirmed through the measurement of sorption properties of the glauconite mineral samples which indicate that cation exchange capacity (CEC) is between 5-40 meq/100g, water absorption is between 3-8% and the oil

absorption is between 5-15 g/100 g. Fig. 5 shows the results of zeta potential which indicates that glauconite surface has a net negative electrostatic charge from pH 1 to pH 12. All of

these results indicate that the glauconite samples need specific modification through surface coating technique to act as a good adsorbent for heavy metals.

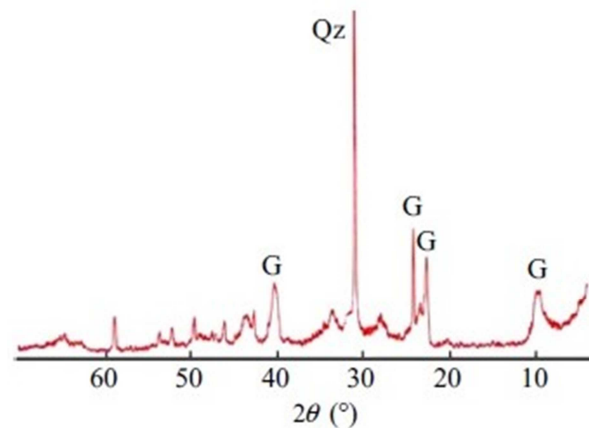
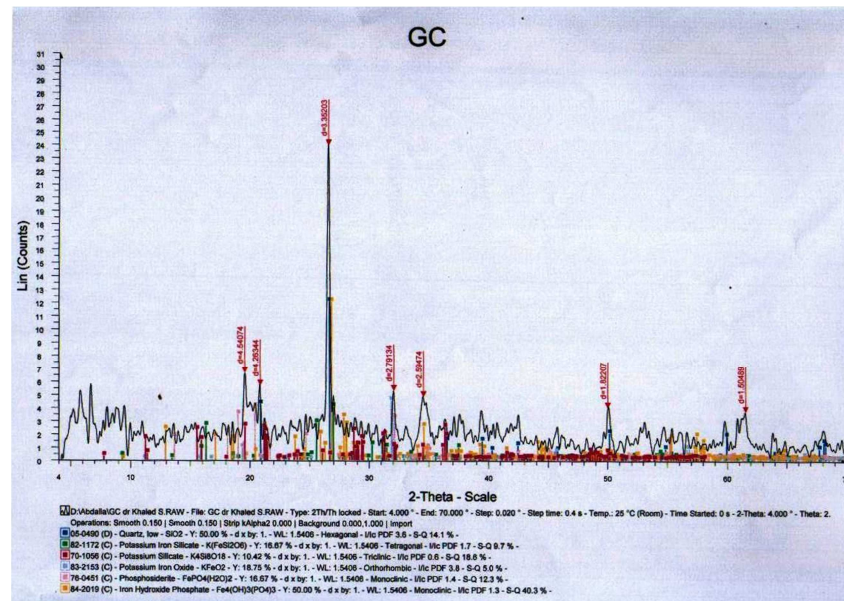


Fig. 3. XRD of Glauconitic Material.

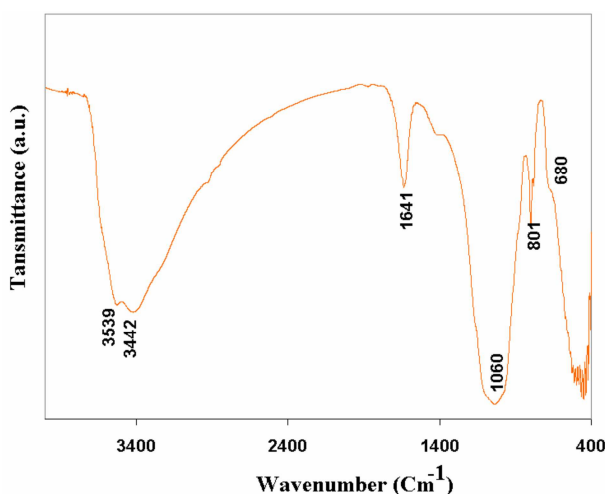


Fig. 4. FTIR of Glauconite Mineral.

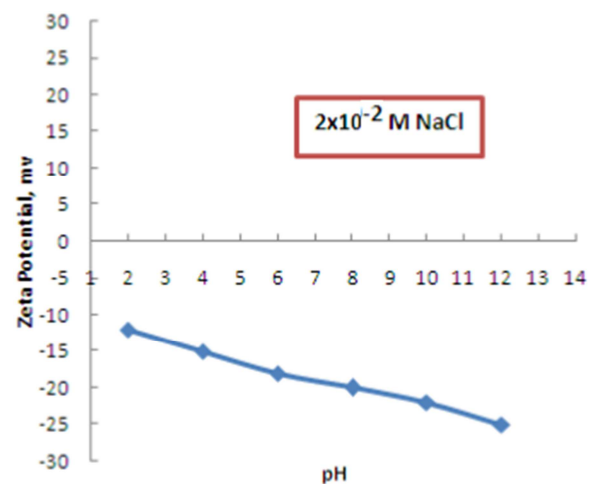


Fig. 5. Zeta potential of Glauconite Sample.



### 3.2. Surface Modification of Glauconite

Manganese greensand is a unique medium used in conjunction with a filtration system. Its manufacturing process uses the ion exchange properties of its stabilized glauconite (greensand) substrate to form an active manganese oxide coating by  $\text{MnSO}_4$ . The surface charge of the  $\text{MnO}_2$  is largely determined by the pH of the solution, the charge becoming more negative as pH is increased as a result of the increased ratio of  $\text{OH}^-$  bound to the  $\text{H}^+$  bound. At very low pH, the  $\text{H}^+$  ions bound at the surface predominate, and the colloidal  $\text{MnO}_2$  bears a net positive charge. Less certain are the exact value at which equilibration of the surface bound hydrogen and hydroxide ions occur. From this we can conclude that it is clear that manganese dioxide exhibits a net negative surface charge within the pH range (5 to 11) of principle interest for common water treatment operations. Manganese greensand has some advantages as:

- It has an optimum grain size and shape to retain oxidation precipitation products of heavy metals. All grains have the same finite uniform coating, which is strongly attached.
- It has unequalled oxidation-reduction buffer capacity, and can tolerate a slight over or underfeed of continuously fed oxidants.
- It provides high effluent water quality.
- Manganese oxide coating is more physically demanding; air/water washing, not removed during backwashing or during the water-saving.

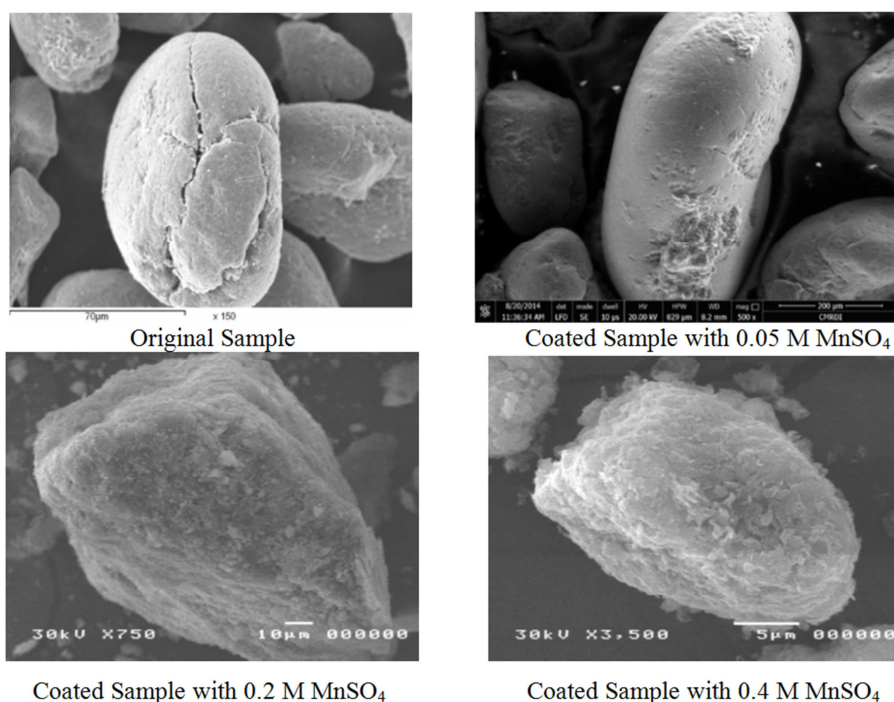
Different concentrations of  $\text{MnSO}_4$  were tested starting from 0.05 M to 0.4 M at different conditioning time, to obtain the optimum conditions for having the same finite uniform coating. The control test for optimization process is the measurement of adsorption efficiency through the

measurement of the residual concentration of  $\text{MnSO}_4$  in solution. It was found that the adsorption efficiency has the maximum value 97.27% at the minimum concentration of  $\text{MnSO}_4$ , 0.05M and decreases till 14.5% at  $\text{MnSO}_4$  concentration of about 0.4M as shown in Table 1. These results are in agreement with SEM which indicated that the addition of high concentrations of  $\text{MnSO}_4$  leads to the formation of multilayer form  $\text{MnSO}_4$  which affects the removal process.

**Table 1.** Effect of  $\text{MnSO}_4$  Concentration on Adsorption Efficiency.

$\text{MnSO}_4$ Concentration, M	Adsorption Efficiency, %
0.05	97.27
0.10	65.00
0.20	29.46
0.40	14.50

Fig. 6 shows the typical morphology of untreated and coated glauconite where, SEM of untreated has sphere-like shape. Small cavities and cracks were found on the surface of each glauconitic particle. This nature of rough texture provides good active sites for chemical adsorption. On the other hand, SEM for coated sample only with low concentration of  $\text{MnSO}_4$  shows a smooth uniform of manganese dioxide coating which due to filling of the active sites on the glauconite particle surface with manganese sulfate. At the same time, Surface analysis using EDS spectrum shows the presence of Mn peak for coated sample which is not present in the original sample as shown in Fig. 7. On the other hand, there is a noticeable decrease for the total pore area, ( $93.17 \text{ m}^2/\text{g}$ ) to ( $26.569 \text{ m}^2/\text{g}$ ) due to coating process and the porosity percentage decreased from (57.31%) to (37.90%).



**Fig. 6.** SEM of Glauconite before and after treatment with  $\text{MnSO}_4$ .

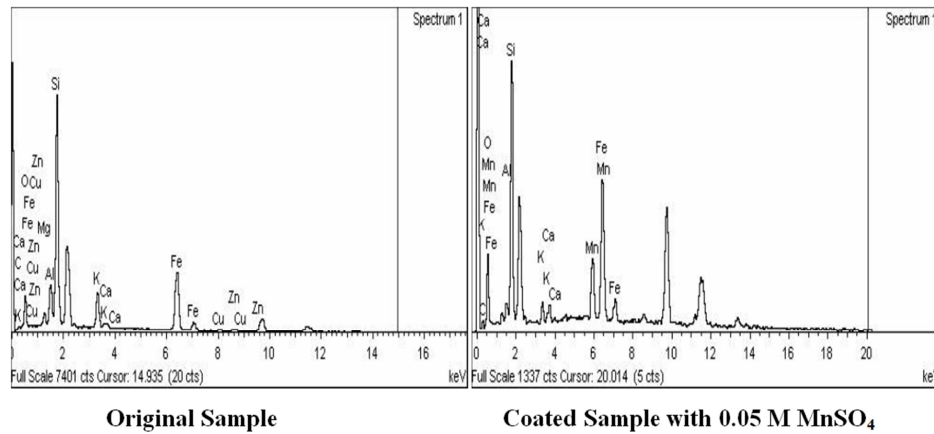


Fig. 7. EDS Analysis spectrum of Glauconite after and before treatment with  $\text{MnSO}_4$ .

### 3.3. Removal of Heavy Metals (Pb and Zn ions)

The suggested operating conditions were selected depending on the physical characteristics of the coated media and chemical composition of water before treatment. The dual media should be sand (0.1mm) and manganese greensand (0.03 – 0.1 mm). The recommended flow rate is ranging from 3-5 gpm/sq.ft. It should be taken into consideration that high concentrations of heavy metal ions require lower flow rate for equivalent run lengths and low concentrations require high flow rate. The maximum pressure drop shouldn't exceed 8-10 psi (0.6-0.7 bar) every 20-24 hours of actual operation. In backwash, an adequate rate of treated water was used to produce 40% bed expansion. It is proved that 500 gm of manganese greensand give about 17 cm bed thickness. The head loss is 1cm/ 1kg coated sample every 6-7 days of actual operation. For good regeneration,  $\text{KMnO}_4$  will be used for this purpose through using 1 gallon

(134 L) of Stock Solution Strength (20 -30  $\text{kg/m}^3$ ) followed by 6-7 gallons (950 L) of water. The adsorption of heavy metals (Zinc and Lead) using surface modified glauconite mineral was evaluated under different operating conditions as pH, heavy metal concentration, mixing speed and adsorbent dose. To study the effect of pH on sorption, the pH of the metal ion solution was adjusted to values in the range of (2–10) by the addition of pH regulators prior to the experiment. The pH should be above 6.0 and below 8.0 and ideally when the pH is between 6.2 and 6.8. Wastewater with a naturally lower pH should be adjusted to a minimum pH of 6.2 before treatment. The effect of the amount of adsorbent on the removal of (Zinc and Lead) ions by surface modified minerals is depicted in Table 2 for varied adsorbent doses of 10, 15, 20 and 25 g/l. Zn removal using modified Glauconite increased from 84% to 94%, while Pb removal varied from 96.67% to 99%.

Table 2. Removal of Zinc and Lead ions.

Metal ions	Adsorbent Dose g/l	Inlet concentration mg/l	Outlet concentration mg/l	Removal efficiency %
Zn	10	50	8.0	84.00
	15	50	6.0	88.00
	20	50	5.5	89.00
	25	50	3.0	94.00
Pb	10	30	1.0	96.67
	15	30	0.7	97.67
	20	30	0.5	98.34
	25	30	0.3	99.00

### 3.4. Adsorption Isotherms

The equilibrium adsorption of lead and zinc onto glauconite minerals was analyzed using Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms.

#### 3.4.1. Langmuir Adsorption Isotherm

The experimental data were fitted into Eq. (4) for Zn and Pb ions. The linear regression equations and determination coefficient ( $R^2$ ) generated are shown in Fig. 8. The values of  $R_L$  (the separation factor) is 0.1321 and 0.0324 and the  $R^2$  value is 0.8864 and 0.97098 for Zn and Pb respectively,

indicating that the equilibrium sorption was favorable, proving that the sorption data fitted well to Langmuir Isotherm model as a confirmation of the chemisorption process. These results were confirmed from values of Langmuir constant ( $K_L$ ) and the maximum monolayer coverage capacity ( $Q_o$ ) were determined as shown in Table 3.

#### 3.4.2. Freundlich Adsorption Isotherm

Application of isotherm equation to analyze the equilibrium isotherms of Zn and Pb ions gave linear plots, the linear regression equations and the regression coefficients ( $R^2$ ) are shown in Fig. 9. The values of  $K_f$  and  $n$ , Table 3, determine the steepness and curvature of the isotherm. From

the data in table 3, that value of  $1/n = 0.767$  and  $0.732$  while  $n = 1.303$  and  $1.34$  for Zn and Pb respectively, indicating that the sorption of  $Zn^{2+}$  and  $Pb^{2+}$  onto modified glauconite is favorable. The values of  $K_f$  confirm that the adsorption capacity of  $Pb^{2+}$  is higher than that in case of  $Zn^{2+}$  as the higher the  $K_f$  value, the greater the adsorption intensity.

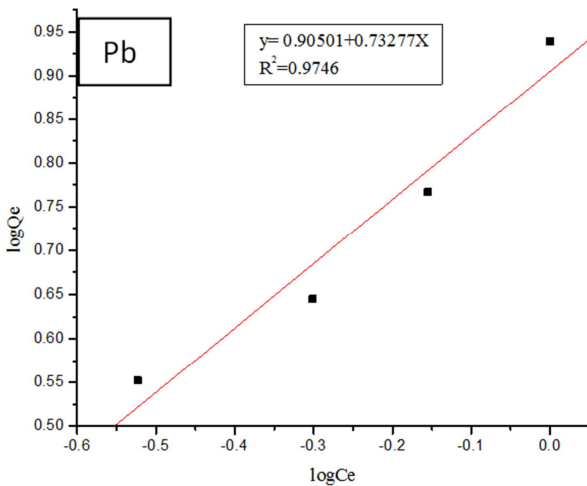
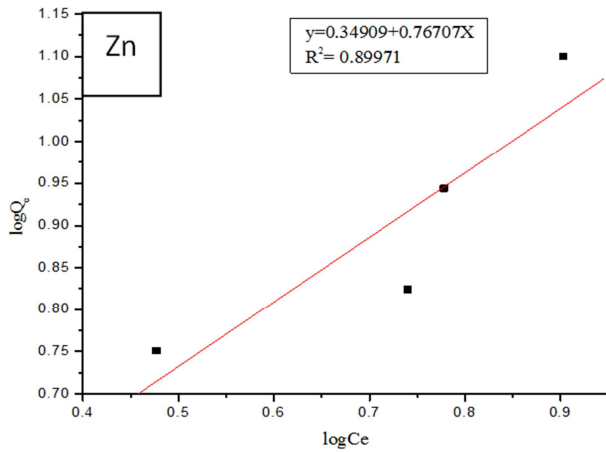


Fig. 8. Langmuir Adsorption Isotherm for Zn and Pb ions.

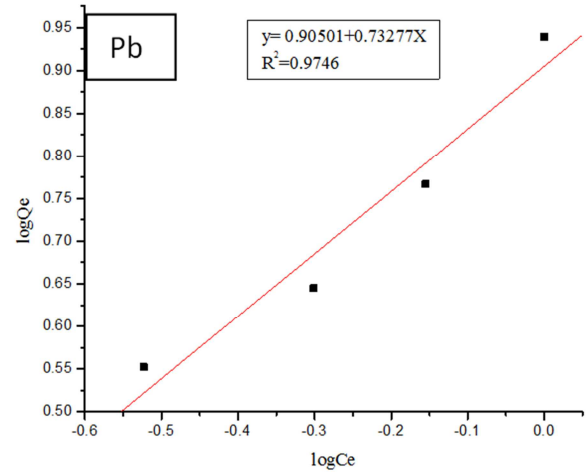
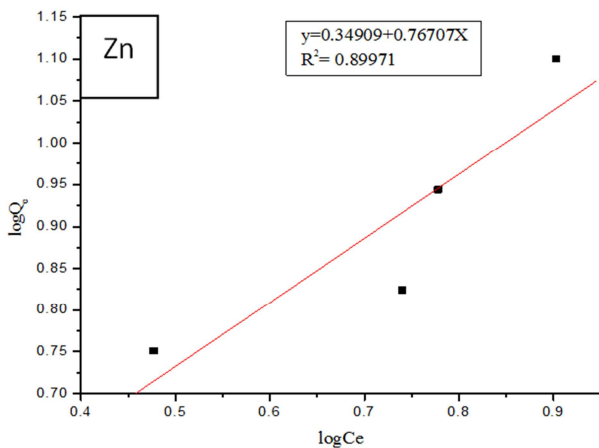


Fig. 9. Freundlich Adsorption Isotherm for Zn and Pb ions.

### 3.4.3. Temkin Isotherm

From the Temkin plot shown in Fig. 10, the following values were estimated:  $A_T = 0.698$ ,  $6.864$  L/g,  $b_T = 384.65$ ,  $599.12$  and  $B = 6.441$ ,  $4.1353$  J/mol for Zn and Pb ions, Table 3 which are indication of the heat of sorption and the sorption are physical sorption process, where  $B < 20$  kJ/mol. So the Temkin equation did not represent a better fit to the experimental data.

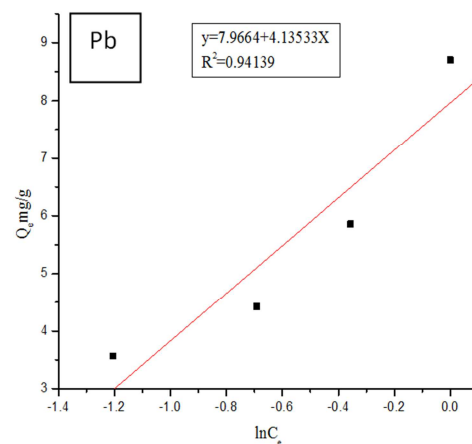
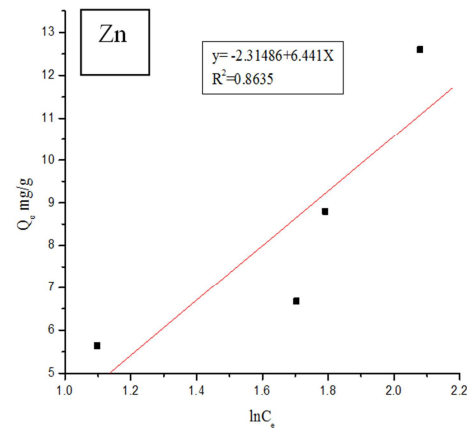


Fig. 10. Temkin Adsorption Isotherm for Zn and Pb ions.



### 3.4.4. Dubinin–Radushkevich Isotherm Model

Fig. 11 represents the Dubinin–Radushkevich plots for the adsorption of Zn and Pb ions on the modified glauconite. The regression equation and  $R^2$  values for Dubinin–Radushkevich model was observed that this isotherm also gave very good investigation of the sorption process.  $R^2$  values and constants

for the model are given in Table 3. The values of the apparent energy of adsorption,  $E$ , indicate to the chemisorptions process, where an  $E_D$  value  $< 8 \text{ kJmol}^{-1}$  is an indication of physical sorption and the values of  $R^2$  and free energy for  $\text{Pb}^{2+}$  is higher than  $\text{Zn}^{2+}$  [23].

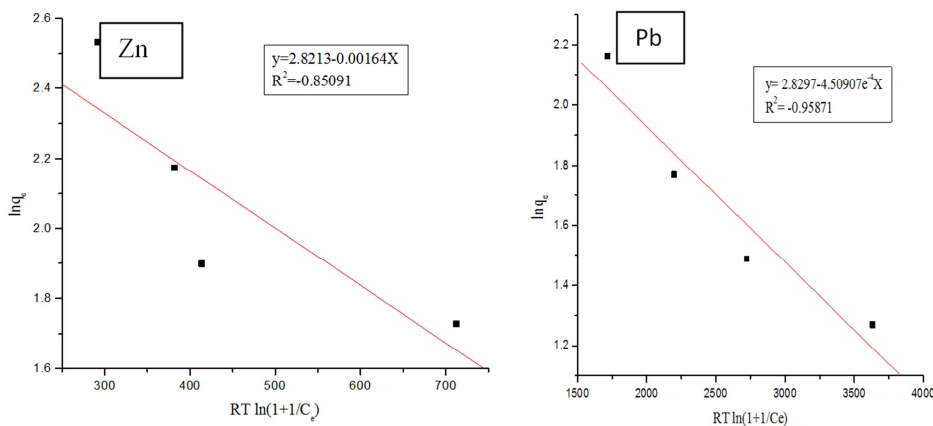


Fig. 11. Dubinin–Radushkevich adsorption isotherm for Zn and Pb ions.

Table 3. Isotherm Models' Constants for Zn and Pb Ions Adsorption onto Modified Glauconite Mineral.

Isotherm	Zn	Pb
Langmuir	$Q^{\circ} = 21.6544$ $K_L = 0.11143$ $R_L = 0.13207$ $R^2 = 0.88649$	$Q^{\circ} = 15.363$ $K_L = 0.9610$ $R_L = 0.0324$ $R^2 = 0.97098$
Freundlich	$n_f = 1.3036$ $K_f = 2.234$ $R^2 = 0.89971$	$n_f = 1.364$ $K_f = 8.035$ $R^2 = 0.9746$
Temkin	$A_T = 0.698$ $b_T = 384.65$ $R^2 = 0.8635$	$A_T = 6.864$ $b_T = 599.12$ $R^2 = 0.94139$
Dubinin–Radushkevich	$B_D = 8.2 \times 10^{-4}$ $q_D = 16.798$ $E_D = 24.693$ $R^2 = -0.8509$	$B_D = 2.25 \times 10^{-4}$ $q_D = 16.9403$ $E_D = 47.093$ $R^2 = -0.9587$

## 4. Conclusions

- 1 The Research team succeeded in designing and manufacturing manganese green sand filter by local materials to be available and more economic.
- 2 The adsorption efficiency of glauconite has the maximum value 97.27% at the minimum concentration of  $\text{MnSO}_4$ , 0.05M and these are in agreement with SEM.
- 3 The maximum Zn and Pb ions removal was 94% and 99% with initial concentration 50 mg/l and 30mg/l, respectively.
- 4 Adsorption data were modeled using Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms and the study on these equilibrium adsorption isotherms provides greater insights on the adsorption of heavy metals onto surface modified glauconite surface.
- 5 The data are best fitted with all models except Temkin isotherm.
- 6 The data proved that the adsorption experiment followed a chemisorptions process. So the relative adsorption capacity for metals was in the order  $\text{Pb} > \text{Zn}$ .

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