



## REMOVAL OF IRON AND MANGANESE IONS FROM GROUNDWATER USING KAOLIN SUB MICRO POWDER AND ITS MODIFIED FORMS

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**Abstract:** The clays have been extensively utilized for the removal of heavy metals from groundwater due to their low-cost, available natural resources and being nontoxic materials. In this work, sub micro kaolin powder has been modified to increase its adsorption ability to remove heavy metals from raw water. The removal efficiency of the natural sub - micro - kaolin powder and its acid (sulfuric & acetic acids) modified forms were investigated for the removal of iron and manganese from raw water samples collected from the northern part of Beni-Suef governorate and parallel authentic samples. The scanning electron microscopy (SEM) and X-Ray techniques were used to characterize the surface morphology of the three adsorbents viz., sub micro kaolin and its two modified forms. The adsorption efficiency of the adsorbent materials was investigated by inductively coupled plasma (ICP). The effects of sub micro kaolin dose, pH, stirring time and temperature on the removal efficiency using standard and case study samples were studied. Both modified forms showed higher adsorption efficiency than the natural clay. Moreover, the empirical values are evaluated according to the Langmuir and Freundlich isotherms that are generally used to describe the adsorption processes.

**Key Words:** Kaolin Clay, Acid Activated, Adsorption, Iron, Manganese, Langmuir and Freundlich isotherms.

### INTRODUCTION

Iron and manganese (Fe/Mn) are the most common elements in the groundwater supplies (Sequestering methods of iron and manganese treatment). Iron is the more frequent of these two contaminants, but they often occurs together (Yuce, (2013). Iron accounts for about 5% of the earth's crust, making it the second most abundant metal (Elinder CG. Iron. In: Friberg LN. G., 1986); (WA, 1981). Iron and manganese are more common in deeper wells where the water has been in contact with the rocks for a long time. The high levels of iron and manganese can discolor the water, stain the plumbing fixtures, and give water an unpleasant metallic taste (California State University, (2004). The iron and manganese elements in water occur in various forms (Ning, 2009); (Ning, 1997) and (Ning and Shen, 1998). In the water tap, the iron and manganese are present in dissolved forms. When the water tap comes out rust-colored, this indicates that the iron and manganese are in precipitate forms. When the water tap has a clear yellow tint, this means that the iron and manganese are combined with organic materials. The Environmental Protection Agency (EPA) determines the maximum contamination levels of iron and manganese by 0.3 mg/L and 0.4 mg/L respectively, due to their health effects. Various physicochemical methods have been used to remove and adjust the heavy metals in drinking water (Veli, S., and Aly<sup>u</sup>z, B.,

2007) and (Anirudhan, 2012), adsorption (Pereira, 2013), (Buamah, 2008), (Nassar, et al., 2004) and (Alfredo, et al., 2012), ion exchange (Ye, 2011), oxidizing filters (Hou, 1988), biological filtration (Alejandra, 2005) and reverse osmosis (Lim, 2011), (Xiang-Feng, 2011) and (Sheikholeslami, 2002) are the most frequently preferred methods. The adsorption process is one of the most popular technologies due to its effective and economic properties (Jiang, 2012) and (Srinivasan, 2011). Their sorption capabilities come from their high surface areas and their ion exchange capacities. The negative charges on the structure of clay minerals give the capability to attract metal ions (Taffarel, 2009). The use of clay materials as adsorbents is becoming a very promising alternative as compared to aluminum sulfate for water treatment, since they are inexpensive, abundant and efficient. In fact clays are 20 times cheaper than activated carbon (Bhattacharyya, et al., 2008). Kaolin is the most clay type abundant phyllosilicate mineral in highly weathered soils (Asmatulur, 2002) and (Woumfo, et al., 2012). Kaolin is widely available in Upper Egypt in the form of aluminum hydrous silicate ( $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ ) (Ning, and Shen, 1998); (Eze k., et al., 2012) and (Kamel, 2004).

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The acid activation of clays is one of the most important processes that have been applied to achieve structural modifications in the clays. During the acid activation, initially the inter-layer's cations are replaced by H<sup>+</sup> ions followed by partial destruction of aluminum octahedral sheets after that a dissolution of structural cations occur. The desired changes in the physicochemical properties of clay occurred as a result of acid activation depend considerably on the condition of acid activation such as acid concentration and the duration and temperature of the activation process (Woumfo, *et al.*, 2012); (Eze, *et al.*, 2012) and (Ajemba, 2012).

In this study, kaolin was used for removing Iron and Manganese from aqueous solutions in some wells in Egypt and increasing of its efficiency to remove heavy metals by applying adsorption on raw washed kaolin and its acid activated forms by using sulfuric and acetic acids.

In order to determine the reaction of Iron and Manganese with kaolin, experimental results were applied to Langmuir, Freundlich adsorption isotherms and isotherm constants were obtained (Veli, and Alyuz, 2007).

## MATERIALS AND METHODS

### Materials

Iron and manganese certified reference materials (CRM) are provided by Merck, Co. (Germany). Nitric acid 65% suprapur® degree is provided by Merck, Co. (Germany). Acetic and sulfuric acids are supplied by Fluka, Sigma-Aldrich, Co. (Germany). Ultra-pure water was used to prepare all solutions; produced by Ultra Purification Water System.

### Sampling

Water samples were collected in polypropylene container 10 liters capacities. The sample container was washed with diluted nitric acid and rinsed with distilled water. The samples were preserved immediately after sampling by acidifying with concentrated nitric acid to pH <2. After acidifying the samples, they were stored in a refrigerator at approximately 4°C to prevent change in volume due to evaporation. Under these conditions, samples with metal concentrations of several milligrams per liter are stable for up to 6 months. Preserving sample may eliminate the need for adding acid before digestion. Treatment with acid was carried out at the time of collection to place the iron in solution and prevent adsorption or deposition on the walls of the sample container (Lenore, 1998).

### Instrumentation and Characterization

The inner cavity and wall thickness of the prepared samples and composite was investigated using scanning electron microscopy (SEM) (JEOL JEM-1200 EX Π). Iron and manganese analyses were carried out using inductively coupled plasma (ICP- AES) (Perkin Elmer) optical emission spectrometer optima 8300. Jar test was used for constant stirring of the sample, Phipps & Bird stirrer, and model: 7790-402 (USA).

The X-Ray diffractometer (philip1976. Model 1390) was used to investigate the phase structure of sample under the following conditions which were kept constant, during the analysis processes: Cu X-ray tube, scan speed =8/min, current=30 mA, voltage =40 kV and preset time=10s.

### Natural Clay Pretreatment

Kaolin clay was collected from kilometer 18 of the Eastern Minia / Beni-Suef road. The pretreatment of kaolin was carried out by milling it to the sub micro size. Kaolin was then washed with distilled water for several times and after that dried in an oven at 100°C, Second milling for the clay was carried out to the sub micro size and after that it is ready for use. Figure (1) shows the SEM image of natural kaolin after 10 h milling. This figure shows sub micro sized clay agglomerated together to form micro granules.

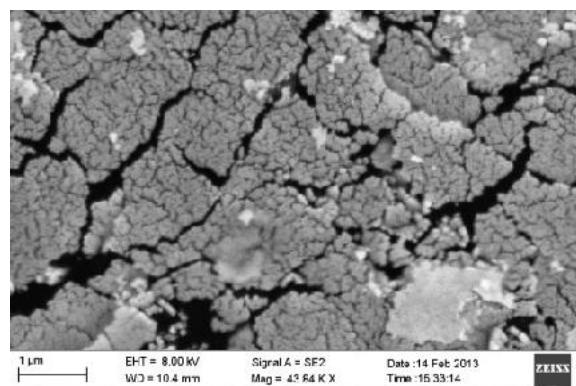


Figure 1: SEM of natural kaolin clay

### Modified Clays

There have been various attempts to improve the quality and characteristics of the clays by modifying them with different techniques. One of the common techniques in this regard is acid activation.

### Acid activation

Activation of kaolin was carried out by taking 10 g of the clay in flask (250ml capacity) and add 100 ml of 1M sulfuric acid solution. After that heat it on a magnetically stirred hot plate at a temperature of 90°C for 2 hours and 30 minutes. At the end of the experimental duration, the resulting slurry was poured into a Buchner funnel to separate the clay from the

acid solution. The residual clay was washed several times with distilled water until pH 7-8 was obtained using pH meter. The clay residue was dried in an oven at 80 °C for 4 hours. The dried acid activated clay was milled to sub micro particle size. The activation process was repeated with acetic acid (Ajemba, 2012).

#### Stock Solution Preparation

The intermediate solutions of iron and manganese standards were prepared by transferring the total amount (200 µl) of standard (1000 mg / L) with micro pipette into a 100 ml volumetric flask class A. Flasks were rinsed with de-ionized water several times and then with acidified distilled water (2% nitric acid) which was used also, for transferring the concentrations of the standards into the volumetric flasks. Series of known standards (0.25, 0.5, 0.75, 1.0 and 1.25 ppm) were prepared by mixing appropriate quantities of the intermediate solution with acidified distilled water.

#### Batch Adsorption Studies

The adsorption studies were carried out by using natural clay (kaolin) and its acidified activated forms (acetic acid and sulfuric acid) for the removal of iron and manganese from known standards and true drinking ground water samples. Batch adsorption experiments were carried out by shaking varied amounts of adsorbent materials with known volumes (ml) and concentrations (ppm) of stock solutions from iron and manganese (adsorbate materials) at room temperature or 25±2°C in Jar test. At the end of predetermined time interval, the adsorbent was removed and filtered. The residual metal ions present in the liquor (filtrate) are analyzed by inductively coupled plasma (ICP). The amount of metal ions adsorbed on the adsorbent materials was calculated by subtracting the final concentration in solution from the initial one. Then the percent of adsorption is determined, the effects of kinetic parameters were studied, and the kinetic and thermodynamic isotherm parameters for each element by each adsorbent material were calculated. The results are the mean of three experiments.

#### Adsorption Isotherm Models

Langmuir and Freundlich isotherm models were used in this study, these isotherm models were applied to establish the relationship between the amount of iron and manganese adsorbed onto equilibrium concentration of the solution.

#### Thermodynamics of Adsorption

Thermodynamic parameters were determined using the equilibrium constant,  $K (q_e / C_e)$  which depends on temperature. The change in free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) with adsorption processes were calculated by using the following equations (Bhattacharyya, 2008), (Errais, 2011) and (Unuabonah, 2008).

$$\Delta G^\circ = -RT \ln K \quad (1)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2)$$

Eqs. (1), (2) can be expressed as:

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (3)$$

Where  $K$  = distribution coefficient of the adsorbate ( $= q_e / C_e$ ),  $T$  = absolute temperature (K),  $R$  (gas constant) =  $8.314 \times 10^{-3}$  kJ K<sup>-1</sup> mol<sup>-1</sup>. The plot of  $\ln K$  versus  $1/T$  is linear with the slope and the intercept giving values of  $\Delta H^\circ$  and  $\Delta S^\circ$ . According to Eq. (3),  $\Delta H^\circ$  and  $\Delta S^\circ$  parameters can be calculated from the slope and intercept of the plot of  $\ln K$  versus  $1/T$  yields, respectively.

## RESULTS AND DISCUSSIONS

#### Structural and morphological studies

**X-Ray Diffraction (XRD) Analysis:** The structural changes that occurred in the clay material due to acid treatment were studied using X-ray diffraction technique. Fig. 2 shows the XRD profiles of the untreated and acid treated kaolin. The intensity of the XRD peaks of kaolin decreases on acid treatment and its inner structure may be affected. The X-Ray diffraction pattern of raw kaolin displays the characteristic peak at 7.15° (Fig. 2). This peak decreased to 5.3°, 5.6° (in case of acid activated kaolin with sulfuric acid and acetic acid, respectively) (Bhattacharyya, and Gupta, 2008)). These are due to the treatment with acid cause preferential release of octahedral Al ions from the kaolin structure with the formation of additional Al – OH and Si – OH bonds without disturbing the mineral structure.

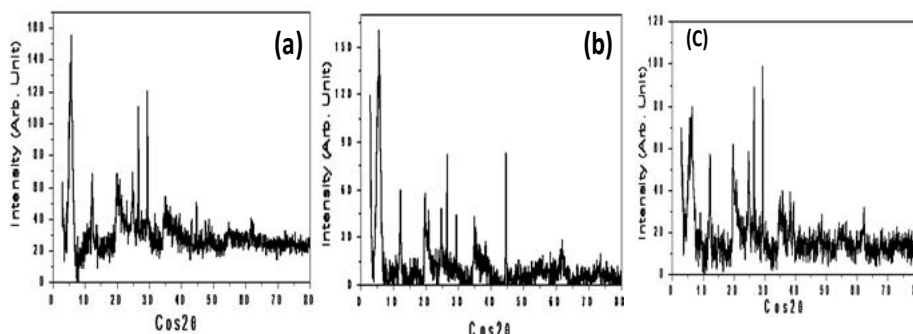


Figure 2: XRD of Acid activated kaolin with (a) sulfuric, (b) acid acetic acid and (c) untreated kaolin.

**Scanning Electron Microscope (SEM) Analysis:**

The morphological structure of different kaolin samples was studied by using scanning electron microscope (C.F. Figure 3. SEM micrograph of natural clay in Figure 3(a) reveals large particles formed by several flaky particles stacked together, while in case of acids treatment as in Figure 3 (b, c) show different particle morphology than natural clay. These figures

show that the large flat layers of natural kaolin change to smaller layers, fragment pieces and the layer conformity decreased. The weak acid (acetic acid) destroyed the uniform and flat morphology of the natural clay as in Figure 3(b), while it was lower than strong acid (sulfuric acid) in Figure 3(c) cause strong destroy in the structure of natural clay (Angaji, 2013).

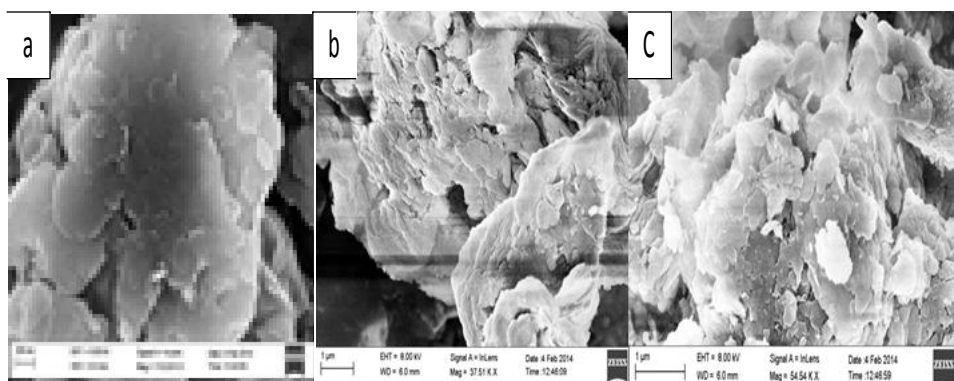


Figure 3: SEM of (a) natural kaolin, (b) activated with acetic acid and (c) with sulfuric acid.

**Effect of Contact Time of Iron and Manganese on Kaolin Clay:**

To study the capacity of the kaolin clay for the sorption of iron and manganese ions, samples of synthetically polluted water are prepared as in section (2.6). The time dependence of the adsorption of iron and manganese on adsorbent materials is given in Figure 4. The results show that the percentage adsorption increases with the increase in adsorption time. The metal ion removal was fast in the first 90 minutes, it may be due to the presence of additional sites on the clay for free cations (Ajemba, and Onukwu, 2013). In addition, presence of adsorption driving force at the beginning lead to higher adsorption rate which occur at first period. However, after 90 minutes, slower due to slower diffusion of iron and manganese ions into pores of kaolin (Elinder, 1986)), the optimum adsorption time for the removal of both iron and manganese from its solutions is 120 minutes.

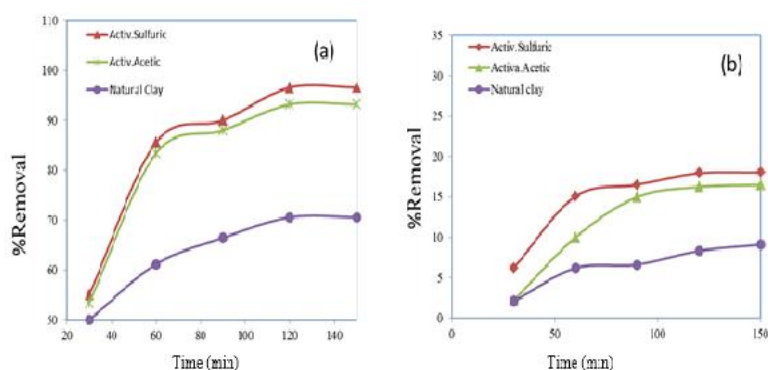


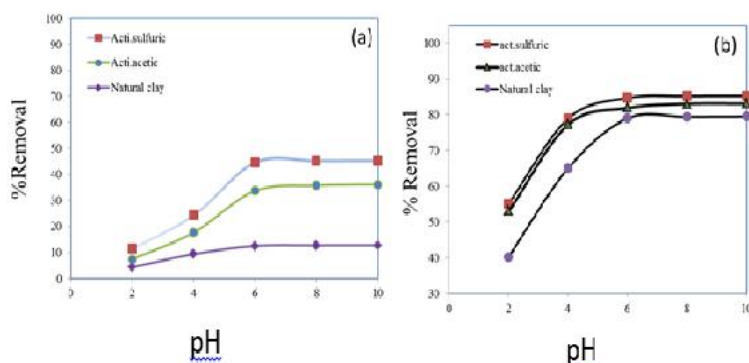
Figure 4: Effect of contact time on the removal of (a) Fe, (b) Mn using kaolin clay at pH 3.25, mixing speed 150 rpm, and clay dose 200 ppm at room temperature.

**Effect of pH on The Sorption of Iron and Manganese on Kaolin Clay:**

The effect of varying the pH on the percentage removal of iron and manganese was investigated and represented in Figure 5. These figures show that the percentage removal of heavy metal ions



gradually increases with increasing the pH until it reaches the maximum value at pH=8. The sorption of iron slightly increases at lower pH values until it reaches the range of 6 to 8, at which the adsorption reaches high level. The sorption of manganese is very low below pH 4 and increases rapidly at pH 6 and coming to maximum at pH 8. It may attributed to the sorption process depends on the concentration of the hydrogen ion in solution. Hydrogen ion strongly competes for the free sites in the structure of the clay leading to decrease in the percentage of adsorption of ions (Kamel, 2004). Increasing the pH of solution results in decrease in H<sup>+</sup> ion leading to low competition for the vacant exchange sites of the clay, and hence more removal of metal ions takes place. At pH>8 (high alkaline media), the precipitation of the metal ion hydroxides may take place, thus, cations present in solution are exchanged with those on kaolin's structure (Bhattacharyya, 2008)



**Figure 5:** Effect of pH on the removal of (a) Mn, (b) Fe using kaolin clay at stirring speed 150 rpm and clay's dose of 200 ppm at room temperature.

**Effect of Temperature on the Sorption of Iron and Manganese by Kaolin Clay:**

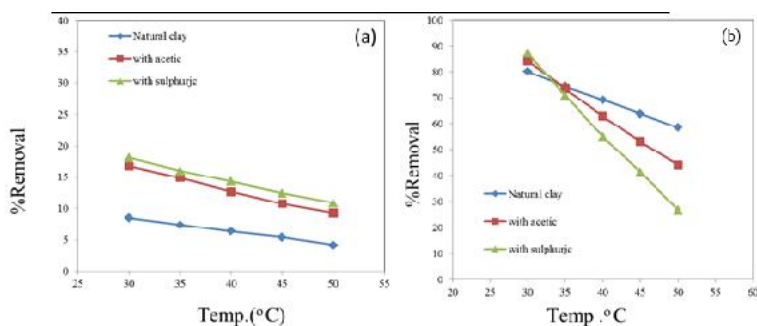
Iron and manganese adsorption at different temperatures 30, 35, 40, 45 and 50°C were studied. The adsorption was found to decrease with the increase in temperature as shown in Figure 6. It reveals that the adsorbate-adsorbent system is exothermic in nature for which the evaluation of thermodynamic parameters was carried out.

**Thermodynamics of Adsorption:** From Eq. (3), Gibb's free energy change of adsorption ( $\Delta G^\circ$ ) was calculated using  $\ln K$  values for different temperatures. The values of the enthalpy of adsorption ( $\Delta H_{ads}$ ) and the entropy of adsorption ( $\Delta S_{ads}$ ) were determined from the slope and intercept of the linear plot of  $\log(q_e/C_e)$  versus  $1/T$ . Table (1) shows the values of  $\Delta H$ ,  $\Delta G^\circ$  and  $\Delta S^\circ$ .

The results in table (1) show that negative values of  $\Delta H_{ads}$  reveals that the adsorption process is exothermic in nature, and also the negative values of  $\Delta G_{ads}$  indicated that the process of adsorption of iron and manganese ions on the clay is spontaneous.  $\Delta G_{ads}$  is less negative with temperature increase, indicating that the sorption process is favorable at room temperature, but it is low at higher temperatures. (Errais, 2011), moreover, the value of entropy of activation is negative, which means that the ions and molecules at the solid-liquid interface are more present than those in the bulk solution phase. The negative entropy change indicated a decreased randomness at adsorbent – sorbate interface during the sorption of iron and manganese ions onto kaolin (Kula, 2010).

**Table 1:** The thermodynamic parameters for the adsorption process of iron and manganese on kaolin clay

Element	Clay Type	$\Delta H^\circ$ kJ/mol	$\Delta S^\circ$ J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta G^\circ$ kJ/mol	R <sup>2</sup>
Fe	Natural clay	-42.46	-57.98	-25.18	1.00
	Clay activated with acetic acid	-76.98	-170.11	-26.29	0.99
	Clay activated with sulfuric acid	-115.45	-295.50	-27.39	0.99
Mn	Natural clay	-30.21	-48.35	-15.80	0.98
	Clay activated with acetic acid	-28.35	-35.91	-17.65	1.00
	Clay activated with sulfuric acid	-24.12	-21.29	-17.78	1.00



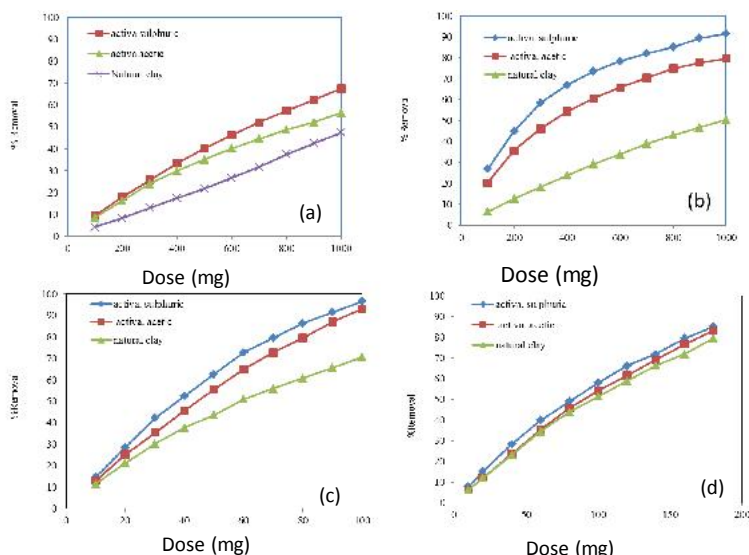
**Figure 6:** Effect of temperature on the removal of Fe (a), Mn (b) using kaolin clay at pH 3.25, stirring speed 150 rpm and clay dose 200 ppm.

**Effect of Adsorbent Dosage:**

The adsorption study was carried out using natural clay (kaolin) and its acidified activated (acetic acid and sulfuric acid) forms. The effect of different doses of kaolin clay and its modified forms on the removal efficiency of iron and manganese from raw water and known standards were carried out on samples collected from wells located in Beni-Suef Governorate "Middle Egypt". The collected samples are treated with different doses of the three clay adsorbents. Iron and manganese standards are prepared as in section 2.6. The clay doses from 0.1g to 1g were added to raw water samples and manganese known standards, while doses of 0.01g to 0.1g were added to raw water samples and iron known

standards. The samples were stirred at 150 rpm. The data are graphically represented in figure 7 (a-d) which shows the relation between the different doses of clay contents and removal efficiency of iron and manganese in raw and known standard solutions. Figure 7(a) shows the relation between % removal of manganese from raw samples and different doses of clay and its modified forms; Figure 7(b) shows the relation between % removal of manganese from known standards and different doses of clay and its other two forms; Figure 7(c) shows the relation between % removal of iron from raw samples and different doses of clay and its modifications and figure 7(d) shows the relation between % removal of iron from known standards and different doses of different clay forms. It is observed that, the adsorption efficiency increases as the clay amount increases. The increase in the efficiency can be explained by the increasing of surface area where the adsorption takes place. Moreover, sorption increases with modified clay more than natural clay. Treated samples with strong acids such as sulfuric give the highest activity, while the treatment using acetic acid gave the lowest activity. Thus, the adsorption efficiency of acid-activated clay is dependent on the acid type and/or concentration. It is obvious that, the dose of clay of 1 g /L is the specific minimum that gives high saturation for manganese and the dose of 0.1 g /L of clay is the specific minimum one that gives high saturation for iron in natural and modified clay. The affinity of the kaolin clay for sorption of iron and manganese ions runs in the order:

**Activated by sulfuric > Activated by acetic > Natural clay**



**Figure 7:** The removal of manganese from (a) raw samples, (b) authentic standards for clay doses (100 mg/L- 1g/L), at 150 rpm and removal of iron from (c) raw samples and (d) authentic standards for clay doses (10mg/L - 100mg/ L).

**Adsorption Isotherms:**

**Langmuir isotherm:** Langmuir adsorption isotherm is illustrated by the following equation (Errais, 2011), (Unuabonah, 2008).

$$q_e = \frac{V_m K C_e}{K C_e + 1} \tag{4}$$

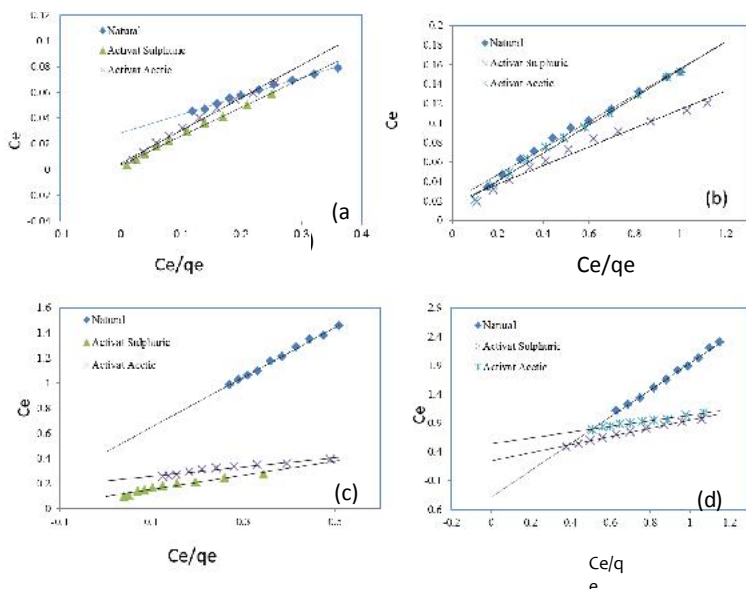
Where  $q_e$  is the amount of adsorbed heavy metal per gram clay (mg/g),  $V_m$  is the monolayer capacity,  $k$  is the equilibrium constant and  $C_e$  is the equilibrium concentration of the solution (mg/L) linear form of Eq. (4) can be written as the following in Eq (5):

$$\frac{C_e}{q_e} = \frac{1}{K V_m} + \frac{C_e}{V_m} \tag{5}$$

The relationship between the sorbed amounts of metal ion per gram ( $C_e/q_e$ ) against the equilibrium concentration ( $C_e$ ) is shown in figure 8. From these figures, linear relationship was obtained indicating that the sorption process can be described by Langmuir type isotherm. From these data it can be concluded that the sorption of the investigated elements by the kaolin clay and its modified forms takes place mainly through the formation of a single monolayer of sorbed species (Unuabonah, 2008); (Sari, 2014). The linear form of Langmuir equation of iron and manganese adsorption on different doses of natural kaolin and its activated forms is given in table 2.

**Table 2:** Linear form of Langmuir equation

Clay/ Element	Fe		Mn	
	Equations	$R^2$	Equations	$R^2$
Natural clay on sample	$0.0296+0.1426C_e$	0.99	$0.4507+1.9818C_e$	0.99
Natural clay on standard	$0.0197+0.1361C_e$	0.99	$0.3911+2.3284C_e$	0.99
Sulfuric clay on sample	$0.0036+0.2235C_e$	0.99	$0.0964+0.561C_e$	0.93
Sulfuric clay on standard	$0.018+0.0959C_e$	0.97	$0.2375+0.709C_e$	0.99
Acetic clay on sample	$0.0049+0.2545C_e$	0.99	$0.3305+0.3706C_e$	0.94
Acetic clay on standard	$0.0122+0.1427C_e$	0.99	$0.5439+0.489C_e$	0.97



**Figure 8:** Langmuir adsorption model for interactions of iron in (a) samples, (b) authentic standards on kaolin clay and interactions of manganese in (c) samples and (d) authentic standards on kaolin clay respectively.

**Freundlich isotherm**

Freundlich isotherm is used for modeling the adsorption on heterogeneous surfaces. This isotherm can be explained as in equation (6).

$$q_e = K_f C_e^{1/n} \tag{6}$$

Where  $K_f$  (mg/g) and (n) are Freundlich constants. These constants are determined from the intercept and slope of linear plot of  $\log q_e$  versus  $\log C_e$ , respectively as in eq. (7),

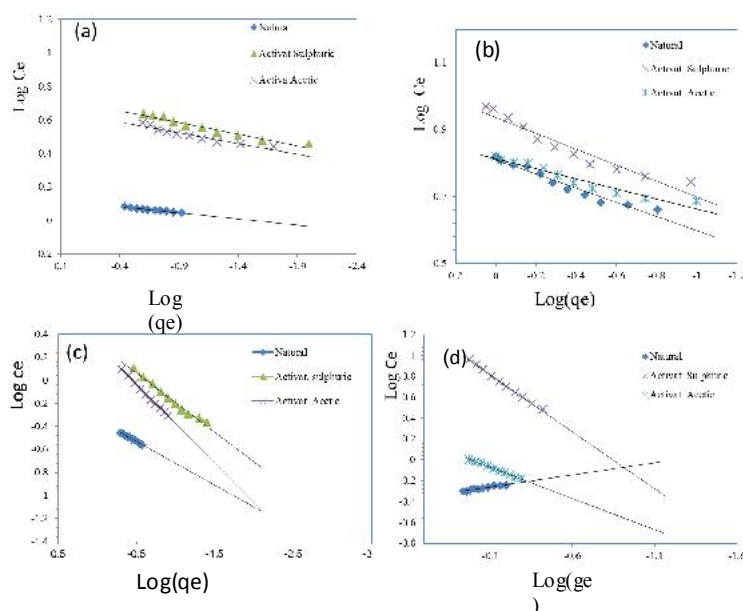
$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{7}$$

The linear form of equation (7) is given in table (3). This linear relationship indicates that the sorption process can be described by Freundlich type isotherm, moreover, the sorption of ions on kaolin clay takes place mainly through the formation of a single monolayer which shows that in figure 9, (Veli, 2007). These figures show that Freundlich isotherm curves are

linear for both iron and manganese adsorption. The Freundlich constant  $K_f$  and adsorption intensity  $1/n$  for iron and manganese adsorption were shown in (Table 5).

**Table 3:** linear form of Freundlich equation.

Clay/ Element	Fe			Mn		
	Equations	$\text{Log}K_f + 1/n \text{Log}C_e$	$R^2$	$\text{Log}K_f + 1/n \text{Log}C_e$	$R^2$	
Natural sample	clay on	$0.11C_e$ 0.073	0.99	$0.3437C_e$ 0.3786	0.99	
Natural standard	clay on	$0.1426C_e$ 0.1471	0.99	$0.017C_e$ 0.5473	0.99	
Sulfuric sample	clay on	$0.823C_e$ 0.256	0.93	$0.3192C_e$ 0.328	0.98	
Sulfuric standard	clay on	$0.9361C_e$ 0.2388	0.99	$0.3053C_e$ 0.6843	0.96	
Acetic clay on sample		$0.6363C_e$ 0.1281	0.94	$0.3053C_e$ 0.6843	0.99	
Acetic standard	clay on	$0.8114C_e$ 0.1498	0.97	$0.0125C_e$ 0.597	0.99	



**Figure 9:** Freundlich adsorption model for interactions of iron in (a) samples, (b) authentic standards on kaolin clay and interactions of manganese in (c) samples and (d) authentic standards on kaolin clay, respectively.

**Table 4:** Langmuir and Freundlich parameters

Types Clay type/Samples	Langmuir isotherm constants of Fe.			Langmuir isotherm constants of Mn.		
	Vm(mg/g)	k	$R^2$	Vm(mg/g)	K	$R^2$
Natural clay on sample	7.01	4.82	0.99	0.50	4.40	0.99
Natural clay on standard	7.35	6.91	0.99	0.43	5.95	0.99
Sulfuric clay on sample	4.47	6.32	0.99	1.41	7.35	0.93
Sulfuric clay on standard	10.43	5.33	0.97	2.70	1.56	0.99
Acetic clay on sample	3.93	5.19	0.99	2.04	1.48	0.94
Acetic clay on standard	7.01	11.70	0.99	2.04	0.90	0.97

**Table 5:** Freundlich parameters

Types Clay type/Samples	Freundlich isotherm constants of Fe			Freundlich isotherm constants of Mn		
	$k_f$	$n$	$R^2$	$k_f$	$N$	$R^2$
natural clay on sample	0.86	2.21	0.98	0.34	2.64	0.98
natural clay on standard	0.81	4.70	0.96	0.29	4.24	0.96
sulfuric clay on sample	0.71	7.18	0.95	0.32	1.95	0.95
sulfuric clay on standard	0.94	4.19	0.93	0.02	3.08	0.93
acetic clay on sample	0.64	7.81	0.92	0.31	1.46	0.92
acetic clay on standard	0.81	6.68	0.93	0.01	1.68	0.93

### CONCLUSION

In this study, tests were performed to evaluate the use of kaolin clay powder and its sulfuric and acetic acids modified activated forms as adsorbents for iron and manganese removal from real groundwater samples. Obtained results applied to authentic standards for both elements proved their good efficiency in the removal processes. The empirical values are evaluated according to the Langmuir and Freundlich isotherms that are generally used to describe the adsorption processes. It is stated that all of isotherm models fit very well. They proved that the sorption process of the investigated elements with the kaolin clay and its acid activated forms take place mainly through the formation of a single monolayer of sorbed species. The three kaolin adsorbents proved to be efficient for the elimination of heavy metals from groundwater since they are low-cost, abundant and locally available.

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