

Optimization and Characterization of Acid-Activated Bentonite

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Abstract- The acid-activated bentonite clay is a low-cost adsorbent. This adsorbent was prepared using sulfuric acid reflux and was used for lead removal from wastewater resulting from batteries industries. RSM was used to optimize results, seventeen experimental runs were obtained for the production of activated bentonite clay at different variables of time (15-45min), the concentration of sulfuric acid (25-45%), and liquid to the solid ratio 3-5 (ml/g). The results of response surface models of the adsorbent production together with the effect and optimization of the process parameters were discussed. The predicted maximum adsorption capacity for activated bentonite clay was 2.887 mg/g at a time of 15 minutes, the liquid to solid ratio of 3 (ml/g) & H₂SO₄ concentration of 40.973 %. The results from the characterization techniques (BET, TGA, FTIR, and XRD) were obtained and discussed. The adsorbent produced from bentonite showed good adsorptive properties and thermal stability. The analysis revealed that there is a rise in the specific surface area of the activated bentonite clay compared to that of the raw bentonite clay (from 41.7065 to 49.227 m²/g).

Keywords- Acid-Activated, Bentonite, Modeling

I. INTRODUCTION

Bentonite clay is a type of adsorbent swelling clay that is composed primarily of montmorillonite. It is generally formed as a result of sitting out of volcanic ash in brine that exchanges the volcanic glass existing in the ash with clay minerals [1,2]. Bentonite clay is one of the mineral clays that possesses major physicochemical properties; particle size and shape, ion exchange, hydration swelling, plasticity, rheological properties, color, and reaction [3]. Montmorillonite is the main component of bentonite; it is made up of two silica tetrahedral sheets with a central alumina octahedral sheet. The isomorphs replacement reveals a net negative superficial charge in the tetrahedral and octahedral sheets. The hydrated exchangeable cations between layers and around the edges balance out as negatively charged. These interchangeable cations are thought to play a major role in the removal of metal cations from an aqueous solution. [3]. Al-Shahrani [4] made an acid activation operation using the optimal operating variables such as 45 wt.% acid concentration, the temperature of boiling, 15 minutes reaction time, 200 rpm speed of mixing, grain size of 325 mesh (44 μm) the water to clay ratio of 5:1. Nwosu et al. [5] prepared the modified clay by impregnation using different concentrations of NaOH or H₂SO₄ in a w/v ratio of 1:2. They examined the adsorptive and physicochemical properties by using standardized techniques, such as bulk density, moisture content and pH. The aim of this study is the removal of lead from waste water resulted from batteries industries by adsorption using natural and acid activated bentonite clay. The response surface methodology (RSM) model was used to forecast the optimum factors affecting the activated bentonite adsorption capacity.

MATERIALS AND METHODS

A. Materials

Bentonite clay was brought from El Fawakher village, Old Cairo, Egypt. Sulfuric acid (H₂SO₄) of 98% purity and lead nitrate were purchased from Qasr Al Aienny Street.

B. Methods

1. Activation Using Sulfuric Acid Reflux Method

10 gm of raw bentonite clay was mixed with various concentrations of sulfuric acid 25, 35, and 45%. The reactants were refluxed in boiling H₂SO₄ for different times of 15, 30, and 45 minutes, and the liquid to solid ratio in the mixture 3, 4, and 5 ml/g making sure that the time is measured starting from the boiling point. Once the reflux time is over, the mixture is left to cool down to room temperature. The cooled mixture is thoroughly poured onto filter paper to get rid

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of excess sulfuric acid and then washed with deionized water multiple times to ensure removal of excess sulfuric acid. The washed bentonite samples were placed in a drying oven for 6 hours at 105°C, and then the dried samples were accurately weighed using an analytical balance. Finally, the dried weighed samples were ground into fine powder.

2. Batch adsorption experiments

After the activation process a constant weight of activated bentonite clay was measured from all the samples and then added to lead solutions with a constant concentration. The mixture was placed on a shaker for constant time for all the samples. After the time is up the concentration of lead in the samples was measured to determine the adsorption capacity for each sample using atomic absorption spectrophotometer (model GBC932AA 2010) at the Agricultural research center.

3. Experimental design and data analysis

RSM based on Box–Behnken experimental design was applied, and seventeenth experimental runs were applied with 5 runs at the center point for optimizing the adsorption capacity and to assess the influence of the process parameters (25–45%; liquid/solid (L/S) ratio, time, 15–45 min and H₂SO₄ concentration, 3–5 ml/g) on the adsorption capacity of the bentonite clay.

4. Characterization of Produced Activated Bentonite Clay

I. Fourier Transform Infrared (FTIR)

Fourier transform infrared spectroscopy (FTIR) for the samples was measured in Egyptian academy and advanced technology labs using Class 1 Laser Product IEC/EN 60825-1/A2:2001 Avatar Series (USA).

II. X-Ray Diffraction (XRD)

X-ray diffraction analysis (XRD) is a technique used in materials science to determine the crystallographic structure of a material. XRD works by irradiating a material with incident X-rays and then measuring the intensities and scattering angles of the X-rays that leave the material. The XRD test were carried out in science and technology center of excellence (STCE) Cairo Egypt. The device model is (X-Ray DFRAC TO METER A-R-X-T-R-A) Swiss made.

III. X-Ray Fluorescence (XRF)

XRF (X-ray fluorescence) is a non-destructive analytical technique used to determine the elemental composition of materials. XRF analyzers determine the chemistry of a sample by measuring the fluorescent (or secondary) X-ray emitted from a sample when it is subjected to a primary X-ray source. The device model is [AXIOS, WD-XRF Sequential Spectrometer (Panalytical 2005)].

IV. The Brunauer–Emmett–Teller (BET)

The Brunauer–Emmett–Teller (BET) theory is an analytical method used to determine the precise surface area for the produced clay. This method utilizes nitrogen adsorption isotherm data to determine the surface area of the material. Nitrogen is used due to its availability in pure form and it mostly has a strong interaction with solid's surfaces. The BET test was carried out in the national research center AL Giza, Egypt., and the device model is (Nova touch 4LX).

V. Thermo-gravimetric analysis (TGA)

Thermo-gravimetric analysis (TGA) is an important tool that is used for the characterization of materials. TGA is used to determine material thermal stability, volatility, and the physical and chemical changes that happened to the material during heating. This is performed by gradually raising the temperature by monitoring the sample's weight using an analytical balance. The test was carried out at the science and technology center of excellence (STCE) in Cairo Egypt. The device model is (Q-500 Thermo-gravimetric made in America).

II. RESULTS AND DISCUSSIONS

The experimental data were analyzed and the subsequent regression equations in terms of coded factors were attained for the forecast values of output responses (adsorption capacity) on behalf of activated bentonite clay.

The adsorption capacity (Y) equation obtained from statistical design analysis in coded value is as follows:

$$(Y) = 1.48 + 0.6950 A - 0.4012 B + 0.293 C + 0.4375 AB + 0.6480 B^2 \quad (1)$$

$$A = \frac{C-35}{10} \quad B = \frac{T-30}{15} \quad C = \frac{R-4}{1} \quad (2)$$

Adsorption capacity (Y) equation obtained from statistical design analysis in actual value is as follows:

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$$(Y) = 2.1171 - \frac{18}{1000}C - \frac{30}{100}T + \frac{293}{1000}R + \frac{4375}{1500000}CT + \frac{648}{225000}T^2 \quad (3)$$

Where, C=H₂SO₄ Concentration

T= Time

R= Ratio

The R-squared value for the model equation is 92.67 percent, which is higher than 75%, indicating that the quadratic models were well-fitting [7].

Table 1 shows the experimental values for the activated bentonite clay adsorption capacity at the design point.

Table 1. Experimental response for the activated bentonite clay production

Run	A: Concentration H ₂ SO ₄ (%)	B: Time (min)	C: Ratio L/S (ml/g)	Adsorption Capacity (mg/g)
1	35	45	3	1.47
2	35	30	4	1.16
3	45	30	5	2.64
4	35	15	3	2.9
5	45	15	4	2.56
6	35	30	4	2.18
7	25	30	5	1.19
8	25	30	3	0.44
9	35	30	4	1.23
10	35	30	4	1.46
11	45	45	4	2.63
12	25	45	4	0.41
13	35	45	5	2.51
14	45	30	3	1.86
15	25	15	4	2.09
16	35	15	5	2.68
17	35	30	4	1.39

A. Effect of process parameters

2-D model can be drawn for a different variation of parameters, which shows the trend of response varying within the selected range of input parameters and the effect of each parameter over the other parameters. With the aid of Response Surface Methodology, the interaction between the three studied parameters namely Time "A", Temperature "B" & stoichiometric ratio "C" can be studied using the obtained model graph contours. A contour graph is the projection of a 2D graph plot. It indicates the maximum, and minimum points as well as the effect of two parameters on a certain response on a 2D plot. Contour is a 2D model in which 2 parameters change while the third remains constant at its minimum, average, or maximum value to determine the maximum adsorption capacity that can be obtained at these values. Changing in colors for the observed contours is a good indication for the adsorption capacity percentage, as getting closer to red-colored regions indicates higher adsorption capacity and getting closer to blue regions indicates

minimum adsorption capacity obtained at the corresponding conditions to each region. Each line shows the adsorption capacity percent obtained at any condition corresponding to the 2 other parameters through the line. Contour plots are useful for establishing the response values and operating conditions as required [8,9].

1. Effect of the Reaction Time and Concentration on the Activated Bentonite's Adsorption Capacity

By plotting the concentration "A" on X-axis and time "B" on Y-axis, while varying the value of the stoichiometric ratio "C" to its minimum, maximum and average values, the effect of these factors on the adsorption capacity could be easily recorded. The results indicated that by increasing the stoichiometric ratio the adsorption capacity increases as well, especially at low time of 15 min and maximum concentration of 45 % as shown in Figure 1.

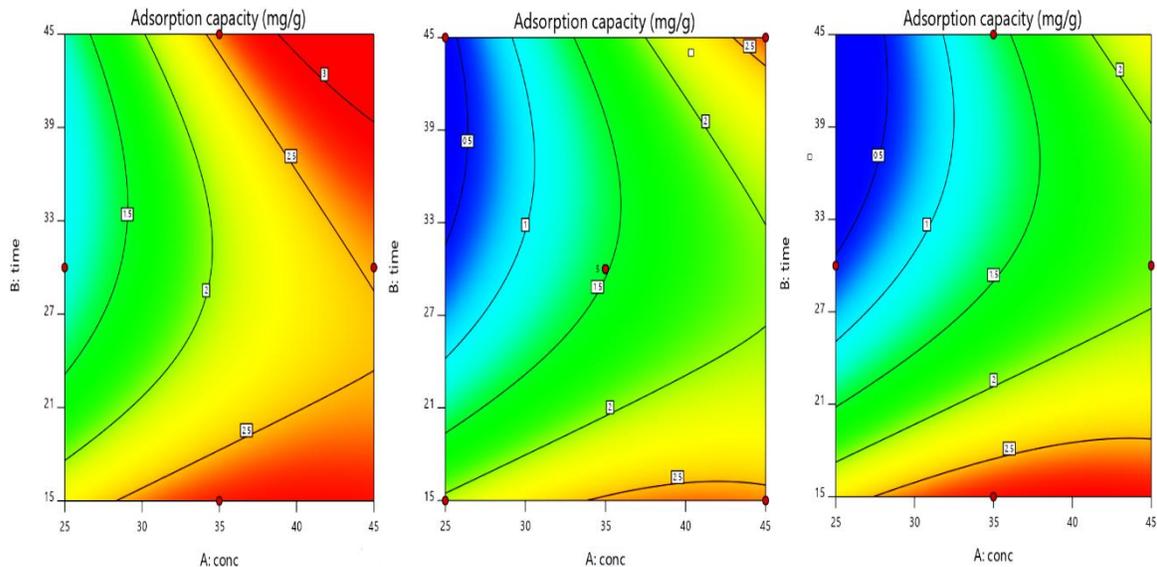


Figure 1. Effect of the Reaction Time and Concentration on the Activated Bentonite's Adsorption Capacity

2. Effect of the Reaction Time and Stoichiometric Ratio on the Adsorption Capacity

The reaction time "B" and stoichiometric ratio "C" factors were studied while varying the value of the concentration "A" to its minimum, maximum and average values to study its effect on the adsorption capacity which indicated that the maximum adsorption found at time 15 min and stoichiometric ratio of liquid to solid 4:1 as shown in Figure 2.

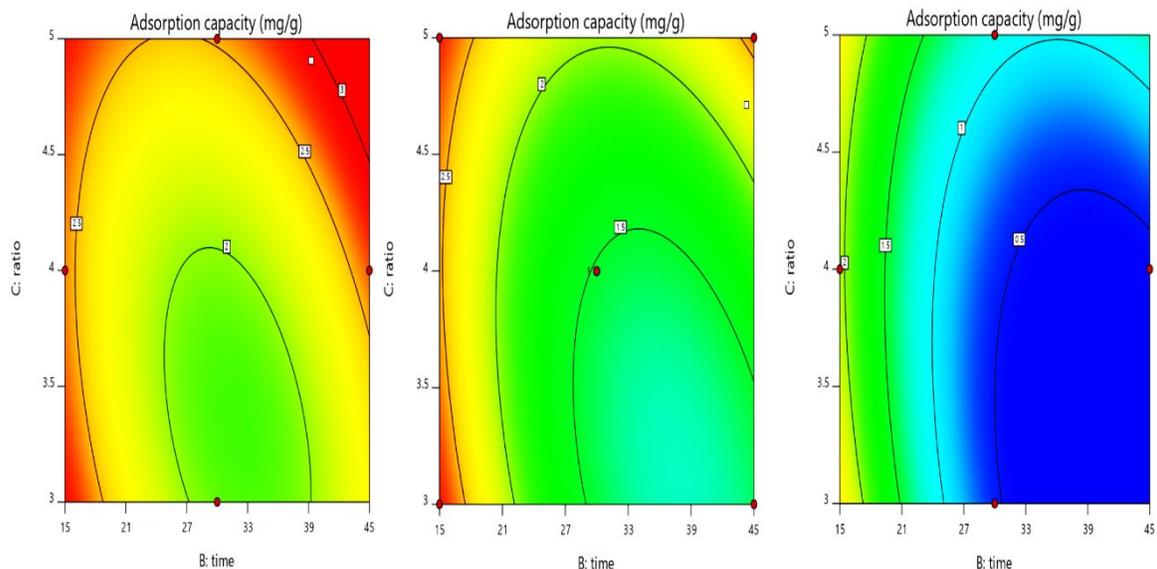


Figure 2. Effect of the Reaction Time and Stoichiometric Ratio on the Adsorption Capacity

3. Effect of the Reaction Concentration and Stoichiometric Ratio on the Adsorption Capacity

The concentration of the reaction “A” and stoichiometric ratio “C” factors was studied while varying the value of the reaction time “B” to its minimum, maximum and average values to study its effect on the adsorption capacity which indicated that the maximum adsorption capacity found at concentration 45% and stoichiometric ratio of liquid to solid 5:1 as shown in Figure 3.

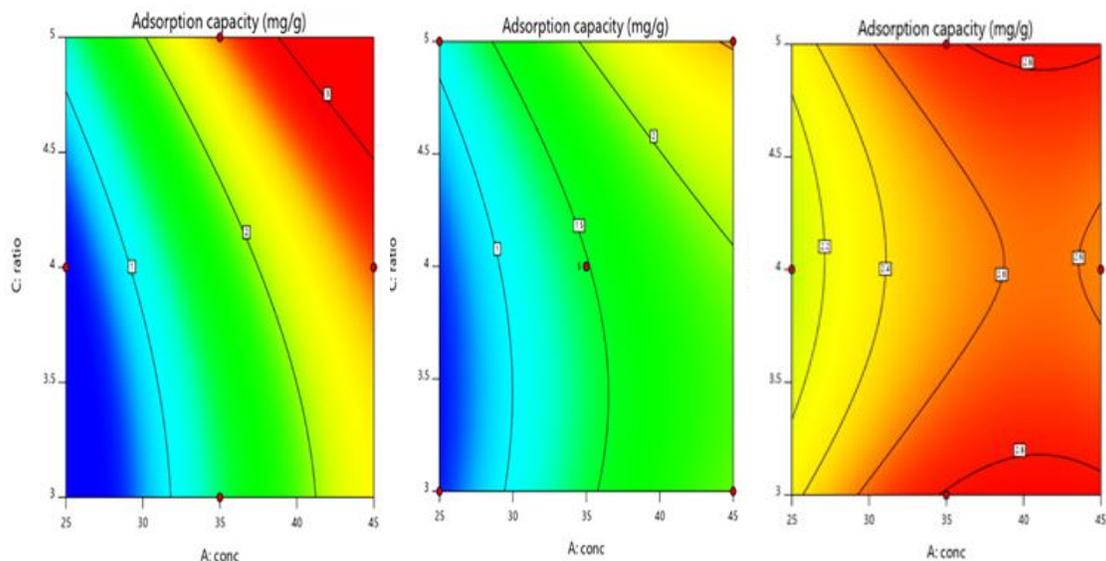


Figure 3. Effect of the Reaction Concentration and Stoichiometric Ratio on the Adsorption Capacity

B. Optimization of activated bentonite produced

The optimum values for the activated bentonite clay adsorption capacity were identified at a time of 15 min to attain maximum adsorption capacity, which satisfies the lowest economical operating cost. The optimal parameters for activated bentonite clay were: time of 15 min, H_2SO_4 concentration of 40.973% & with liquid/solid ratio of 3 ml/g. The target reached was a maximum adsorption capacity of 2.88708mg/g. The confirmatory experimental results were found to be closer to the predicted results. The decisive errors were too small 3.7% for the predicted responses (adsorption capacity) obtained using the developed models for activated bentonite clay.

C. Characterization of Raw Material

Different analytical tests were performed for the characterization of raw bentonite clay

1. Fourier Transform Infrared (FTIR) for Raw Bentonite Clay

Fourier transform infrared (FTIR) spectroscopic was applied on raw bentonite clay. As shown in figure 4. the presence of OH, carbonyl (C=O), and CH_3 functional groups and their respective peaks in the IR spectrum are shown in Table 2 [10].

Table 2: FTIR spectrum of the functional groups present in the raw bentonite clay sample [10].

Compound class	Functional group	Absorption (cm^{-1})
Alcohol	O-H	3422.4
Carboxylic acid	C=O	1636.7
Alkane	CH_3	1439.82

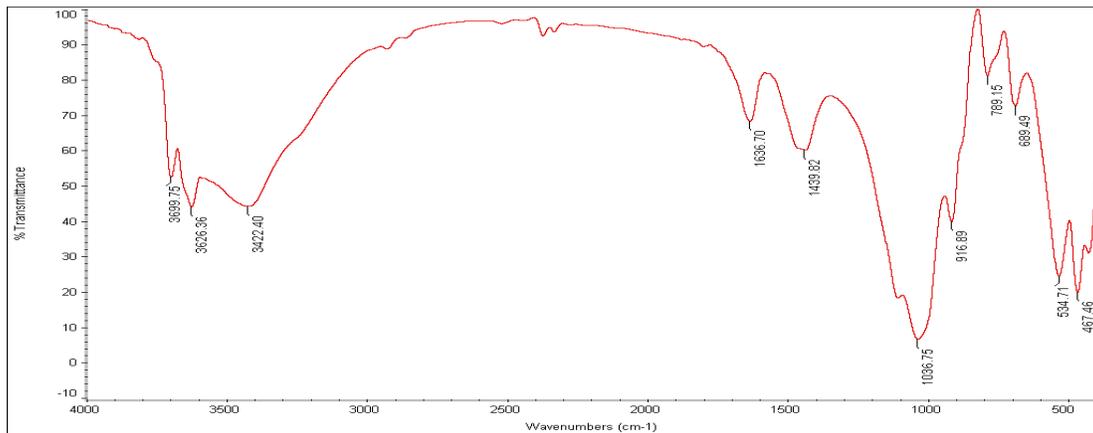


Figure 4: FTIR of raw bentonite clay sample

2.X-ray Diffraction Analysis (XRD) for the Raw Bentonite

The XRD analysis on raw bentonite determines the content of minerals contained and sees the diffraction pattern at a value of 2θ as shown in Figure 5. Therefore, there is a diffraction peak at $2\theta = 26.5^\circ$ specifies the peak of quartz mineral (SiO_2). The diffraction peaks of this quartz mineral have a high level of reflection intensity, as well main components like montmorillonite and kaolinite are also present. [11,12].

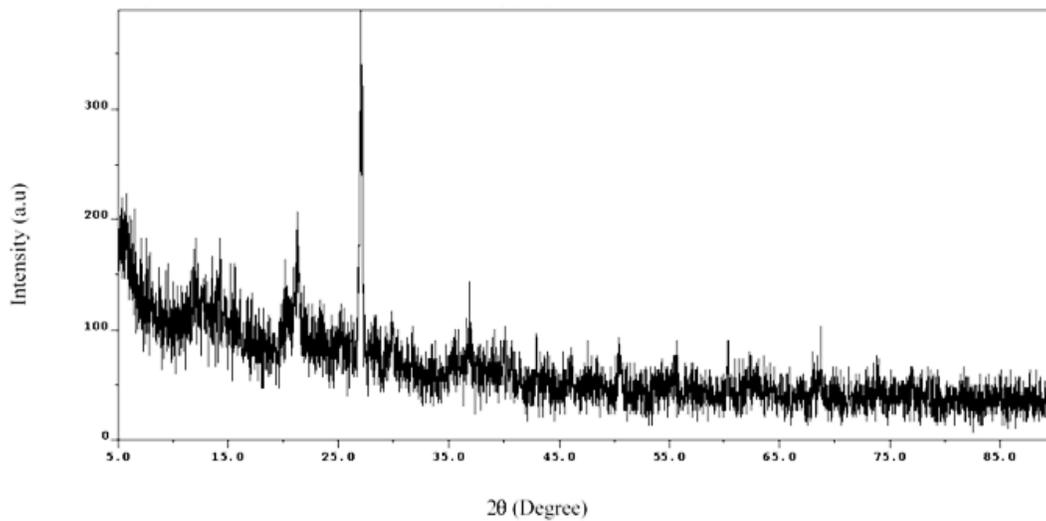


Figure 5. XRD of raw bentonite clay

3.X-Ray Fluorescence Analysis for Raw Bentonite Clay

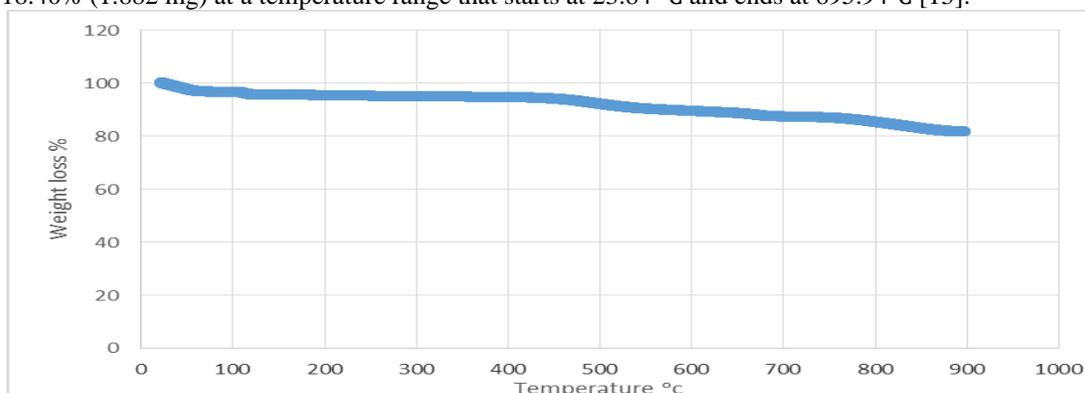
The chemical composition of raw bentonite clay was determined by X-ray fluorescent analysis (XRF), and the observed data were listed in table 3. It was observed that SiO_2 , Al_2O_3 & Fe_2O_3 are the main components of raw bentonite clay, representing the largest compositions of 54.91%, 17.01% & 9.31% respectively as well a low content of 0.48% is observed for the composition of SO_3 .

Table 3: Chemical composition for raw bentonite clay

Elements	Raw bentonite %
SiO ₂	54.91
TiO ₂	1.53
Al ₂ O ₃	17.01
Fe ₂ O ₃	9.31
MnO	0.08
MgO	2.47
CaO	0.99
Na ₂ O	2.75
K ₂ O	1.03
P ₂ O ₅	0.16
CL	1.20
SO ₃	0.48

4. Thermo-gravimetric Analysis for the Raw Bentonite

The TGA profile obtained for the raw bentonite in Figure 6 shows the percentage of mass loss of raw bentonite at different temperature ranges. At temperature range 23.84 to 149.99 °C the mass loss is 4.115% (0.4210 mg), and at range 149.99 to 599.95 °C the mass loss is 6.097% (0.6238 mg), and at range 599.95 to 721.01 °C the mass loss is 2.246% (0.2298 mg), and at range 721.01 to 895.94 °C the mass loss is 5.611% (0.5741 mg). Therefore the total mass loss is 18.40% (1.882 mg) at a temperature range that starts at 23.84 °C and ends at 895.94°C [13].

**Figure 6: TGA of raw bentonite**

D. Characterization of Activated Bentonite

The activated bentonite clay was subjected to the different characterization techniques as typically applied earlier for the raw bentonite clay.

1. Fourier Transform Infrared (FTIR) For Activated Bentonite Clay

Also, as shown in Figure 7, the FTIR spectra of the activated bentonite sample. It was noticed the presence of the following characteristic peaks, stretching absorption peaks observed of OH, carbonyl (C=O), CH₃ disappeared, and a new peak appeared, which could be attributed to the S=O stretching sulfonic acid which is an indication of the SO₃ active sites on the acid activated bentonite clay & their IR spectrum is shown in Table 4 also, after the acid activation, many characteristic peaks disappeared, indicating a change in functional groups as CH₃ that has disappeared in the activated bentonite sample [10].

Table 4: The FTIR spectrum of the functional groups present in the activated bentonite sample

Compound class	Functional group	Absorption (cm ⁻¹)
Alcohol	O-H	3390.16
Carboxylic acid	C=O	1635.59
Alkane	S=O	1107.06

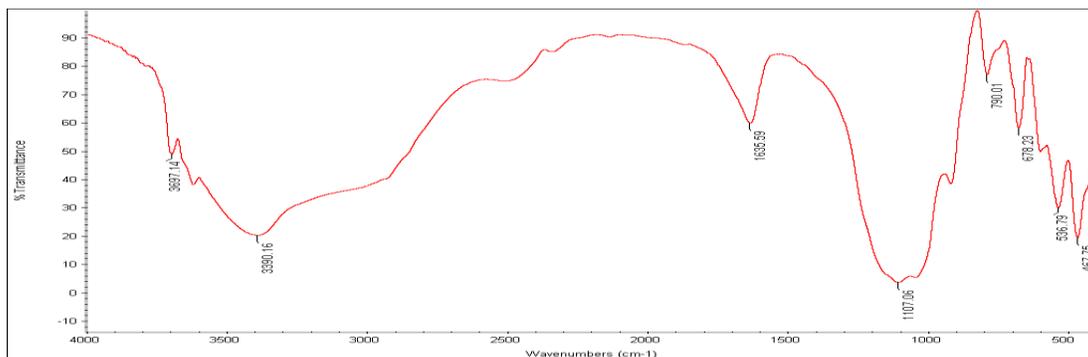


Figure 7: FTIR spectrum of activated bentonite sample

2.X-Ray Diffraction Analysis (XRD) for the Acid-Activated Bentonite

XRD analysis on acid-activated bentonite determines the content of minerals contained and shows the diffraction pattern at a value of 2θ as shown in Figure 8. Therefore, there is a diffraction peak at 2θ = 26.5° signalizes the peak of quartz mineral (SiO₂) as the raw bentonite but the angle 2θ was shifted and the intensity becomes larger (a slight shift toward a higher angle of 2θ). This shift is due to the reaction between bentonite and acid, The XRD pattern shown in Figure 8 shows shifts into lower & sharper peak, which is composed of quartz (SiO₂) [11].

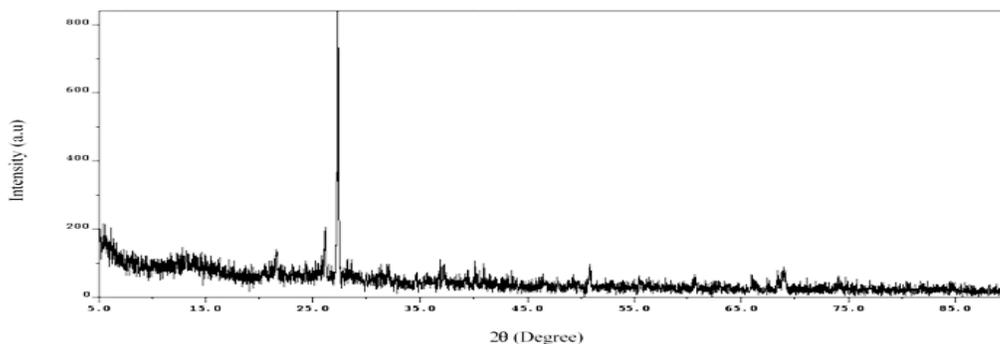


Figure 8: XRD of acid-activated bentonite

3.X-Ray Fluorescence Analysis for Activated Bentonite Clay

The results from the (XRF) analysis for the activated bentonite clay were obtained and illustrated in Table 5. It’s noted that there is a noticeable decrease in Al³⁺, Fe³⁺, Si⁴⁺, and Mg²⁺ cations after the activation process. This decrease might be due to the acid attack from the activation process. There is a significant increase in SO₃²⁻ anions after the activation process due to the sulfuric acid (H₂SO₄) activation process [12].

Table 5: Chemical composition for activated bentonite clay

Elements	Activated bentonite %
SiO ₂	44.910
TiO ₂	0.833
Al ₂ O ₃	11.695
Fe ₂ O ₃	2.679
MnO	0.015
MgO	0.320
CaO	4.094
Na ₂ O	0.190
K ₂ O	0.901
P ₂ O ₅	0.039
CL	0.015
SO ₃	18.024

4. The Brunauer–Emmett–Teller (BET) for Raw and Activated Bentonite

The specific surface area for both raw and activated bentonite clay was obtained from the Brunauer–Emmett–Teller (BET) N₂ adsorption analysis. As illustrated in Table (6) there is an increase in the specific surface area of the activated bentonite clay compared to the raw bentonite clay (from 41.7065 to 49.227 m²/g). The increase in the surface area for the activated bentonite clay can be the result of the splitting of clay particles and the opening up of the edges of the clay platelets due to the acid activation [12].

Table 6: (BET) Surface area for activated and non-activated bentonite clay

Property	Raw bentonite clay	Activate bentonite clay
BET surface area (m ² /g)	41.7065	49.227

5. Thermo-gravimetric Analysis (TGA) for the Acid-Activated Bentonite

The TGA profile obtained for the acid-activated bentonite in (Figure 9) shows the percentage of mass loss at different temperature ranges. At temperature range 25.15 to 295.06 °C the mass loss is 9.690% (0.8232 mg), and at range 295.06 to 575.56 °C the mass loss is 5.005% (0.4252 mg), and at range 575.56 to 895.95 °C the mass loss is 7.913% (0.6723 mg). Therefore, the total mass loss is 23.03% (1.957 mg) at a temperature range that starts at 25.15 °C and ends at 895.95°C. Thus, the total mass loss of the acid-activated bentonite is higher than the mass loss of the raw bentonite so, the total mass loss of acid-activated bentonite paralleled the severity of the acid treatment [13].

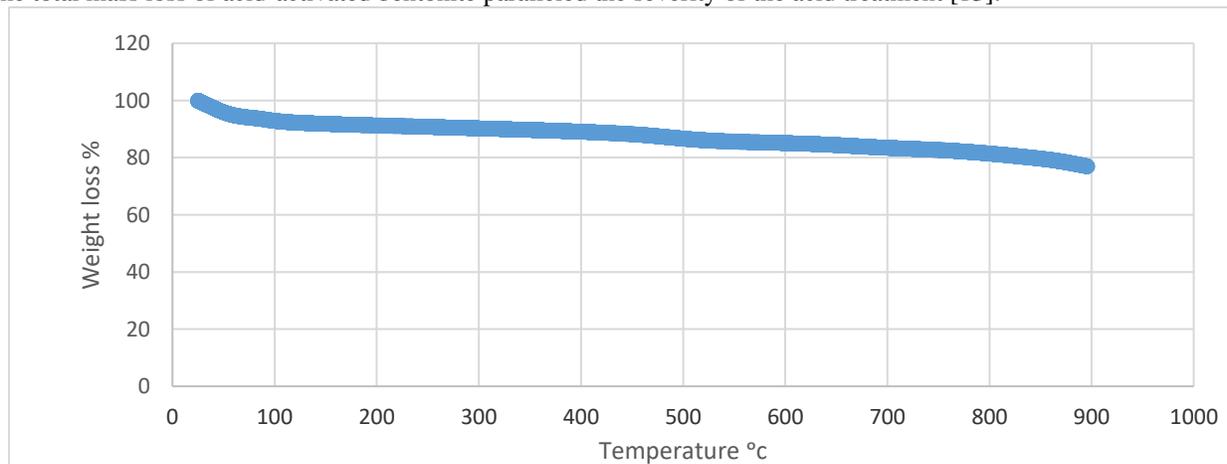


Figure 9: TGA for activated bentonite

III. CONCLUSION

The activated bentonite is a low-cost, and effective adsorbent used in the removal of lead. Raw bentonite clay and sulphuric acid are the necessary components needed to prepare the acid-activated bentonite clay. RSM was applied to increase the desired results. For the sulfuric activated bentonite clay, a total of 17 experimental runs were carried out, each with a different combination of variables, including the amount of time (15-45 minutes), the concentration of sulfuric acid (25-45 percent), and the liquid to solid ratio 3-5 (ml/g). Under ideal circumstances, the impact of contact time, pH, starting concentration, and dose on the activated bentonite clay were studied. The following were part of the optimal conditions: The results of applying response surface models to the manufacturing of adsorbents were the topic of conversation, as were the effects of and potential for optimizing the various process parameters. The predicted maximum adsorption capacity for activated bentonite clay was 2.887 mg/g at a time of 15 minutes, liquid to solid ratio of 3 (ml/g) & H₂SO₄ concentration of 40.973 %. The adsorbent produced from bentonite has good adsorptive properties and thermal stability. The analysis showed that there is an increase in the specific surface area of the activated bentonite clay compared to the raw bentonite clay (from 41.7065 to 49.227 m²/g).

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