REMOVAL OF METHYLENE BLUE DYE BY ACTIVATED EGYPTIAN BENTONITE CLAY

Mahmoud I. Eleraky ⁽¹⁾; Taha A. M. Abd El Razek ⁽²⁾ and Ahmed M Abd Elbasier⁽³⁾

 Egyptian Mineral Resources Authority 2) Faculty of Graduate Studies and Environmental Research, Ain Shams University 3) Environmental Engineering Department, Faculty of Graduate Studies and Environmental Research, Ain Shams University.

ABSTRACT

The aim of this study was activation of Egyptian calcium bentonite clay which obtained from El Alamein area, northern Egypt to use it in the removal of methylene blue dye. Egyptian bentonite was crushed, grinded by ball mill, purified using magnetic separation, treated by 0.1N acetic acid and finally activated by Acid activation (HCl, H₂SO₄) and alkali activation (Na₂CO₃, NaOH) using 1, 3, 5, 7and 9 % of acids and alkalis. The samples characterized by XRF, Cation Exchange Capacity (CEC) and free swelling. A 5 % Na₂CO₃ activated sample was chosen for methylene blue dye removal due to its best swelling and cation exchange capacity results. Adsorption studies were performed to evaluate the influence of various experimental parameters (pH, temperature, initial concentration, bentonite dose and time effect. Methylene

blue removal was optimum at 40 $^{\circ}$ C, pH 7, 40 min, 200 ppm MB and using 1 g/L activated bentonite as adsorbent dose.

Keywords: calcium bentonite, methylene blue dye, alkali activation, free swelling, cation exchange capacity.

Vol. (51); Iss. (8); No. (4); August, 2022 ISSN 1110-0826 ONLINE ISSN 2636 - 3178

INTRODUCTION

Urban agglomerations and changes in living style have increased the need for different types of synthetic substances which lead to pollute the water. Pollution of water is an important environmental problem to the modern world, which result in ecological imbalance that can cause adverse effects on the whole ecosystem. The main pollutants are synthetic dyes and heavy metals that should be given priority in wastewater treatment due to their deadly poisoning (Premkumar *et al.*, 2018). Dyes can be ordered into three principal classes: (a) anionic (acid, reactive, and direct dyes) which have negative charge, (b) cationic (basic dyes) because of the protonated amine group, and (c) nonionic (disperse dyes) due to their behavior of dissociation in solutions (Sakin Omer *et al.*, 2018). Dyes are utilized in an incredible variety of areas: textile, paper, leather, dyestuff, printing, plastic, cosmetics, and coatings which are spread widely because of low-cost production, brightness, and high resistance against environmental conditions (Reck *et al.*, 2018).

The most important cationic dye is Methylene Blue (MB). MB was known as methyl thioninium chloride, is a heterocyclic aromatic chemical compound with the molecular formula [C16H18N3SCI]. It is classified as a cationic dye (Peres *et al.*, 2018). It is used in various fields for example: drugs, dyestuff industries, paper, textile, and pesticide industries (Elwakeel *et al.*, 2021). Various techniques are evolved for the treatment

2

of dye wastes such as coagulation- flocculation (Dotto *et al.*, 2019), biodegradation (Bharti et al., 2019), electrochemical oxidation (Shetti *et al.*, 2019), ion exchange (Yan *et al.*, 2019), Fenton oxidation (Sözen *et al.*, 2020), reverse osmosis (Cinperi *et al.*, 2019), ozonation (Venkatesh and Venkatesh, 2020), electrocoagulation (Donneys-Victoria *et al.*, 2019), and adsorption (Naushad *et al.*, 2019).

Of these, adsorption has been widely used with bentonite as one of the most extensively studied adsorbent material because it is naturally available, inexpensive and has good adsorption capacity mainly due to its physical and chemical stability, high superficial area and good cation exchange capacity (De Castro *et al.*, 2018).

Egyptian bentonite clay was considered low grade of Ca–Mg smectite and without any beneficiation cannot be used and unsuitable for most industrial applications (Ismaeel *et al.*, 2017).

So, the aim of this study is the activation of Egyptian bentonite then uses it in the removal of Methylene Blue from wastewater.

MATERIALS AND METHODS

Materials:

Methylene blue dye is purchased from Rasayan Laboratories (India) and used as received. The natural Egyptian bentonite was collected from El Alamein region and activated by acid activation (Ali et al., 2019) and alkali activation (Magzoub et al., 2017). Acid activation was done by Hydrochloric

> Vol. (51); Iss. (8); No. (4); August, 2022 ISSN 1110-0826 ONLINE ISSN 2636 - 3178

acid and Sulfuric acid while alkali activation was done by sodium carbonate and sodium hydroxide. All the used chemicals were analytical grade chemicals.

Methods:

The natural Egyptian bentonite was crushed and ground using ball mill then pass through 63 µm sieves and this is sample A. Sample A was purified by 0.1 N acetic acid at room temperature to get rid of carbonates then washed and dried at 90 °C. Then the sample was passed through magnetic separation process to decrease iron content and this purified sample is sample B. The natural bentonite (sample A) and purified bentonite (sample B) were characterized by X-ray fluorescence analysis, XRF (ZSX Primus IV, Rigaku), X-ray diffraction analysis, XRD (Panalytical X PERT PRO), swelling test and cation exchange capacity (CEC). Swelling index was carried out according to ASTM D5890. This method also called free swell test. A 2 g dried sample and finely ground bentonite is dispersed into a 100 mL cylinder in 0.1 g increments. Each increment takes at least 10 min to allow full hydration and settlement of the bentonite. This step continues until the 2 g sample has been added to the cylinder. The cylinder then covered and protected from disturbance for 16-24 hour until the reading is stable (Muhammad and Siddiqua 2021). CEC carried out by using BaCl₂ as a saturation cation. This method involves the saturation of the exchangeable site with barium ions, equilibrium, removing excess barium by ethanol, and leaching and replacement with ammonium. Firstly, samples were washed thoroughly with deionized water, then 1 g of dried sample

4

was dispersed in 10 ml of 0.5 N BaCl₂·2H₂O solution, the dispersion was shaken on a reciprocating shaker for 30 min and then the clay suspension filtered under vacuum extraction using a Whatman No. 5 filter paper. The clay suspension was leached with 100 ml of 1 N BaCl₂·2H₂O. The excess BaCl₂·2H₂O was rinsed from the sample by washing with 200 ml volume of ethanol. In a clean flask the sample was washed with 225 ml of 1 N ammonium acetate solution having a pH of 7 to replace the exchangeable barium. The leached solution was completed to 250 ml with deionized water using a volumetric flask. The concentration of Ba ions in the final leachate was determined using ICP-OES (Dardir et al. 2018). After that the purified sample (Sample B) activated by acidic activation and alkali activation.

Acidic activation

1. HCl Activation

In this activation 5 samples B1, B2, B3, B4 and B5 were activated by 1, 3, 5, 7 and 9 % HCl respectively at 70 $^{\circ}$ C for 3 hours. 20 g of sample was weighed in conical flask and 100 ml of the solution was added (liquor ratio 1:5). Then the samples filtered and washed by distilled water till pH neutralized. Then the samples dried at 90 $^{\circ}$ C.

2. H₂SO₄ Activation

In this activation another 5 samples B6, B7, B8, B9 and B10 were activated by 1, 3, 5, 7 and 9 % H₂SO₄ respectively at 70 $^{\circ}$ C for 3 hours. 20 g of sample was weighed in conical flask and 100 ml of the solution was added (liquor ratio

> Vol. (51); Iss. (8); No. (4); August, 2022 ISSN 1110-0826 ONLINE ISSN 2636 - 3178

1:5). Then the samples filtered and washed by distilled water till pH neutralized.

Then the samples dried at 90 $^{\circ}$ C.

Alkali activation

1. Na₂CO₃ activation

In this activation another 5 samples B11, B12, B13, B14 and B15 were activated by 1, 3, 5, 7 and 9 % Na_2CO_3 respectively at 70 °C for 3 hours. 20 g of sample was weighed in conical flask and 100 ml of the solution was added (liquor ratio 1:5). Then the samples filtered and washed by distilled water till pH neutralized. Then the samples dried at 90 °C.

2. NaOH activation

In this activation another 5 samples B16, B17, B18, B19 and B20 were activated by 1, 3, 5, 7 and 9 % NaOH respectively at 70 $^{\circ}$ C for 3 hours. 20 g of sample was weighed in conical flask and 100 ml of the solution was added (liquor ratio1:5). Then the samples filtered and washed by distilled water till pH neutralized. Then the samples dried at 90 $^{\circ}$ C. All the samples were characterized using XRF (ZSX Primus IV, Rigaku), swelling test (ASTM-D5890) and Cation Exchange Capacity (CEC), Cation exchange capacity of bentonite was investigated using BaCl₂ method (Dardir *et al.*, 2018).

After sample B 13 (5 % Na₂CO₃ activation) was selected, because it has the best swelling and more cation exchange capacity, it was characterized using XRF (ZSX Primus IV, Rigaku), XRD (Panalytical X PERT PRO), IR (Agilent

6

Cary 630 FTIR), and Scanning electron microscope, SEM model Quanta 250 FEG attached with EDX unit (Energy Dispersive X-ray analysis). The removal process of methylene blue by sample B13 (activated bentonite) was studied with changing several parameters (pH, temperature, initial concentration, bentonite dose and time effect). In this process we depended on Shimadzu UV-visible spectrophotometer (model NO.160A, Japan) by preparing standard curve and measured the samples at 665 nm. In order to study the batch kinetics of the adsorption process, the remaining concentration of MB in the solution was studied at pre-determined intervals of time. According to the percentage dye removal can be calculated as follows (Khan, 2020):

(C_o- C_e) % Dye removal = ----- X 100 C_o

Where C_o is the initial dye concentration (mg/L), C_e is the equilibrium concentration. The amount of dye adsorbed per unit weight of the adsorbent; q_e (mg/g) was calculated using the following equation (Khan, 2020):

$$V$$

 $q_e = (C_o - C_e) x$ -----

Where V is the volume of dye solution (L), and m is the adsorbent mass (g). All experiments were carried out in duplicate, and the average values were used in further calculations.

m

Vol. (51); Iss. (8); No. (4); August, 2022 ISSN 1110-0826 ONLINE ISSN 2636 - 3178

RESULTS AND DISCUSSION

The natural bentonite sample A and purified sample B were characterized using XRF, XRD, Swelling Index and cation exchange capacity. Results indicated that there was upgrading in the purified sample B. XRF results show that there is an improvement in iron percentage because of magnetic separation process (Table 1) and XRD results show the presence of montmorillonite group in sample A and sample B and disappear of carbonates (dolomite) in sample B due to acetic acid treatment (Figure 1, 2).

COMPOSITION	SAMPLE A (RAW SAMPLE)	SAMPLE B (PURIFIED SAMPLE)
SiO ₂ %	51.1	50.95
TiO ₂ %	1.76	1.8
Al ₂ O ₃ %	17.25	19.14
Fe ₂ O ₃ %	8.97	7.9
MnO ₂ %	0.21	0.1
MgO %	1.9	1.75
CaO %	1.55	1.4
Na ₂ O %	0.7	0.71
K ₂ O %	1.75	1.84
P ₂ O ₅ %	0.1	0.11
SO ₃ %	0.25	0.19
L.O.I %	14.45	14.1

Table 1: XRF analysis of samples A and B

•••

8



Journal of Environmental Sciences (JES) Faculty of Graduate Studies and Environmental Research, Ain Shams University

Figure 1: XRD analysis for sample A



Figure 2: XRD analysis for sample B

Vol. (51); Iss. (8); No. (4); August, 2022 ISSN 1110-0826 ONLINE ISSN 2636 - 3178

Swelling index (Figure 3) and cation exchange capacity results showed that there was improvement in the sample B (Table 2).

Table 2: Swelling index and Cation Exchange Capacity (CEC) of natural and purified bentonite.

SAMPLE NO.	SWELLING INDEX	CEC (MEQ/100G)
А	7	45
В	10	47.5





Sample A

Sample B

Figure 3: Swelling of natural bentonite (sample A) and purified bentonite (sample B)

After that sample B is subjected to both acidic and alkali activation to select the best activated sample was used in methylene blue removal.

10

• Acidic activation

1. HCl activation

XRF analysis of HCl activated samples (B1, B2, B3, B4 and B5) showed that treatment of clays changes the clay structure by dissolving part of $A1_2O_3$ as well as of CaO, MgO, from the lattice and exchanging of the Ca and Mg ions, located at the surface of the crystal against hydrogen ions from the mineral acid (Table 3).

COMPOSI	SAMPLES				
TION	B1	B2	3	34	B5
SiO ₂	55.76	57.2	8.6	50.7	51.2
TiO ₂	1.55	1.54	.51	.51	1.5
Al ₂ O ₃	17.9	17.65	7.4	7.22	17.06
Fe ₂ O ₃	7.1	6.5	.93	1.33	4.25
MnO	0.06	0.04	.03	0.03	0.03
MgO	1.3	1.16	.01).86	0.75
CaO	0.9	0.85	.79).76	0.69
Na ₂ O	0.12	0.11	.04	0.03	0.02
K ₂ O	1.43	1.37	.26		1.13
P_2O_5	0.1	0.04	.01	0.01	0.01
SO ₃	0.11	0.09	.07).06	0.06
L.O.I	13.5	13.3	3.2	3.2	13.15

Table 3: XRF analysis of five HCl activated samples.

2. H₂SO₄ activation

XRF analysis of H_2SO_4 activated samples (B6, B7, B8, B9 and B10) showed that sulfuric acid activation changed the clay structure by dissolving part of Al_2O_3 as well as of CaO, MgO from the lattice and exchanging of the Ca and Mg ions from the crystal surface (Table 4).

Vol. (51); Iss. (8); No. (4); August, 2022 ISSN 1110-0826 ONLINE ISSN 2636 - 3178

Journal of Environmental Sciences (JES) Faculty of Graduate Studies and Environmental Research, Ain Shams University

Table 4: XRF analysis of five sulfuric acid activated samples

COMPOSI		S.	AMPLES		
TION	B6	B7	B8	B9	B10
SiO ₂ %	54.1	55.8	57.1	57.9	58.5
TiO ₂ %	1.8	1.79	1.79	1.77	1.78
Al_2O_3 %	18.5	17.9	17.4	17.1	16.9
Fe_2O_3 %	7.5	6.9	6.4	6.1	5.9
MnO	0.06	0.05	0.05	0.04	0.04
MgO	1.29	1.08	1.05	1.01	0.9
CaO	1.31	1.22	1.19	1.1	1.03
Na ₂ O %	0.16	0.14	0.1	0.08	0.08
K ₂ O %	1.37	1.3	1.26	1.2	1.18
P ₂ O ₅ %	0.09	0.09	0.1	0.08	0.09
SO ₃ %	0.15	0.15	0.15	0.14	0.14
L.O.I %	13.6	13.4	13.35	13.31	13.27

It is clear that, acid activation led to alteration in the clay structure, and it

appeared in swelling test (Figure 4) and Cation Exchange Capacity (Table 5).



Figure 4: Swelling of acid activation samples

Vol. (51); Iss. (8); No. (4); August, 2022 ISSN 1110-0826 ONLINE ISSN 2636 - 3178

Table 5: Swelling index and Cation Exchange Capacity (CEC) of acid activation

SAMPLE NO.	SWELLING INDEX ML/2G	CEC MEQ/100 G
В	7	32.
В	7	3
В	5	22.
В	5	18.7
В	5	17.
В	5	17.
В	4	16.
В	4	1
В	4	1
B1	4	12.

samples (B1-B5, HCl activation, B6-B10, H_2SO_4 activation)

Alkali activation

1. Na₂CO₃ activation

B11, B12, B13, B14 and B15 are five samples which activated by 1, 3, 5, 7 and 9 % Na₂CO₃ respectively. XRF analysis of Na₂CO₃ activated samples (B11-B15) showed that sodium carbonate activation led to increase sodium ions by exchanging of Na ions with Ca ions (Table 6).

> Vol. (51); Iss. (8); No. (4); August, 2022 ISSN 1110-0826 ONLINE ISSN 2636 - 3178

Journal of Environmental Sciences (JES) Faculty of Graduate Studies and Environmental Research, Ain Shams University

COMPOSITION	SAMPLES				
COMPOSITION	B11	B12	B13	B14	B15
SiO2 %	49.5	49.2	49	48.8	48.5
TiO2 %	1.93	1.99	2.05	2.11	2.15
A12O3 %	19	18.8	18.7	18.5	18.4
Fe2O3 %	7.95	8.07	8.15	8.5	8.55
MnO %	0.1	0.11	0.09	0.1	0.09
MgO %	1.68	1.55	1.5	1.47	1.44
CaO %	1.14	1.03	0.88	0.84	0.8
Na2O %	1.84	2.37	2.64	2.68	2.7
K2O %	1.64	1.6	1.58	1.55	1.51
P2O5 %	0.11	0.09	0.1	0.1	0.11
SO3 %	0.24	0.24	0.23	0.24	0.25
L.O.I %	14.8	14.85	14.88	14.9	15.2

Table 6: XRF analysis of five Na₂CO₃ activated samples

2. NaOH activation

XRF analysis of NaOH activated samples (B16, B17, B18, B19 and B20) showed that sodium concentration increased by increasing sodium hydroxide percentage and calcium concentration decreased and partially decreasing in silica concentration (Table 7).

CONDOCUTION	SAMPLES				
COMPOSITION	B16	B17	B18	B19	B20
SiO2 %	47.5	47	46.48	46.3	46.1
TiO2 %	2.07	2.03	2.06	2.05	2.06
A12O3 %	19.5	18.95	18.75	18.55	18.5
Fe2O3 %	8.5	9	9.84	10	10.1
MnO %	0.09	0.1	0.1	0.11	0.11
MgO %	1.7	1.65	1.59	1.54	1.5
CaO %	1.49	1.42	1.37	1.26	1.2
Na2O %	1.7	1.81	1.86	1.94	1.99
K ₂ O %	1.69	1.66	1.65	1	1.53
P ₂ O ₅ %	0.09	0.09	0.1	0	0.09
SO ₃ %	0.24	0.24	0.25	0	0.25
L.O.I %	15	15.42	15.8	1	16

Table 7: XRF analysis of five NaOH activated samples.

14

It observed that alkali activation led to improvement of bentonite as it obvious in swelling (Figure 5) and cation exchange capacity (Table 8).





- Figure 5: Swelling of alkali activation, Na₂CO₃ (samples B11-B15) NaOH (samples B16-B20)
- **Table 8:** Swelling index and Cation Exchange Capacity (CEC) of alkali activation samples

SAMPLE NO.	SWELLING INDEX ML/2 G	CEC MEQ/100 G
B11	13	47.5
B12	22	55
B13	27	60
B14	24	51
B15	23	50
B16	19	37.5
B17	20	37.5
B18	13	32.5
B19	13	32.5
B20	12	25

Vol. (51); Iss. (8); No. (4); August, 2022 ISSN 1110-0826 ONLINE ISSN 2636 - 3178

From the previous results, sample B13 (5 % Na_2CO_3 activated sample) is the best sample. So, sample B13 used in methylene blue removal by changing several parameters. Sample B13 was characterized by XRD, IR and SEM to know the composition of the sample.

X-Ray Diffractograms



XRD analysis of activated bentonite B13 (5 % Na_2CO_3 activated sample) shows the presence of montmorillonite as the major component. Kaolinite and quartz are also present (Figure 6).

Figure 6: XRD pattern of sample B13

Vol. (51); Iss. (8); No. (4); August, 2022 ISSN 1110-0826 ONLINE ISSN 2636 - 3178

FTIR Spectrum Analysis:

The FTIR spectrum of sample B13 (5 % Na₂CO₃ activated sample) was measured in the range of 400–4000 cm⁻¹ (Figure 7). The spectrum of B13 shows absorption bands at 3450 and 1650 cm⁻¹ assigned to the stretching and bending vibrations of the OH groups for water of hydration molecule, which adsorbed on the sample surface, and a band at 3620 cm⁻¹ indicated the stretching vibration of the hydroxyl groups coordinated to octahedral Al³⁺ cations. Clear absorption band at 1030 cm⁻¹ is recognized for stretching vibration Si-O bands, which is strong evidence for a silicate structure. The bands are at 520 for Si-O-Al (octahedral) and 460 cm⁻¹ for Si-O-Si bending vibrations. The bands at 520, 698, and 791 cm⁻¹ associated with Si-O-Al vibration (Figure 7).



Figure 7: IR spectra of sample B13

Vol. (51); Iss. (8); No. (4); August, 2022 ISSN 1110-0826 ONLINE ISSN 2636 - 3178

Scanning Electron Microscope

The result of scanning electronic microscope shown in Figure 8 which indicated that 5 % Na_2CO_3 activated bentonite (B13) was dispersed, flat surface, better continuity and clear hole which led to better adsorption (Figure 8).



Figure 8: SEM (Scanning Electron Microscope) of 5 % Na₂CO₃ activated sample B13.

• MB Removal Results:

MB removal was explored by studying the effect of changing several parameters such pH of Methylene Blue (MB) solution, temperature, initial concentration of MB dye, adsorbent dose (5 % Na₂CO₃ activated sample, B13) and contact time effect to achieve the optimum condition of methylene blue adsorption onto the adsorbent, sample B13.

• Effect of pH:

Initial pH of MB dye solution affects the dye adsorption onto the adsorbent (5 % Na₂CO₃ activated sample, B13). The initial pH affected by several factors ¹⁸ Vol. (51); Iss. (8); No. (4); August, 2022

like surface charge of the adsorbent, degree of ionization of the adsorbate molecule, and the extent of dissociation of functional groups on the active sites of the adsorbent. Generally, the percentage of dye removal is low at low pH range due to the prescence of excess H⁺ ions that may compete with the cationic dye for adsorption sites (Elmoubarki et al., 2015). In order to study the effect of initial solution pH, a series of MB dye solutions (50 ml volume, 200 mg/L MB concentration) were prepared with different pH ranging from 3 to 11. The pH of these solutions was adjusted using 0.1 M HCl and 0.1 M NaOH solutions. 0.05 g of adsorbent dosage, B13 (1 g/L) was used and shacked for 60 min at 20 $^{\circ}$ C using water bath shaker (Figure 9). The remaining solution measured using Shimadzu UV- visible spectrophotometer by preparing standard curve and measured the samples at 665 nm. The removal efficiency of each pH solution was calculated (95.34, 96.45, 99.1, 99.13, 99.13 % for pH 1, pH 3, pH 5, pH 7, pH 9 respectively) and the optimum pH was selected (neutral solution, pH = 7) and was used for all next experiments.

Vol. (51); Iss. (8); No. (4); August, 2022 ISSN 1110-0826 ONLINE ISSN 2636 - 3178



٠

5

6

4

7

8

9

10

11

۵

3

2

1

Journal of Environmental Sciences (JES) Faculty of Graduate Studies and Environmental Research, Ain Shams University

pH solution

Figure 9: Effect of initial solution pH on Methylene Blue (MB) adsorption onto adsorbent, B13 (contact time 60 min, adsorbent dosage 1 g/L, MB concentration: 200 mg/L and temperature 20 $^{\circ}$ C).

• Effect of bentonite dose:

0

Adsorbent dosage effect was examined to know the optimum dosage with respect to dye concentration. It is clear from the chart that, as the adsorbent dosage increases, the removal efficiency also increases. This is expected because there are excess in adsorption sites present at the adsorbent surface. 0.25, 0.5, 0.75, 1 and 1.25 g/L of bentonite were used with 50 ml of 200 mg/L MB at pH 7 and 20 °C for 60 min (Figure 10). The remaining solution was measured using Shimadzu UV- visible spectrophotometer and the removal

20

efficiency was calculated for each adsorbent dose (23.5, 47.5, 71, 99.15, 100 % for 0.25, 0.5, 0.75, 1, 1.25 g respectively).



Figure 10: Effect of initial adsorbent dosage on Methylene Blue (MB) adsorption (contact time 60 min, pH 7, MB concentration: 200 mg/L and temperature 20 $^{\circ}$ C).

• Effect of contact time

The adsorption of MB changed as a function of contact time and the removal efficiency increased with increasing the contact time and the maximum adsorption of dye takes place in the first ten minutes. After that there was a very gradual increase in dye adsorption and nearly reached equilibrium within 40 min of the initial contact. This may be because of the presence of the negatively charged surface of adsorbent which caused rapid

> Vol. (51); Iss. (8); No. (4); August, 2022 ISSN 1110-0826 ONLINE ISSN 2636 - 3178

Eleraky et al.

```
Eleraky et al.
```

electrostatic adsorption of cationic dye methylene blue from the solution at neutral pH (Khan, 2020). removal efficiency studied by changing contact time from 10, 20, 30, 40 and 50 min with fixing the other parameters, 50 ml of 200 mg/L MB, pH 7, 20 $^{\circ}$ C and 0.05 g = 1 g/L of adsorbent dosage, (Figure 11). The removal efficiency was calculated for each time period (95.3, 97.4, 98.05, 99.13, 99.22 % for 10, 20, 30, 40, 50 min).





mg/L and temperature 20 $^{\circ}$ C).

• Effect of initial concentration

It was observed that removal efficiency of methylene blue decreased by varying the initial dye concentration (50 ml of 50, 100, 150, 200 and 250 mg/L MB) and keeping the other variables (1 g/L bentonite, 20 °C, pH 7 and 60 min). ²²Vol. (51); Iss. (8); No. (4); August, 2022 ISSN 1110-0826 ONLINE ISSN 2636 - 3178

```
Eleraky et al.
```

This may be because there are not enough active sites for the adsorbate to interact with (Figure 12). The removal efficiency was calculated for each solution (100, 100, 100, 99.13, 78 % for 50, 100, 150, 200, 250 mg/L).



Figure 12: Effect of initial Methylene Blue (MB) concentration on the adsorption onto the adsorbent (contact time 60 min, pH 7, adsorbent dosage 1 g/L and temperature 20 $^{\circ}$ C).

• Effect of temperature

Methylene blue removal efficiency enhanced by increasing temperature and this is due to increasing collisions and reaction rates at the interface between the adsorbent and adsorbate. Any increase in temperature should produce a swelling effect within the layers permitting easier penetration of the MB molecules. The enhancement was observed by changing temperature from 20, 30, 40, 50 and 60 $^{\circ}$ C and the removal efficiency was 78, 79.2, 80.4, 80.8, 80.8 % respectively with keeping the other variables constant, 50 ml of

> Vol. (51); Iss. (8); No. (4); August, 2022 ISSN 1110-0826 ONLINE ISSN 2636 - 3178

```
Eleraky et al.
```

250 mg/L MB, pH 7, 1g/L adsorbent dosage and contact time 60 min, (Figure 13).



Figure 13: Effect of initial temperature on Methylene Blue (MB) adsorption onto the adsorbent (contact time 60 min, pH 7, MB concentration: 200 mg/L and adsorbent dosage 1 g/L).

CONCLUSION

Based on the results of the study the following can be concluded:

- Modification of bentonite can be done using 0.1 N acetic acid wash to remove carbonates and magnetic separation to reduce iron content then activated using 5 % Na₂CO₃.
- Activated bentonite has better properties compared to the natural Egyptian bentonite clay where the swelling value and cation exchange capacity were improved and appeared in methylene blue removal.

Vol. (51); Iss. (8); No. (4); August, 2022 ISSN 1110-0826 ONLINE ISSN 2636 - 3178

• Activation of bentonite is very important in industry where it considered as low cost technique by using smaller quantity of activated bentonite than the raw bentonite.

REFERENCES

- Ali, M. M.; Attia, A. A.; Taha, M. H.; El-Maadawy, M. M.; Abo-Raia, A. M. and Abouria, A. (2019). Application of Acid Activated Bentonite for Efficient Removal of Organic Pollutants from Industrial Phosphoric Acid: Kinetic and Thermodynamic Study. In SPE Middle East Oil and Gas Show and Conference. OnePetro.
- Bharti, V.; Vikrant, K.; Goswami, M.; Tiwari, H.; Sonwani, R.K.; Lee, J.; Tsang, D.C.; Kim, K.H.; Saeed, M.; Kumar, S. and Rai, B.N. (2019). Biodegradation of methylene blue dye in a batch and continuous mode using biochar as packing media. Environmental research, 171:356-364.
- Cinperi, N. C.; Ozturk, E.; Yigit, N. O. and Kitis, M. (2019). Treatment of woolen textile wastewater using membrane bioreactor, nanofiltration and reverse osmosis for reuse in production processes. Journal of cleaner production, 223:837-848.
- Dardir, F. M.; Mohamed, A. S.; Abukhadra, M. R.; Ahmed, E. A. and Soliman, M. F. (2018). Cosmetic and pharmaceutical qualifications of Egyptian bentonite and its suitability as drug carrier for Praziquantel drug. European Journal of Pharmaceutical Sciences, 115: 320-329.
- De Castro, M. L. F. A.; Abad, M. L. B.; Sumalinog, D. A. G.; Abarca, R. R. M.; Paoprasert, P. and de Luna, M. D. G. (2018). Adsorption of methylene blue dye and Cu (II) ions on EDTA-modified bentonite:

Vol. (51); Iss. (8); No. (4); August, 2022 ISSN 1110-0826 ONLINE ISSN 2636 - 3178

isotherm, kinetic and thermodynamic studies. Sustainable Environment Research, 28(5): 197-205.

- Donneys-Victoria, D.; Bermúdez-Rubio, D.; Torralba-Ramírez, B.; Marriaga-Cabrales, N. and Machuca-Martínez, F. (2019). Removal of indigo carmine dye by electrocoagulation using magnesium anodes with polarity change. Environmental Science and Pollution Research, 26(7): 7164-7176.
- Dotto, J.; Fagundes-Klen, M. R.; Veit, M. T.; Palacio, S. M. and Bergamasco, R. (2019). Performance of different coagulants in the coagulation/flocculation process of textile wastewater. Journal of cleaner production, 208: 656-665.
- Elmoubarki, R.; Mahjoubi, F.Z.; Tounsadi, H.; Moustadraf, J.; Abdennouri, M.; Zouhri, A.; El Albani, A. and Barka, N.(2015). Adsorption of textile dyes on raw and decanted Moroccan clays: kinetics, equilibrium and thermodynamics. Water resources and industry, 9: 16-29.
- Elwakeel, K. Z.; Elgarahy, A. M. and Guibal, E. (2021). A biogenic tunable sorbent produced from upcycling of aquatic biota-based materials functionalized with methylene blue dye for the removal of chromium (VI) ions. Journal of Environmental Chemical Engineering, 9(2), 104767.
- Ismaeel, S. H.; Mabrouk, M. S.; Ali, A. A. A. and Abn-Elwalead, K. (2017). Synthesis and characterization of bentonite nanocomposites from Egyptian bentonite clay. Nanotechnology, 1(1): 16-29.
- Khan, N.; Chowdhary, P.; Ahmad, A.; Giri, B. S. and Chaturvedi, P. (2020). Hydrothermal liquefaction of rice husk and cow dung in Mixed-Bed-Rotating Pyrolyzer and application of biochar for dye removal. Bioresource technology, 309, 123294.
- Magzoub, M. I.; Nasser, M. S.; Hussein, I. A.; Benamor, A.; Onaizi, S. A.; Sultan, A. S. and Mahmoud, M. A. (2017). Effects of sodium

26

carbonate addition, heat and agitation on swelling and rheological behavior of Ca-bentonite colloidal dispersions. Applied Clay Science, 147:176-183.

- Muhammad, N. and Siddiqua, S. (2021). Moisture-dependent resilient modulus of chemically treated subgrade soil. Engineering Geology, 285, 106028.
- Naushad, M.; Alqadami, A. A.; AlOthman, Z. A.; Alsohaimi, I. H.; Algamdi, M. S.and Aldawsari, A. M. (2019). Adsorption kinetics, isotherm and reusability studies for the removal of cationic dye from aqueous medium using arginine modified activated carbon. Journal of Molecular Liquids, 293, 111442.
- Omer, O. S.; Hussein, M. A.; Hussein, B. H. and Mgaidi, A. (2018). Adsorption thermodynamics of cationic dyes (methylene blue and crystal violet) to a natural clay mineral from aqueous solution between 293.15 and 323.15 K. Arabian Journal of Chemistry, 11(5), 615-623.
- Peres, E. C.; Slaviero, J. C.; Cunha, A. M.; Hosseini–Bandegharaei, A. and Dotto, G. L. (2018). Microwave synthesis of silica nanoparticles and its application for methylene blue adsorption. Journal of Environmental Chemical Engineering, 6(1): 649-659.
- Premkumar, M. P.; Thiruvengadaravi, K. V.; Senthil Kumar, P.; Nandagopal, J. and Sivanesan, S. (2018). Eco-friendly treatment strategies for wastewater containing dyes and heavy metals. In *Environmental Contaminants* (pp. 317-360). Springer, Singapore.
- Reck, I. M.; Paixao, R. M.; Bergamasco, R.; Vieira, M. F. and Vieira, A. M. S. (2018). Removal of tartrazine from aqueous solutions using adsorbents based on activated carbon and Moringa oleifera seeds. Journal of Cleaner Production, 171: 85-97.
- Shetti, N. P.; Malode, S. J.; Malladi, R. S.; Nargund, S. L.; Shukla, S. S. and Aminabhavi, T. M. (2019). Electrochemical detection and

Vol. (51); Iss. (8); No. (4); August, 2022 ISSN 1110-0826 ONLINE ISSN 2636 - 3178

degradation of textile dye Congo red at graphene oxide modified electrode. Microchemical Journal, 146:387-392.

- Sözen, S.; Olmez-Hanci, T.; Hooshmand, M. and Orhon, D. (2020). Fenton oxidation for effective removal of color and organic matter from denim cotton wastewater without biological treatment. Environmental Chemistry Letters, 18(1):207-213.
- Venkatesh, S. and Venkatesh, K. (2020). Ozonation for degradation of acid red 14: effect of buffer solution. Proceedings of the National Academy of Sciences, India Section A: Physical Sciences, 90(2): 209-212.
- Yan, L.; Liang, M.; Wang, D.; Zhang, L.; Zhu, Z. and Huang, D. (2019, April). Dynamic adsorption of As (V) by hydroxyapatite/bagasse biomass carbon composite adsorbent. In IOP Conference Series: Materials Science and Engineering (Vol. 490, No. 3, p. 032037). IOP Publishing.

إزالة حبغة أزرق الميثلين بواسطة طغلة البنتونيت المصرية المنشطة

محمود إبراهيم العراقي^(۱) – طه عبد العظيم محمد عبد الرازق^(۲) – أحمد ماهر عبد البصير^(۲)) كيميائي بالهيئة المصرية للثروة المعدنية ٢) كلية الدراسات العليا والبحوث البيئية، جامعة عين شمس

المستخلص

هدفت هذه الدراسة إلى تتشيط طفلة البنتونايت المصرى الكالسيوم, الذى تم الحصول عليها من منطقة العلمين شمال مصر لاستخدامه في إزالة صبغة أزرق الميثيلين. تم سحق البنتونيت المصرى، وطحنه بواسطة طاحونة بالكور ، وتنقيته باستخدام الفصل المغناطيسي، ومعالجته بحمض الخليك 0.1 عيارى وأخيرا تنشيطه عن طريق التنشيط الحمضي (حمض الهيدروكلوريك , حمض الكيريتيك والتنشيط القلوى (كريونات الصوديوم , هيدروكسيد الصوديوم) باستخدام ١ و قدرة تبادل الأيونات الموجبة الأحمض المغناطيسي، ومعالجته بحمض الخليك 0.1 عيارى وأخيرا تنشيطه عن طريق التنشيط الحمضي (حمض الهيدروكلوريك , حمض الكيريتيك والتنشيط القلوى (كريونات الصوديوم , هيدروكسيد الصوديوم) باستخدام ١ و ٣ و ٥ و ٧ و ٩ ٪ من الأحماض والتنشيط القلوى (كريونات الصوديوم , هيدروكسيد الصوديوم إلاشعي السينية عالم دالم وقدرة تبادل الأيونات الموجبة والختبار الانتفاخ. تم اختيار عينة تنشيط ٥٪ كريونات الصوديوم لإزالة صبغة أزرق الميثيلين بسبب انها

Vol. (51); Iss. (8); No. (4); August, 2022 ISSN 1110-0826 ONLINE ISSN 2636 - 3178

أعطت أفضل نتائج لاختبار الانتفاخ و اختبار قدرة تبادل الأيونات الموجبة. تم دراسة الامتزاز لتقييم تأثير عوامل تجريبية مختلفة (تأثير الرقم الهيدروجيني، ، تأثير درجة الحرارة ، تأثير التركيز الأولى، تأثير جرعة البنتونيت وتأثير الوقت). كانت إزالة الميثيلين الأزرق مثالية عند ٤٠ درجة مئوىة ، ودرجة الحموضة ٧ ، و ٤٠ دقيقة ، وتركيز ٢٠٠ حزء في الملبون واستخدام ١ حم / لتر من الدنتونيت المنشط. الكلمات المفتاحية: البنتونايت الكالسيومى، صبغة أزرق الميثيلين، التنشيط القلوي، الانتفاعة الحر، قدرة تبادل الايونات الموجبة.

> Vol. (51); Iss. (8); No. (4); August, 2022 ISSN 1110-0826 ONLINE ISSN 2636 - 3178