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Heavy Oil Fly Ash as an Adsorbent for Methylene Blue Removal from Aqueous Solution

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Abstract

The industry produces a large amount of solid waste that has very bad effects on the environment. The application of waste material adsorbents for waste materials treatment has become of greater interest. Heavy oil fly ash (HOFA) is hazardous industrial solid waste which produces from the combustion of heavy fuel oil in power plants. The work aims to investigate using waste material heavy oil fly ash (HOFA) after modification to activated carbon (AC) as an adsorbent of methylene blue (MB) in an aqueous solution. Chemical and physical analyses were conducted to characterize the HOFA produced as a by-product of an electrical power station. BET analysis showed the surface area was 1.6 m^2/g and the surface area was enhanced by the activation process to 63.7 m^2/g and the pore width to 553.5A. SEM showed a change in the nature of the surface of the martial by increasing the porosity. Adsorption studies were performed by batch experiments as a function of process parameters. The removal percentage increased with the increase of the adsorbent to 1.5g, the amount was selected as the optimum dosage. The removal percentage decreased with an increase the entail dye concentration and limited difference in pH variables. The experimental adsorption data was represented with Langmuir, Freundlich, and Tempkin isotherms. The data fitted well to the Freundlich model as multilayer adsorption.

1. Introduction

Environmental pollution is the main problem connected with rapid industrialization, urbanization and rise in living standards of people. The industry produces huge amount of solid waste that has very bad effects on environment. Heavy oil fly ash (HOFA) is one of hazardous industrial solid waste which produces from combustion of heavy fuel oil in power plants [1].

Fly ash with varying particle diameters is trapped by using an electrostatic precipitator. The characteristics of HOFA are determined by the type of fuel and the method of combustion. Chemical analysis reveals that HOFA is primarily composed of carbon (e.g., 50–90 percent). It also contained heavy metals found in crude petroleum, such as arsenic, copper, mercury, and cadmium [2]. The characteristics showed that toxic materials should not be discharged directly into the environment [3]. Hence, when disposed of in landfill, it poses environmental concern as causes the spread of fine particles containing toxic substances that are dangerous to health. Limited studies have focused on the characterization and utilization of HOFA. HOFA particle usually ranges from 10 to 120 m. HOFA particles contain small pores of a few microns in size that may have shaped during the combustion process. The color of HOFA is close to carbon black; however, the color of HOFA mainly based on the burning process and the properties of the heavy oil [4].

Activated carbon is defined as high porosity carbonaceous material with an internal surface area. The desired properties for an AC has a large surface area, suitable pore distribution, high surface reactivity and significant mechanical strength. The commercial AC has internal surface areas between 500 and 1.500 m^2/g; and the greater surface area is preferred as a stronger adsorbent [1]. Production of adsorbent form low-cost materials have been attracted many researchers. Many studies developed waste materials for this purpose[5, 6]. The present work encourages producing activated carbon from HOFA. AC has proven applications in environmental purification. Adsorption is one of the most effective methods of removing colors, odors, oils, and organic pollutants from process or waste effluent. Adsorption consider as an excellent technique for water treatment in terms of simple design, ease of operation, initial cost and insensitivity to harmful substances [7].

Because of its excellent adsorption capability, activated carbon is the most widely used adsorbent. However, the cost of using commercial activated carbon (CAC) to treat industrial pollutants is high, prompting researchers to create more affordable adsorbents. Therefore, many researchers have looked into less expensive alternative substitutes and that capable of having a preferable adsorptive capacity. These articles investigate the use of fly ash, bottom ash, cellulose-based waste, starch, rice husk.... etc [9]. Recently, few studies have been conducted on HOFA as a possible absorbent source. Caramuscio et al. (2003) synthesized AC from HOFA and discovered that the surface area was 156 m^2/g [8]. Mofarrah et al. (2014) prepared AC from HOFA by using H_3PO_4 as chemical agent and the surface area was 144.8 m^2/g [1]. Dyes and pigments are used in most industries to color their products[9]. The most commonly used substance for dying wood, cotton, and silk is methylene blue ($C_{16}H_{18}N_3SCl.3H_2O$), a cationic dye. Although MB is not considered highly toxic dye, it can cause some harmful effects on human beings such as vomiting, increased heart rate, jaundice, diarrhea, shock, quadriplegia, cyanosis, and tissue necrosis. As result, MB containing wastewater must be treated before discharge [10]. Methylene blue is chosen as a model compound to evaluate its ability to remove methylene blue from aqueous solutions.

This study aims to explore the use of industrial solid waste in adsorption. It investigates the beneficial of heavy oil fly ash as adsorbent in the adsorption of methylene blue in the aqueous solution. The specific objectives of the research are as follows: to examine the characteristics of the heavy oil fly ash and to evaluate the improved adsorbent performance in adsorption of methylene blue in aqueous solution.

2. Experimental Procedure

2.1. Preparation of Activated Carbon

For this research, HOFA samples were assembled instantly from the electrostatic precipitator (ESP) Power Plant in South Baghdad. The acids used for the washing and leaching process are 15 % hydrochloric acid, and 28 % nitric acid [1]. At a ratio of 10 g of raw HOFA to 50 ml of nitric acid (28% HNO_3) at 60 °C for two hours, the raw HOFA was treated with an aqueous acid solution. The residues were washed six times after filtration to eliminate the NO^{3-} ions till pH mixture exceeds 6. Afterwards, the filtrate residue was blended with 15 % hydrochloric acid solution at 60 °C for one hour in the same method mentioned above then filtered to get the filtered cake. Repeatedly the filtered cake was rinsed with water to get rid of the chloride ions. To obtain the unburned carbon, the filtered cake was then put in furnace at 105 °C for 5 h. The dried unburned carbon was activated by blending with H_3PO_4 for 30 min at 80 °C and then the material was dried. The tubular furnace was programmed heat rate was increased 5 °C/min until reaching at 800°C [1] with a constant nitrogen flow of 5 ml/min was applied in the process. Then the calcined product was cleaned with 0.5N HCl by mixing at 80 °C for 30 min. the filtered cake was then washed with water four times until the pH become 7. Finally, the activated carbon was put in furnace at 100 °C for 5h four drying.

2.2. Characterization of HOFA & AC

Ultimate analysis was utilized to characteristic the carbon, hydrogen, nitrogen, and sulfur contents in HOFA. Measurements multipoint BET surface area were implemented to gain an overview of the porous characteristics of the HOFA and activated sample such as surface area, pore size distribution and pore volume. The analytical method involve of three steps, including dehydration, degassing under low volume vacuum pressure, and nitrogen gas adsorption at 77 K. Scanning surface microscopy (SEM) technology (TESCAN, Czech Republic) was used to analyze the material's surface and microstructure. SEM analysis reveals details about the morphology, crystalline structure, and orientation of the sample's constituent materials.

2.3. Adsorption Studies Experiments

Adsorption studies were carried out in batches to determine the removal of methylene blue and the adsorption capacity of activated carbon derived from HOFA. Various MB solutions with different initial concentrations were prepared by diluting stock solution (100 ppm). Equilibrium experiments were conducted using 250 ml conical flasks and 50 ml of dye solution was added to each flask and shaken for 4h at 25 °C. Dye concentrations in the solutions were calculated by measuring absorbance using UV -visible spectrophotometer. The removal percentage of MB was determined using following equation (1) [11]

$$\%\,\boldsymbol{Removal} = \frac{\boldsymbol{Ci - Ce}}{\boldsymbol{Ci}} * \mathbf{100} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (\mathbf{1})$$

and the adsorption capacity of adsorbent was determined using following equation (2) [12]:

$$\boldsymbol{qe} = \frac{\boldsymbol{Ci - Ce}}{\boldsymbol{m}} * \boldsymbol{V} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (\mathbf{2})$$

Where *Ci* is the initial concentration of the solution and *Ce* is the concentration of methylene blue in mg/l at equilibrium, respectively, m is the amount of the adsorbent in g. *V* is the volume of the solution in mg/l. The following effects were investigated:

- **Effect of Adsorbent Dosage**

The doses of adsorbent were (0.05, 0.1, 0.3, 0.4, 0.5, 1, 1.5g). 250 ml conical flasks were filled with 50 ml of the aqueous solutions containing 25 ppm of MB. At a temperature of 25 °C and a speed of 250 rpm, the contact time was 4 hours.

- **Effect of Dye Concentration**

Initial MB concentrations of (10, 25, 50, and 100) were used in conjunction with the adsorbent dose 1.5g. The contact time was 4h at 25 °C and agitation speed 250 rpm.

- **Effect of pH**

Initial pH of MB solutions was adjusted to (3, 5, 7, 8.5, and 9) by adding dilute HCl and NaOH solutions. 50 ml of the aqueous solutions of 25 ppm of MB was taken, 1 g of adsorbent with continuous stirring at room temperature for 4 h.

- **Effect of Contact Time**

Half liter of aqueous solution of 25ppm of MB was taken then 1.5g of adsorbent was add to the solution. The solution exposed to variable agitation time (5, 10, 15, 30, 60, 120, and 240 min) with agitation speed 250 rpm.

2.4. Adsorption Isotherm

To describe adsorption isotherm relationships, several equilibrium models have been developed. The Langmuir, Freundlich, and Tempkin isotherm equations were used to analyze the data that was obtained. One of the commonly used models for describing monolayer sorption to the adsorbent is the Langmuir isotherm. The concentration of a medium above a solid surface at a constant temperature and the coverage of molecules on the solid surface are related by the Langmuir equation. The model implies that there will be no transmigration of the adsorbate and uniform energies of adsorption onto the surface. The maximum adsorption capacity on AC was determined using the Langmuir model [13]:

$$\frac{\boldsymbol{C_e}}{\boldsymbol{q_e}} = \frac{\mathbf{1}}{\boldsymbol{kq}} + \frac{\boldsymbol{C_e}}{\boldsymbol{q}} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots. (\mathbf{3})$$

C_e is the equilibrium concentration in milligram per liter (mg/l), q_e the amount of metal ion adsorbed in milligram per gram (mg/g). q_e is the amount adsorbed at a complete monolayer (mg/g) and k is a parameter related to the energy of the adsorption.

Freundlich isotherm is an experimental equation. This is one of the significant isotherms for describing adsorption equilibrium. Freundlich isotherm is usually used for heterogeneous surface energy system. The Freundlich equation is expressed [13]:

$$q_e = kC_e^{\frac{1}{n}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

The equation can be expressed in its linear form as:

$$logq_e = logk + \frac{1}{n} logC_e \ldots\ldots\ldots\ldots\ldots\ldots\ldots 5$$

k and n are the freundlich constants. The intercept and the slope of the linear plot of $logq_e$ verses $logC_e$ under specified experimental conditions.

Tempkin isotherm model assumes an organized distribution of binding energies on the adsorbent surface. The Tempkin equation is expressed [14]:

$$q_e = \frac{RT}{b} \ln AC_e \ldots\ldots\ldots\ldots\ldots\ldots\ldots 6$$

The linear form of equation is:

$$q_e = \beta \ln \alpha + \beta \ln C_e \ldots\ldots\ldots\ldots\ldots\ldots\ldots 7$$

R is the universal gas constant J (mol K)$^{-1}$, T is the absolute temperature in Kelivn, b is the Tempkin constant correlating to heat of sorption (J/mg). β and α are calculated from the slope and intercept of q_e versus ln C_e.

3. Results and Discussion

3.1. Characterization of HOFA and AC

Table (1) shows the HOFA is typically composed of carbon (more than 93%) with miner content of hydrogen, nitrogen and sulfur.

Table (1). Ultimate analysis for HOFA.

Content	HOFA (wt. %)
Carbon	93.3
Hydrogen	1.5
Nitrogen	0.7
Sulfur	0.1

The BET (Brunauer, Emmett, and Teller) surface area analysis was performed as shown in Table 2. The specific surface area as received HOFA was 1.6 m^2/g, which represents very low surface area and the result was consisted with Mofarrah and his colleges when tested Saudi Arabian HOFA (the surface area was 1.45 m^2/g) [1]. Whereas, after chemical and physical treatment, a sharp increase in surface area from 1.6 to 63.7 m^2/g was observed. The increase was due to the dissolution of oxidizing deposits closing the pore openings. In addition, the micropore volume (0.0245 cm^3/g) was broaden during the treatment.

Table (2). Pore characterization of HOFA and AC.

Characterization	HOFA	AC
BET surface area (m^2/g)	1.6	63.7
Pore volume (cm^3/g)	ND	0.0245
Average pore width (A)	ND	553.5

ND: not detectable

SEM micrograph Figure (1) shows the characteristics of the particles of HOFA are mostly spherical in shape, spongy and hollow particles. The carbonaceous nature of the material is deduced from the porous particles as viewed in Figure (1 a).The particles are mostly porous in nature as shown in Figure (1 c) and this consistent with Salehin et al. [15]. By contrast, Figure (1 b, d) displays the material after preparation AC, the porosity of the particles is increased because of chemical treatment and calcination process.

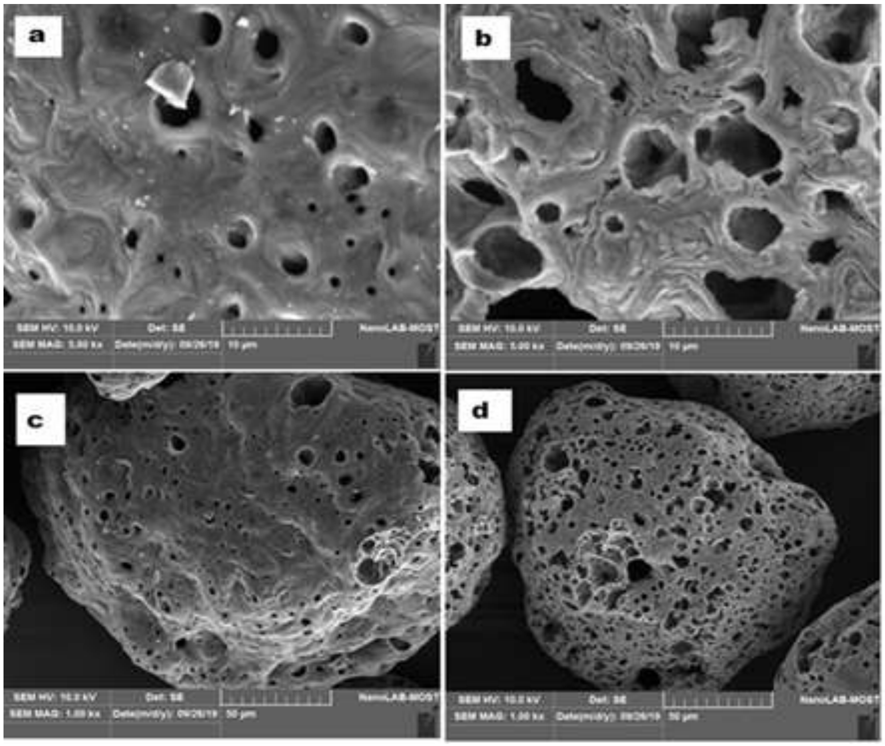

Figure (1). SEM analysis of the HOFA: (a, c) raw material, (b, d) after treatment.

3.2. Effect of Adsorbent Dosage

The effect of adsorbent dosage on removal percentage was investigated using variable amounts of AC produced from HOFA ranging from (0.025 to 1.5g) at a fixed volume of 50 ml with an initial dye solution which contains 25ppm. Other operation parameters for these tests were kept constant at 25 °C, 250 rpm agitation speed, 4 h of contact time, and an unadjusted pH for the initial MB solution. The results are shown in Figure (2). The maximum adsorption of MB was obtained for adsorbent dosage 1.5g. The observed increase in dye removal percentage with adsorbent dose was attributed to a rise in the surface area of the adsorbent that is available, as the number of adsorption sites rises correspondingly [16] and that was confirmed by BET surface area characterization. The findings suggest that 1.5 g of adsorbent, or the amount necessary for efficient MB removal, must be the fixed dosage of adsorbent for AC. Therefore, for the adsorption studies described in this work, 1.5 g/50 ml was chosen as the ideal AC dosage.

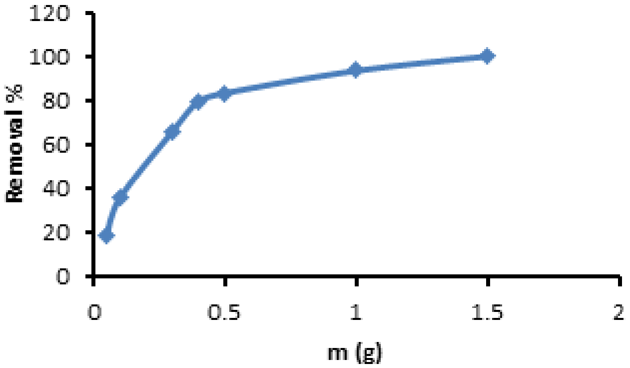

Figure (2). Effect of adsorbent dosage on MB removal.

3.3. Effect of Dye Concentration

The effect of dye concentration on its removal and adsorption capacity of MB onto AC produced from HOFA was carried out in the various concentrations (10, 25, 50, 100 mg/L) are shown in Figure 3. The dye molecules must first diffuse into the boundary layer during dye removal, then into the adsorbent surface, and finally into the porous structure of the adsorbent. At lower concentrations, it was seen that the percentage of dye removal could reach 100%. The percentage of dye removal fell as the initial dye concentration rose. Due to nearly complete binding site coverage at high dye concentrations, the percentage of dyes removed decreased as the initial dye concentration was increased. With an increase in initial dye concentration, the concentration gradient's driving force increases, which may explain how initial dye concentration affects the removal of dyes [17].

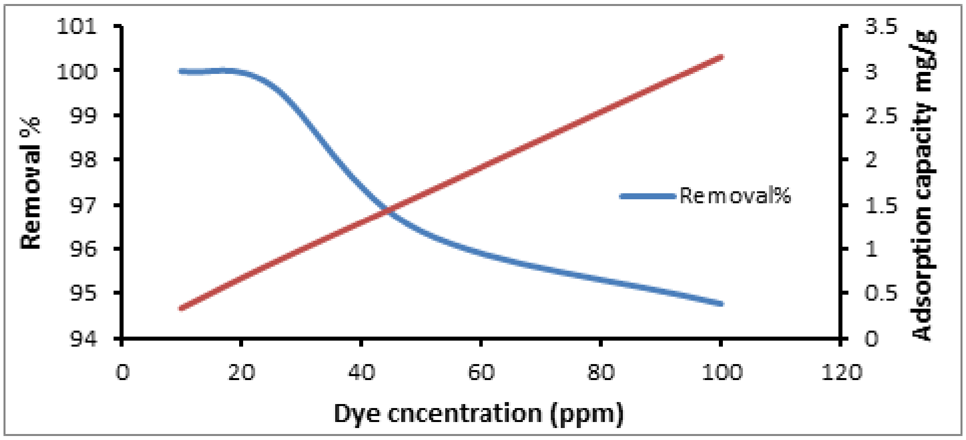

Figure (3). Effect of initial dye concentration on removal and adsorption capacity.

3.4. Effect of pH

The aqueous solution's pH has a significant impact on the dye adsorption process by altering an adsorbent's surface charge and the ionization behavior of the adsorbent and dye [7]. Figure 4 shows the effect of the solution pH on MB removal by carbonaceous materials. The maximum MB removal was observed at pH 9 since increased OH- ion which decreased the effect of the positive charge on the adsorbent surface as consequence the adsorption increases due to increase of the negative surface charge of adsorbent. Moreover, when the basic dye is dissolved in water, positively charged ions are produced. Therefore, in an acidic medium, the positively charged surface of the sorbent tends to prevent the cationic adsorbate from adhering. Increased electrostatic attraction between positively charged dye and negatively charged adsorbent is caused by the surface of the dye solution acquiring a negative charge as the pH of the solution rises [18]. The removal of MB at low pH 3 was 97%. Whereas, the removal percentage was decreased to 95% between pH 4-7 because the number of negatively charged of adsorbent sites was decreased.

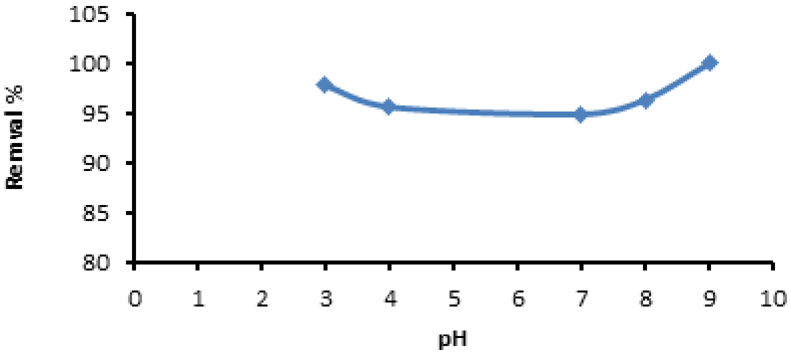

Figure (4). Effect of pH on MB removal.

3.5. Effect of Contact Time

Figure (5) depicts the effect of contact time on the removal of MB. AC removes 98% of the dye in 100 minutes. After 120 minutes, the equilibrium was reached. The change in adsorption rate because of the adsorbent sites are initially vacant and the solute concentration is very high. Later, the lower adsorption rate because of the reduction in the number of vacant adsorbent and dye concentration sites. The decreased adsorption rate, especially near the end of the experiments, indicates the possibility of MB monolayer formation on the adsorbent surface. This might be because there aren't enough active sites left after equilibrium to allow for further uptake. [19].

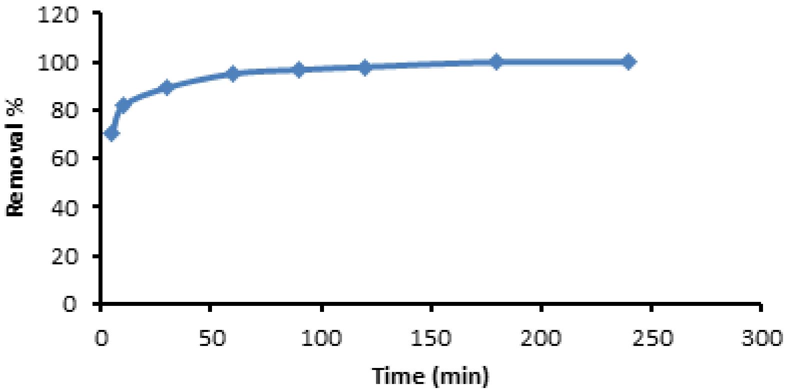

Figure (5). Effect of contact time on MB removal.

3.6. Adsorption Isotherms

Figure (7) shows equilibrium isotherm curves for experimental and theoretical results as relation between adsorption capacity and dye concentration at equilibrium after 4 h agitation where Table 3 shows estimated parameters for Langmuir, Frenulich and Tempkin isotherm models.

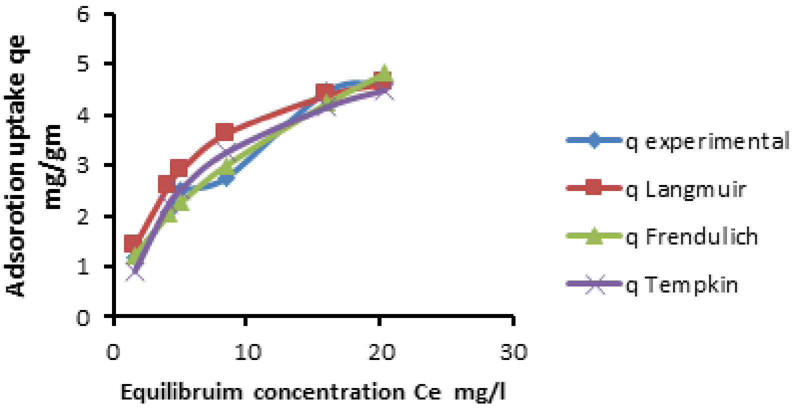

Figure (6). Adsorption isotherms of MB adsorbed by AC produced from HOFA.

Table (3). Isotherm parameters for the removal of methylene blue at different temperature.

Equation	Parameters	25 °C
Langmuir	K_L	0.202
	q_{th}	5.47
	R^2	0.98
Freundlich	K_f	0.939
	N	1.821
	R^2	0.99
Tempkin	B	1.499
	A	1.186
	R^2	0.949

Even though all models show good correlation which is represented by square correlation coefficients R2 for Freundlich model 0.99 while for Langmuir and Tempkin models were 0.98 and 0.949, respectively. And Langmuir model's qth calculated value 5.47 mg/g as the theoretical value which so encloses to an experimental value which explains the acceptable matching but R2 and N value 1.82 (recommended N value 1-10) but Freundlich model gave it more acceptability among others models. The average relative error (ARE) was applied statically for comparing experimental and calculated adsorption capacity, which was obtained by actual and model equilibrium isotherm results according to eq.15. The average relative error ARE values refers to the best value for the Freundlich model (0.05844) while (0.1588 and 0.0964) for Langmuir and Tempkin models, respectively.

$$\boldsymbol{ARE = \frac{1}{N}\left|\frac{qe-qm}{qe}\right|} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\mathbf{15}$$

Where qe experimental adsorption capacity mg/g, qm calculated adsorption capacity by equilibrium isotherm model mg/g, N number of data points.

4. Conclusions

The present study shows that activated carbon prepared from HOFA can be effectively used as an adsorbent for removable of MB from aqueous solution. Removal percentage of MB shows increasing with HOFA increasing dosage and decreasing of MB initial concentration while there is limited difference at pH variable. MB adsorption by HOFA show good fitting with Freundlich equilibrium isotherm model as multilayer adsorption and heterogeneous surface nature of HOFA surface.

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