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Bio-adsorption of Basic blue dye from aqueous solution onto raw and modified waste ash as economical alternative bio-adsorbent

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Abstract

Background: *Dyes are one of the most hazardous material in industrial effluents which can cause several health problems in bio-life. The removal of dye from colored effluents has been attracted increasing attention in the recent decay. In this study raw, beneficiated and activated waste ash was evaluated as an adsorbent for removal of methylene blue (MB) from aqueous solution by batch adsorption method. Comprehensive characterization studies were carried out on each bio-adsorbents such as proximate analyses, bulk density, specific surface area, point of zero charge, pH and Fourier-Transform Infrared (FTIR) spectroscopy (which shows functional groups on adsorbents surface).*

Results: *The effects of pH, adsorbent dosage, initial dye concentration, and contact time were determined in order to know the optimum condition and adsorption potential of the adsorbents. The methylene blue (MB) removal efficiency of raw, beneficiated and activated bio-adsorbents from aqueous solutions was recorded to be 95.212%, 89.172%, and 84.504%, respectively. It is reported that adsorption efficiency of MB on each adsorbents was quite different due to electrostatic and dispersion interaction between the dye molecules and the surface property of the adsorbents. The obtained results were well fitted with Freundlich isotherm model and adsorption process follows the pseudo second order kinetics model for both adsorbents.*

Conclusions: *In fact the results showed that raw, beneficiated and activated waste ash bio-adsorbents could be employed as effective and economical alternative material in the near future use.*

Key words: *Bio-adsorption, waste ash, adsorption capacity, surface modification, basic blue dye.*

Background

Many manufacturing industries such as textile, paper, plastics, cosmetics, leather and food use dyes for coloring their products [1]. About 50% of the total world production of dyes goes off during the dyeing process and have been release in textile effluents [2]. Those considerable amounts of dyes are lost and discharged in to water streams, which ultimately affects the aquatic life. In addition; the colored effluents are known to be carcinogenic and highly toxic to living things in contact by different mechanisms [3]. Among those dyes methylene blue is one of the basic (cationic) and heterocyclic aromatic compound in its structure. It has many applications which

includes coloring paper, dyeing textile products (wool, silk, cotton), and leather industries. In spite of several applications this dye has a number of negative impacts (if swallowed or made in contact with skin or eye) on human beings and animals; such as irritation of mouth, diarrhea, throat, stomach with symptoms of nausea, vomiting, shock, enhancing heartbeat, cyanosis, jaundice, and tissue necrosis in humans [1, 4]. Undesirable dye pollutions are required to remove from waste waters before being discharged to the environment. Several physical and chemical treatment methods such as adsorption, oxidation, biodegradation, chemical coagulation/flocculation, and chemical precipitation have been used for the treatment of wastewater containing dyes [4-6]. Adsorption is one of the physico-chemical methods, which is found to be most simple and economical to remove the dyes from effluents [7]. Several adsorbents have been reported in the literature such as eggshell powder [8], modified silica gel [9], tobacco steam ash [10], rice hull ash [11], tea waste [12], coffee grounds [13], fishery waste [14], coconut shell activated carbon [15] agricultural waste products [16], jatropha curcas pods [17], vegetable residues [18], calcined bones [19], waste bamboo culms [20], orange and banana peel [21], etc.

Removal harmful dyes from effluents is an economic fashion remains a major problem for textile industries [5]. However, high capacity low cost adsorbents are still under development to remove/minimize textile effluents. Waste ash is a leading waste in Woldia town, Ethiopia may be thought as other inexpensive material which used as adsorbents. It has been preferred as it is an easily available waste material mainly coming from hotels, student cafe's and other household activities and stored in a common waste disposal area. It is obtained from plant stems and charcoal for fuel/thermal energy purposes generates waste ash with no known economic uses. The main plant sources which used for such purposes is Girar (*Acacia bussei*). The aim of this work is to study the bio-adsorption potential of waste ash for the removal of harmful methylene blue from aqueous solution.

1. Material and methods

2.1 Preparation of bio-adsorbents

Waste ash; white in color and non-combustible residue was obtained from the waste disposal area of Woldia town, Ethiopia as shown in **Figure 1**. The waste ash used in this experiment was prepared without any treatment (raw) and modified with distilled water (beneficiated) and 1 N H₂SO₄ (activated) as a ratio of 1:5 with continuous stirring for 24 hr. The sample mixtures have

been filtered and washed several times with distilled water. Filtered waste ash samples were dried at 105°C for 24hr, powdered by mortar until the samples were equally fine, sieved in the size of 200 µm and kept in desiccators for further use.

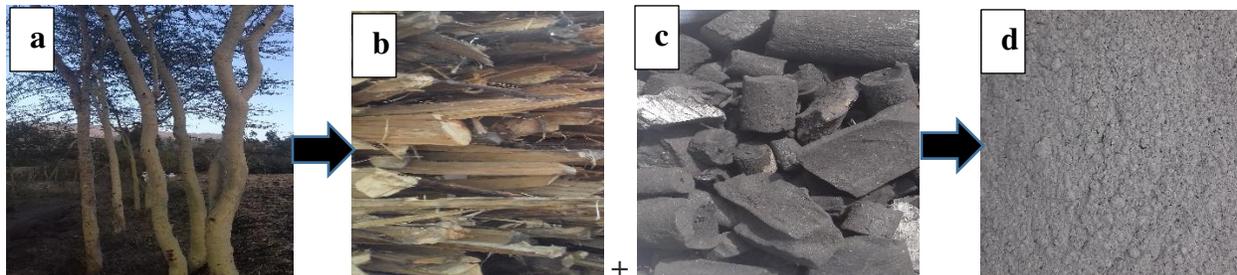


Figure 1. Girar, *Acacia bussei* (a), stem (b), charcoal (c) used for fuel source and disposed waste ash (d).

2.2 Preparation of basic blue dye (MB) solution

Basic blue dye (cationic dye) was taken from Kombolcha (S/Wollo) textile Share Company, Amhara region, Ethiopia. Basic blue dye is powdered solid, soluble in water, has molecular weight: 319.9g/mol, maximum absorption wavelength: 665nm, chemical formula: $C_{16}H_{18}ClN_3S$, and its IUPAC name: 3,7-bis (dimethyl amino)-phenothiazin-5-ium chloride. The stock solution (500 mg/L) of the dye was prepared and the required concentrations were obtained by serial dilution of the stock solution. The maximum wavelength of the dye (665nm) was obtained after full scanning using Uv/Vis spectrophotometer (Lamda 35 Perkin Elmer). A Linear calibration curve was obtained with different concentration of methylene blue dye solution as shown in **Figure 2**.

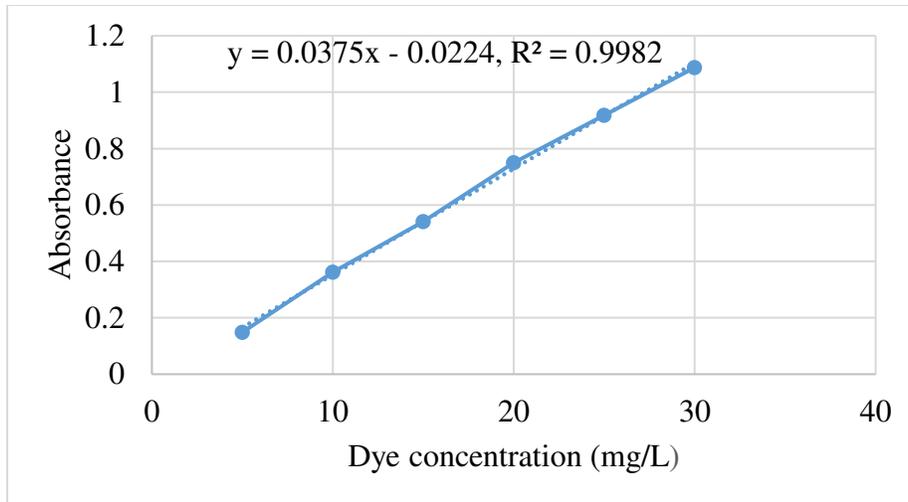


Figure 2. Calibration curve of MB dye solution at different concentration

2.3 Characterization of bio-adsorbents

The properties of the adsorbents such as moisture content, ash content, volatile matter, fixed carbon and bulk density were determined according to [22-25] with slight modifications.

Moisture content: About 1.0 g of adsorbent samples were weighed and placed in a clean, dried, and weighed crucible in a preheated oven at 105 °C for 4 hr. Then, the samples were cooled and kept in desiccators at room temperature and measured again. The moisture content of the adsorbents were obtained using **Equation 1**.

$$\text{Moisture content (MC)} = \frac{M_0 - M_1}{M_0} \times 100 \dots \dots \dots 1$$

Where, M_0 and M_1 are the initial and final mass (g) of the adsorbents, respectively.

Ash content: About 1 g of adsorbent samples were placed in crucibles, weighted and heated in a muffle furnace (Nabertherm B180) under a temperature of 500 °C for 4 h. After that, the crucibles containing samples were allowed to cool in a desiccator to room temperature and reweighed. The ash content of samples were calculated using the Equation 2.

$$\text{Ash content (AC)} = \frac{M_s}{M_a} \times 100 \dots \dots \dots 2$$

Where, M_a and M_s are the mass (g) of the adsorbents and ashes, respectively.

Volatile matter: 1.0 g of the adsorbent samples were taken and placed in a pre-dried crucibles and heated in a muffle furnace regulated at 500 °C for 8 min. Then, the crucibles were cooled in desiccators and weighed. Finally, the volatile matter of the adsorbents were calculated using Equation 3.

$$\text{Volatile matter (VM)} = \frac{M1 - M2}{M1} \times 100 \dots \dots \dots 3$$

Where, M1 and M2 are initial mass (g) of adsorbents and final mass (after drying), respectively.

Fixed carbon: Fixed carbon content of adsorbents were determined by subtracting the percentage of MC, AC, and VM using Equation 4.

$$\text{Fixed carbon content (FC)\%} = 100 \% - (MC + AC + VM) \% \dots \dots \dots 4$$

Bulk density: The mass to volume ratio of adsorbents were used to determine the bulk density the adsorbents. A measuring cylinder (10 mL volume/size) was weighted. Sufficient amount of the adsorbents were poured to it with constant tapping and filled to the 10 ml mark. The difference between the initial weight of the container/measuring cylinder and the final weight (container + sample) was calculated. The mass difference was taken as the mass of the adsorbents. Then, the bulk density was calculated from the relationship of mass to volume and determined using Equation 5.

$$\text{Bulk density} \left(\frac{g}{mL} \right) = \frac{\text{Mass (g) of adsorbent}}{\text{volume (mL) of container}} \dots \dots \dots 5$$

Surface area determination: The specific surface area of the adsorbents were estimated according to sear method [26-28]. About 1.5 g of raw, beneficiated and activated waste ash was mixed with 30 g NaCl and dissolved by 100 mL of distilled water using 250 mL conical flask. The mixtures were stirred for five minutes. Then, each of the pH of solution was adjusted to 4, and the solutions were titrated by 0.1 M NaOH until pH of the solution reaches to 9. The volumes of NaOH required to change pH value from 4-9 were recorded. The specific surface area of each sample was obtained using the following formula:

$$\text{specific surface area} \left(\frac{m^2}{g} \right) = 32.V - 25 \dots \dots \dots 6$$

Where, V = volume of 0.1 M NaOH required to raise the pH from 4.0 to 9.0.

Determination of pH: About 1.0 g of raw, beneficiated and activated waste ash was mixed in 100 mL of distilled water and continuously stirred for 2 hr. The samples were allowed to stabilize before the measurement and the supernatants were analyzed for pH using pH meter [24, 29].

Determination of point zero charge (PZC): The surface property (surface charge) of the adsorbents were determined by measuring a pH of zero point charge [30]. Raw, beneficiated and activated waste ash for the determination of pH_{zpc} , 0.01M NaCl was prepared and its initial pH was adjusted between 2 to 12 by using 1 M NaOH and 1 M HCl in each batch. Then, 50 mL of 0.01 M NaCl was taken in to 250mL Erlenmeyer flasks and 0.20 g of each adsorbent was added to the solutions. These flasks were kept for 24 h and the pH of the solutions were measured by using a pH meter. The results were then plotted between “pH final versus pH initial”. The point of intersection of the curves of “pH final versus pH initial,” is the PZC of adsorbents.

FTIR analysis: The surface functional groups of the bio-adsorbents were studied by FTIR spectroscopy (JASCO model 4100). The analyzed samples were prepared by mixing 1 mg of each dried adsorbents with 500 mg of KBr (spectroscopic grade) in an agate mortar and then pressing the resulting mixture in order to form pellets. Then, FTIR spectra were recorded between 4000 and 400 cm^{-1} .

2.4 Batch adsorption experiment

Adsorption experiments were carried out in batch mode by optimizing different parameters; solution pH (4-13), contact time (20-120 min), adsorbent dosage (0.1-2 g), dye concentration (25, 50, 75, and 100 mg/L) and temperature (30-50). A measure amount of dye sample (50 mL) and 1.6 g adsorbent was taken in 250 mL of conical flask for batch experiment and agitated with magnetic stirrer on digital hot plate at 200 rpm. The initial pH of all the solutions were adjusted with 1M HCl or 1M NaOH. At the end of each experiment, small amount of the solutions (supernatants) were withdrawn at predetermined time and the absorbance determined by using UV-Vis spectrophotometer at a maximum

wave length of 665nm. The adsorption capacity at equilibrium, the methylene blue dye removal (%) and q_e (mg/g) are shown in **Equation 7** and **8**, respectively [25, 31, 32].

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_1}{C_0} \times 100 \dots \dots \dots 7$$

$$q_e \left(\frac{mg}{g} \right) = \frac{(C_0 - C_1)V}{m} \dots \dots \dots 8$$

Where, C_0 : initial dye concentration (mg/L); C_e : liquid-phase concentrations of the dye (mg/L) at equilibrium; V : volume of the dye solution (L); m : the mass of the adsorbents (g).

2. Result and discussion

3.1 Characterization of bio-adsorbents

Physicochemical characteristics of the adsorbents such as moisture content, ash content, volatile matter, fixed carbon, bulk density, solution pH, point of zero charge were determined and presented in (**Table 1**). The raw and modified (beneficiated and activated) waste ash had almost similar low moisture contents, which indicates that the adsorption of moisture by the samples is also less. The moisture contents has no significant effect on adsorptive power unless it increases the weight and hinders the porous nature of adsorbents [33]. The volatile matter contents were found to increase significantly from raw, beneficiated to activated waste ash (raw < beneficiated < activated). During activation step, organic molecules present in adsorbents become unstable and volatile matter is released as gas and liquid products which evaporates off leaving a material [24, 34] and also significant amounts of mineral matter, carbonates, certain oxides and sulfides become removed [35]. The result of volatile matter of adsorbents were revealed that; the active sites of the adsorbents might be removed on the case of activation. The ash contents were also significantly increased from raw, beneficiated to activated waste ashes; causes a decrease in adsorptive properties of adsorbates. A good adsorbent must have low ash content [36]. Ash content can lead to increase hydrophilicity and can have catalytic effects, causing restructuring process during regeneration of used adsorbents [30, 35]. The fixed carbon contents were found to decrease significantly from raw, beneficiated to activated waste ashes. This could be attributed to the higher competition between activators (water and sulfuric acid) and carbon as well as other elements present in the adsorbent to release more

volatile components with concomitant improvement in the textural characteristics and carbon burn-off [23].

The bulk densities were decreased from raw, beneficiated to activated waste ashes. High bulk density is considered to be a good quality of the adsorbent materials [22]. The surface area of raw and modified waste ashes was determined according to Sear method. Activated waste ash was found to have a low surface area (935 m²/g) than beneficiated (1319 m²/g) and raw (1465 m²/g) waste ashes. The reduced value was due to the high concentration of H₂SO₄ that attenuated the pore volume and the surface area [34]. The surface area of activated ash was also reduced due to the presence of significant amount of ash because the presence of these inorganics fill or block some of the existing networks of micropores [35] and it occupies some of the open pores of the adsorbent material [37]. The result was shown water treatment also affects the surface area of the waste; this may be due the presence of high ash content than the raw material. In addition; water treatment may alter the surface of waste ash through protonation and deprotonation.

Table 1. Characteristics of raw, beneficiated and activated waste ash bio-adsorbents.

Characteristics	Bio-adsorbents		
	Raw	Beneficiated	Activated
Moisture content (%)	0.011	0.014	0.085
Volatile matter (%)	0.051	0.0875	0.2898
Ash content (%)	1.4594	2.427	9.612
Fixed carbon (%)	98.4756	97.4742	90.0132
Bulk density (g/mL)	0.7463	0.7053	0.6846
pH	11.65	11.35	8.90
Surface area (m ² /g)	1465	1319	935
PZC	10	10	8.2

The pH of raw, beneficiated and activated waste ashes was 11.65, 11.35 and 8.9, respectively. The results were confirmed that the waste ash adsorbents are basic in nature, pH >7. The point zero charge (PZC) was determined for both raw, beneficiated and waste

ashes and presented in **Figure 3**. It was found to be 10, 10 and 8.2 for raw, beneficiated and activated waste ashes, respectively. When the pH of the solution is below the PZC, the surface of the adsorbent will become positively charged and when the solution pH is greater than PZC, the surface of the adsorbent will become negatively charged [25]. It implied that the raw, beneficiated and activated waste ashes were most probably adsorb methylene blue dye on basic regions.

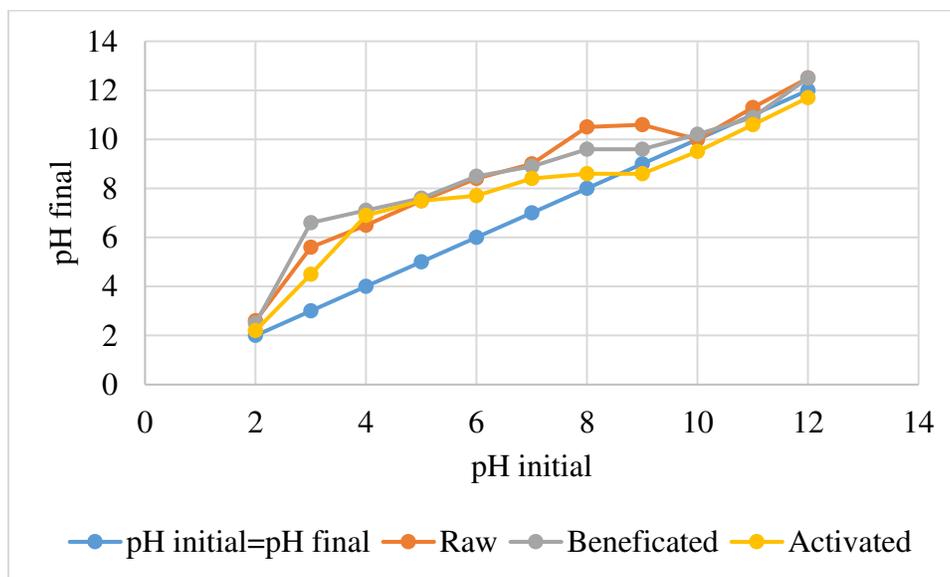


Figure 3. pH final versus pH initial for PZC determination of waste ash adsorbents.

FTIR analysis of adsorbents: FTIR spectra of the raw, beneficiated and activated waste ashes was presented in **Figure 4**. The results show that waste ash adsorbents has many different functional groups due to different adsorption band areas. The intensity of absorption peaks were significantly increased from raw, beneficiated to activated due to modification of the surface of the adsorbents with water and sulfuric acid. The spectra showed broad band at a range 3550-3400 cm^{-1} confirming the presence of the hydroxyl (O-H) groups of carboxylic acids, alcohols, phenols and adsorbed water on the surface of adsorbents [38, 39]. The band at a range of 1615-1430 cm^{-1} is attributed to C=C stretching vibrations and the peak < 900 cm^{-1} results C-H (out of plane) confirm the presence of aromatic ring in the adsorbent [35]. The absorption peaks at a range of 1130-1040 cm^{-1} is attributed to the C-O stretching vibrations.

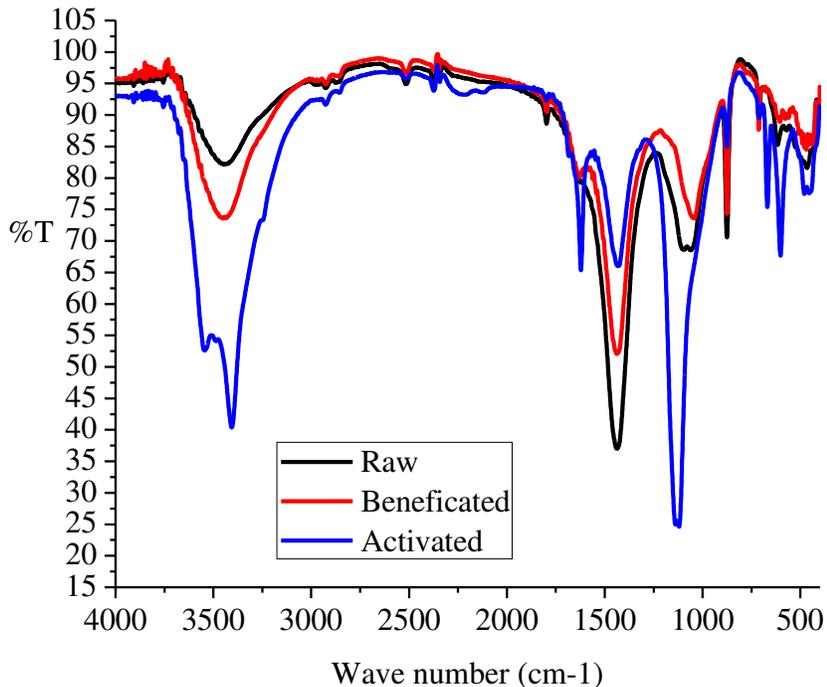


Figure 4. FTIR spectra of raw, beneficiated and activated bio-adsorbents.

3.2 Effects of experimental conditions on adsorption efficiency

Effects of solution pH, adsorbent dosage, initial dye concentration, and contact time have been investigated individually for determination of ideal experimental conditions under room temperature.

3.2.1 Effect of solution pH

Removal efficiency of the adsorbents have been strongly affected by the pH of the solution in adsorption studies [25]. The effect of initial pH on adsorption of methylene blue dye by raw, beneficiated and activated waste ashes was studied in pH range between 4-13, dye concentration 25 mg/L and adsorbent dose 0.4 g at room temperature presented in **Figure 5a and b**. The maximum dye removal by raw, beneficiated and activated waste ashes was 2.101 mg/g (67.244 %) at pH 8, 1.824 mg/g (58.368%) at pH 12, and 1.417 mg/g (45.328) at pH 12, respectively. The fact that the maximum adsorption of methylene blue was high at higher pH (at basic region) indicates that the surface of each adsorbent has become negatively charged. Therefore, the

mechanism of dye removal were explained via the electrostatic interaction between the negatively charged surface of the adsorbents and the positively charged methylene blue dye adsorbate.

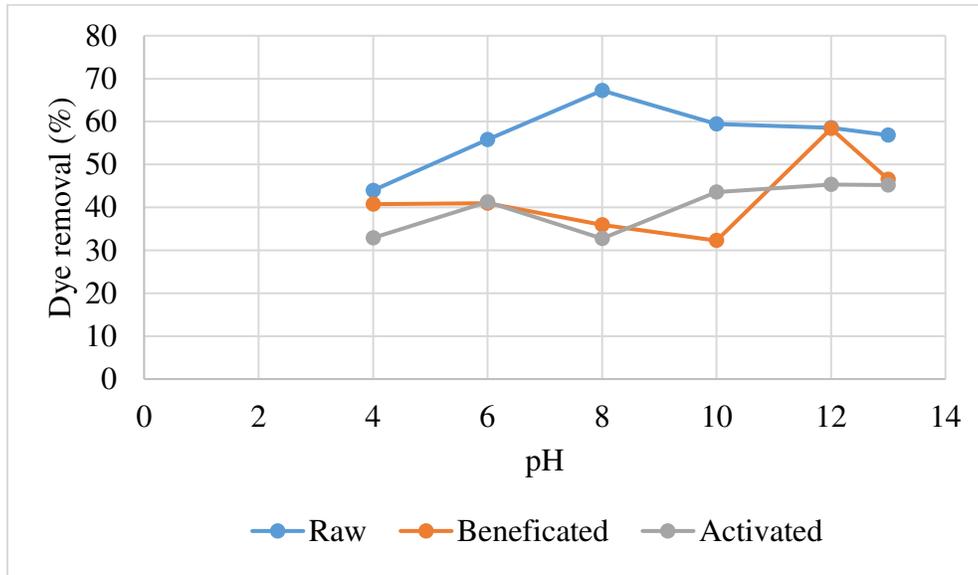


Figure 5a. Effect of pH on the removal (%) of MB by raw, beneficiated and activated waste ashes.

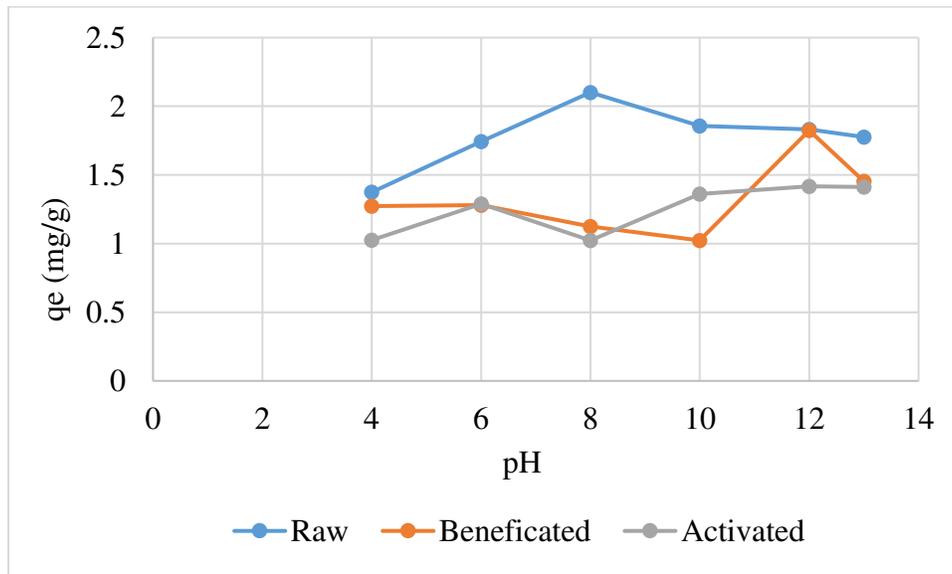


Figure 5b. Effect of pH on the adsorption capacity (mg/g) of MB by raw, beneficiated and activated waste ashes.

3.2.2 Effect of adsorbent dose

The increase in adsorbent dosage found to increase the removal efficiency of methylene blue until equilibrium was reached and presented in **Figure 6a**. The methylene blue (MB) removal efficiencies of raw, beneficiated and activated from aqueous solutions were resulted to be 95.212%, 89.172%, and 84.504%, respectively at optimum dosage value of 1.6 g. Thereafter, no significant change has been observed in both adsorbents, because adsorption saturation was reached or overlapping of adsorption sites as a result of overcrowding of adsorbent particles. As shown in **Figure 6b**, the adsorption capacity of adsorbents was found to decrease with increasing adsorbent dosage might be due to the interaction of adsorbent particles like aggregation or agglomeration which results in decrease of the total surface area [4].

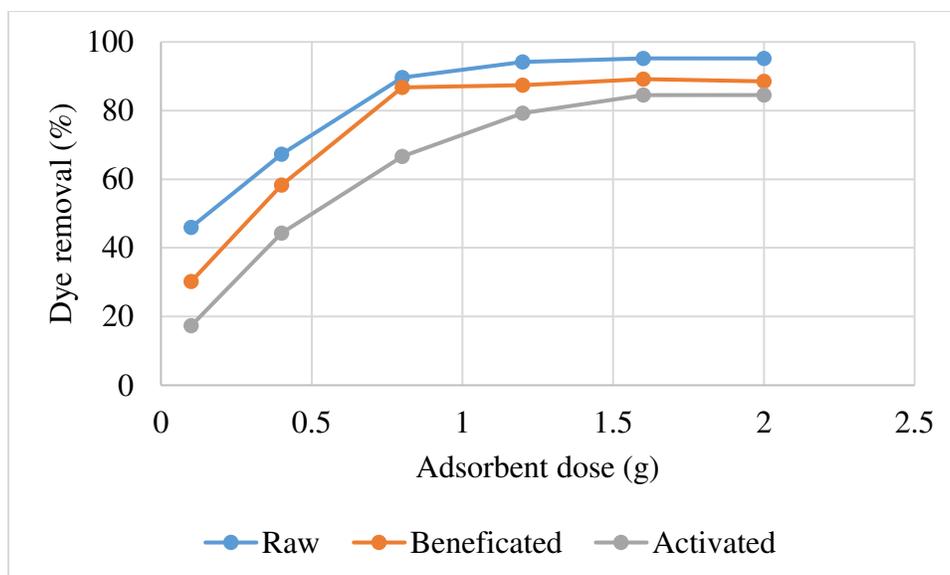


Figure 6a. Effect of adsorbent dosage on MB removal efficiency (%) of raw, beneficiated and activated waste ashes.

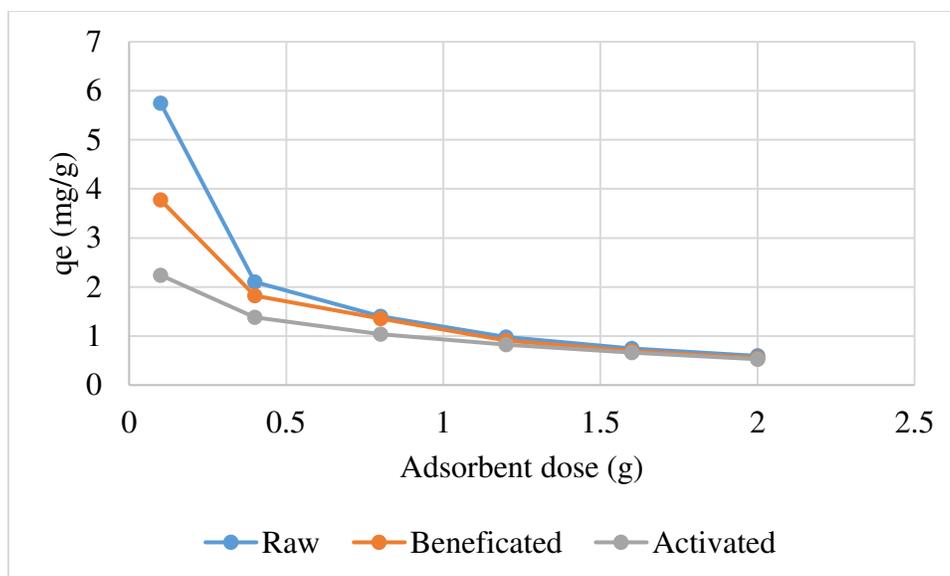


Figure 6b. Effect of adsorbent dosage on MB adsorption capacity of raw, beneficiated and activated waste ashes.

3.2.3 Effect of initial concentration of dye

Effects of initial concentration of dye have been examined by using different dye concentrations from 25 to 100 mg/L described in **Figure 7a** and **7b**. The adsorption capacity increased with increasing concentration of dye from 0.744 to 2.833 mg/g for raw, 0.697 to 2.732 mg/g for beneficiated and 0.66 to 2.479 mg/g for activated bio-adsorbents. On the other hand, the percentage of removal efficiency of the dye was decreased from 95.212% to 62.564% for raw, 89.172 to 49.7% for beneficiated and 84.504% to 17.247% for activated waste ashes with increasing initial dye concentration. At a lower initial concentration of methylene blue, there will be unoccupied active sites on the adsorbent surface, and when the initial dye concentration increases, the active sites required for adsorption of the dye molecules will be occupied or reaches saturation of active bio-adsorbents sites [25].

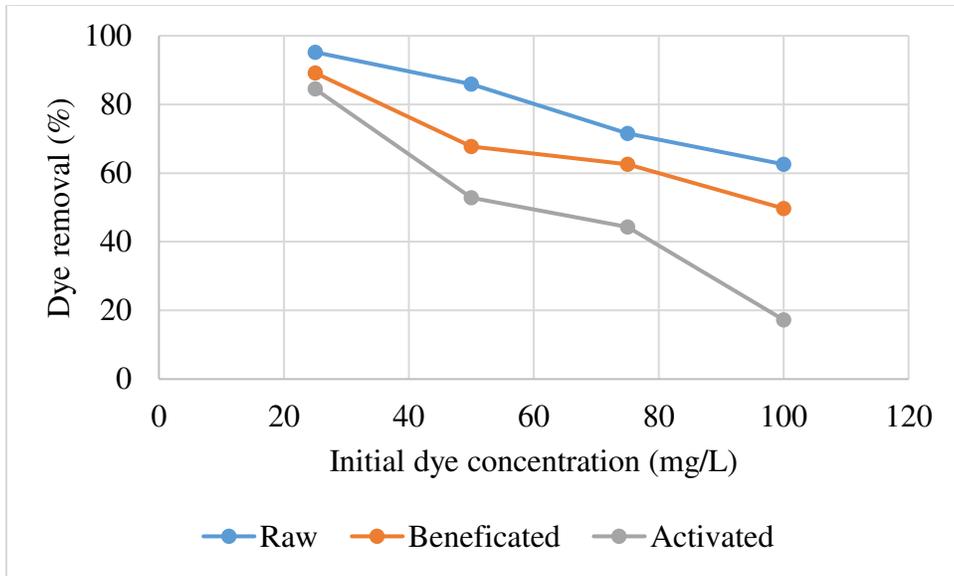


Figure 7a. Effect of initial dye concentration on MB dye removal by raw, beneficiated and activated adsorbents.

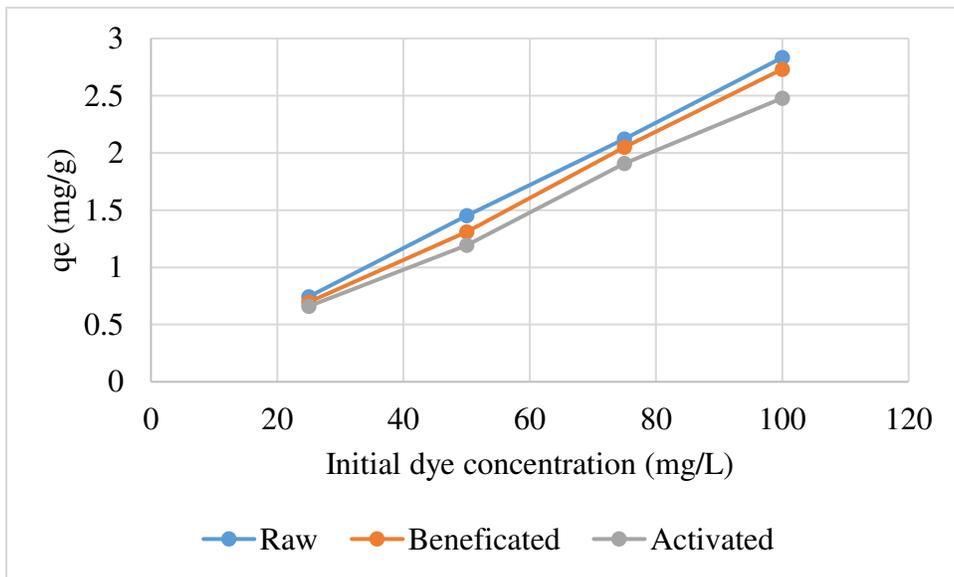


Figure 7b. Effect of initial dye concentration on MB dye adsorption capacity by raw, beneficiated and activated adsorbents.

3.2.4 Effect of contact time

To examine the minimum time required for maximum performance of adsorbent process, the contact time varies from 20-120 min at optimum values of adsorbent dose 1.6g, pH 4 for raw and 12 for beneficiated and activated, initial concentration of dye 25 mg/L at room temperature. As

shown **Figure 8a** and **b**, it has been observed that the removal efficiency and adsorption capacity increase with increase in contact time up to 100 min and beyond this time no more change. In fact that most vacant surface sites are available for adsorption during the initial stage and the remaining vacant surface sites are hard to be adsorb due to repulsive forces between the dye molecules on the adsorbents and the bulk phase.

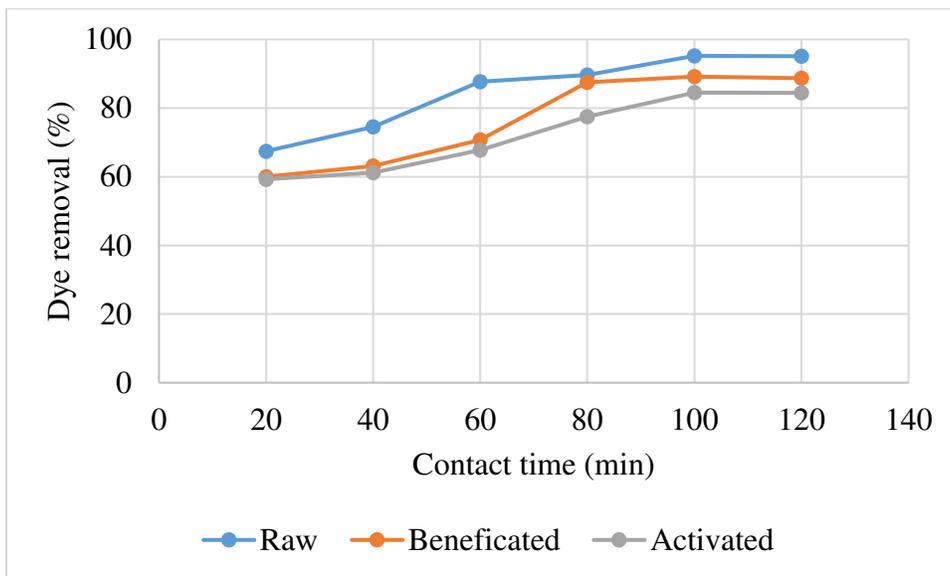


Figure 8a. Effect of contact time on MB dye removal efficiency by raw, beneficiated and activated adsorbents.

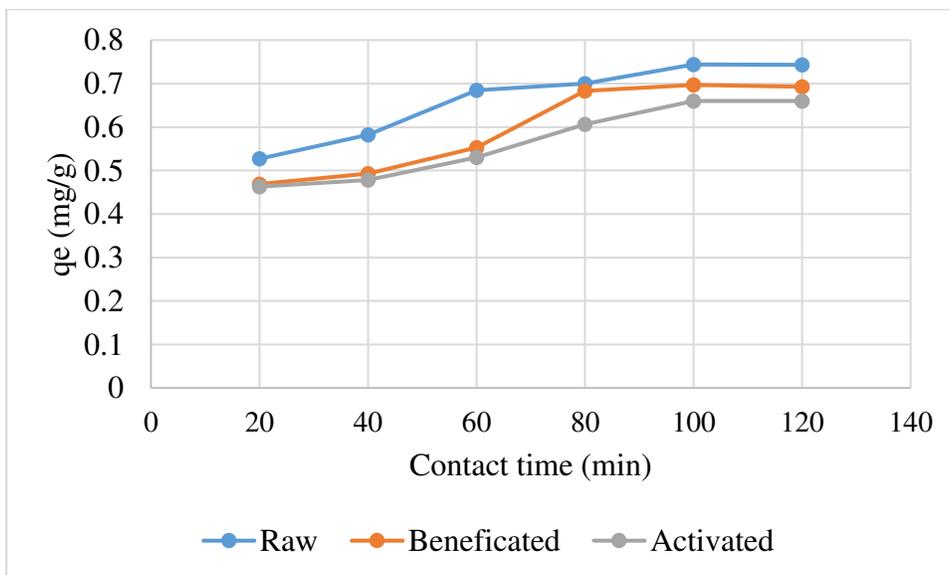


Figure 8b. Effect of contact time on MB dye adsorption capacity by raw, beneficiated and activated adsorbents.

3.3 Kinetics study

Kinetic models have been exploited to test the experimental data and to find the mechanism of adsorption and its potential rate-controlling step that include mass transport and chemical reaction [40]. In addition, information on the kinetics of dye uptake is required to select the optimum conditions for full scale batch or continuous dye removal Processes. Adsorption kinetics is expressed as the solute removal rate that controls the residence Time of the sorbate in the solid–solution interface. In order to further understand the characteristics of the adsorption process, the pseudo-first-order and pseudo-second-order kinetic models were applied to fit experimental data obtained from batch experiments and presented on **Figure 9** and **10**, respectively. The pseudo-first-order kinetic models are expressed in linear form as follows:

$$\log(q_e - q_t) = \log q_e - k_1 t \dots \dots \dots 9$$

Where q_e is the amount of adsorbate adsorbed at equilibrium, (mg/g), q_t is the amount of solute adsorb per unit weight of adsorbent at time, (mg/g), k_1 is the rate constant of pseudo-first order sorption (1/hr) [25]. The value of k_1 and q_e calculated from the slope and intercept of $\log(q_e - q_t)$ vs t graph respectively and the results were presented in **Table 2** for all adsorbents.

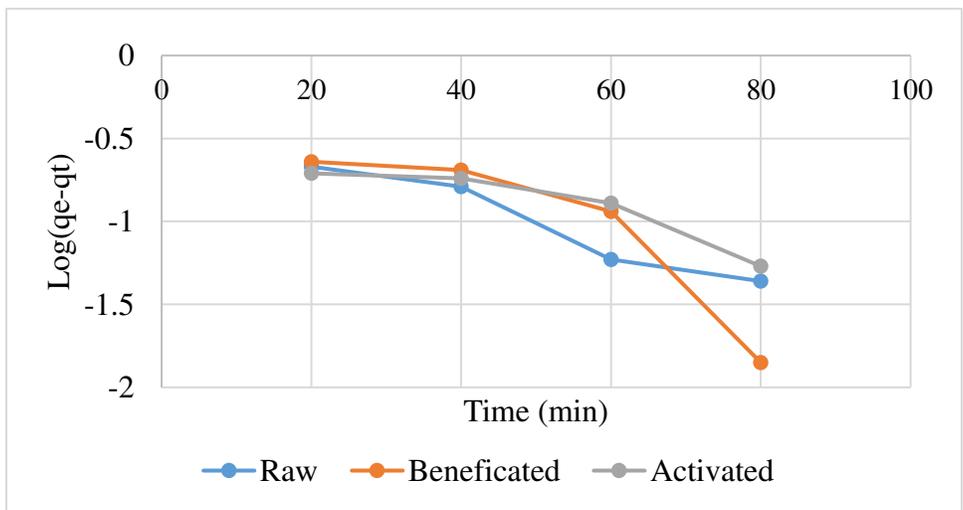


Figure 9. Pseudo first order kinetics model for all adsorbents at 50 ml of 25mg/l of MB concentration

The result of pseudo second-order model is shown in **Figure 10** and expressed in **Equation 10** in linearized form as follows:

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \dots \dots \dots 10$$

Where K_2 [$\text{gmg}^{-1}\text{min}^{-1}$] is the rate constant of the pseudo second order adsorption, q_e is the amount of dye adsorbed on the adsorbent at equilibrium [mg/g], and q_t is the amount of dye adsorbed on the adsorbent at any time, t [mg/g]. The value of k_2 and q_e were calculated from slope and intercept of t/q_t Vs t graph respectively.

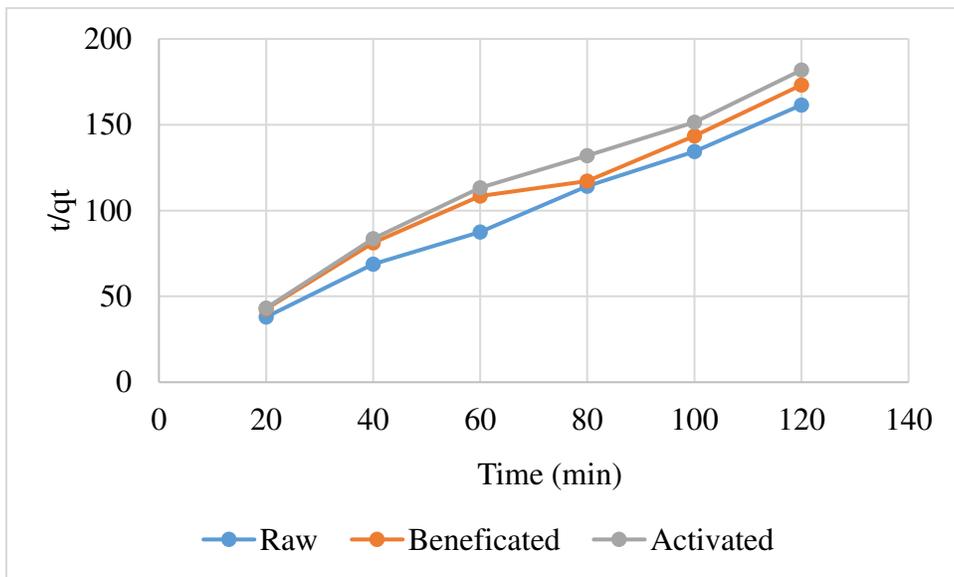


Figure 10. Pseudo second order kinetics model for all adsorbents at 50 ml of 25mg/l of MB concentration

The kinetic parameters and the correlation coefficients (R^2) were determined from nonlinear regression. **Figure 9** and **10** represent for pseudo 1st and 2nd order kinetics respectively and their parameters were presented in **Table 2**. The calculated q_e values (q_e, cal) of pseudo 2nd order model is close to the experimental ones (q_e, exp) as compared to pseudo 1st order kinetics model. The R^2

values also for the pseudo-second-order kinetic model close to 1 which indicates that experimental data were good agreement with pseudo second kinetics order model.

Table 2. kinetic parameters for MB adsorption on Raw, beneficiated and activated ash

Adsorbent type	Concentration (mg/L)	Qe exp. (mg/g)	Pseudo 1 st order			Pseudo 2 nd order		
			K ₁ (min ⁻¹)	Qe calc. (mg/g)	R ²	K ₂ (min ⁻¹)	Qe calc. (mg/g)	R ²
Raw	25	0.744	-0.0126	0.412	0.9407	0.087	0.69	0.9967
Beneficiated	25	0.697	-0.0194	0.871	0.7938	0.056	0.68	0.9764
Activated	25	0.660	-0.0091	0.359	0.8428	0.065	0.59	0.9823

3.4 Adsorption isotherms

In order to study how the molecules of MB interact with the adsorbent surface the adsorption isotherms were used to analyze the experimental data. Isotherms study can describe how an adsorbate interacts with adsorbent [41, 42]. The isotherm provides a relationship between the concentration of dye in solution and the amount of dye adsorbed on the solid phase when both phases are in equilibrium. The most widely used isotherm equations are Langmuir and Freundlich equations. These two isotherms have their own assumptions that explain the adsorption mechanism and it was presented in **Figure 11 and Figure 12**, respectively. The Langmuir model is used to describe the formation of monolayer adsorbate on the outer surface of the adsorbent. It is often applicable to a homogeneous adsorption surface with all the adsorption sites having equal adsorbate affinity while Freundlich isotherm described that during the adsorption process different sites of the adsorbent are involved with several adsorption energy is an empirical relation for adsorption over heterogeneous surfaces. The linear expression of Langmuir isotherm model can be illustrated as **Equation 11** below.

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \dots \dots \dots 11$$

Where C_e is the equilibrium concentration of solute (mmol L^{-1}), q_e is the amount of solute adsorbed per unit weight of adsorbent (mmol g^{-1} of adsorbate), q_m is the adsorption capacity (mmol g^{-1}), or monolayer capacity, and b is a constant (L mmol^{-1}). The isotherm parameter b and q_m , determined from the intercept and the slope of C_e/q_e versus C_e graph respectively. The linear expression of Freundlich isotherm model can be illustrated as **Equation 12** below.

$$\log q_e = \log k_f + \frac{\log C_e}{n} \dots \dots \dots 12$$

Where K_f and n are empirical constants incorporating all parameters affecting the adsorption process such as, sorption capacity and sorption intensity respectively [43]. The isotherm parameters k_f and n were calculated from the $\log q_e$ vs $\log c_e$ graph and it was presented in **Table 3** below. For the Freundlich isotherm if $n = 1$ then the partition between the two phases are independent of the concentration. If value of $1/n$ is below one it indicates a normal adsorption. On the other hand, $1/n$ being above one indicates cooperative adsorption. For this study as shown in the table 3 the value of $1/n$ were below 1 for all adsorbents which confirms that adsorption of MB on these adsorbents were by normal adsorption.

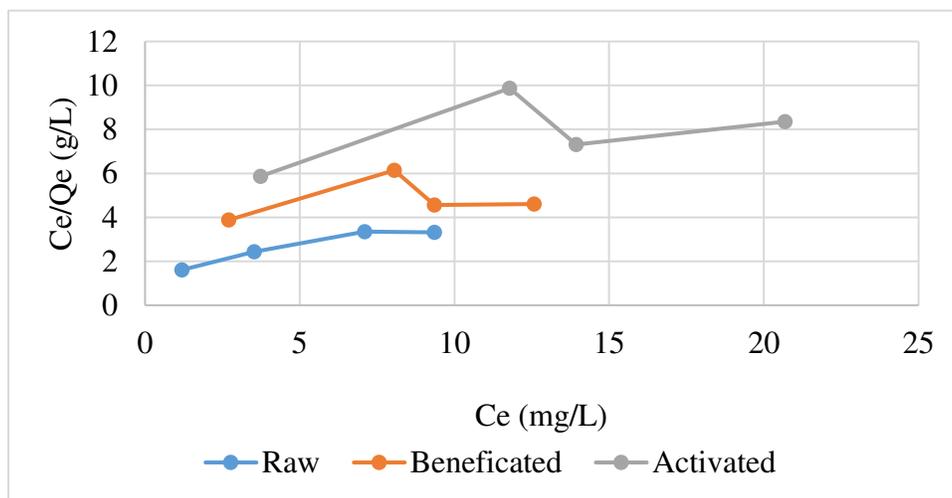


Figure 11. Langmuir isotherm model for different adsorbents (raw, beneficiated and activated ash) at constant dosage (25 mg/l), pH optimum (8 for raw and 12 for beneficiate and activated),

contact time 100 min, shaker speed 100 rpm, room temperature and concentration 25-100 mg/l within 25 mg/l intervals.

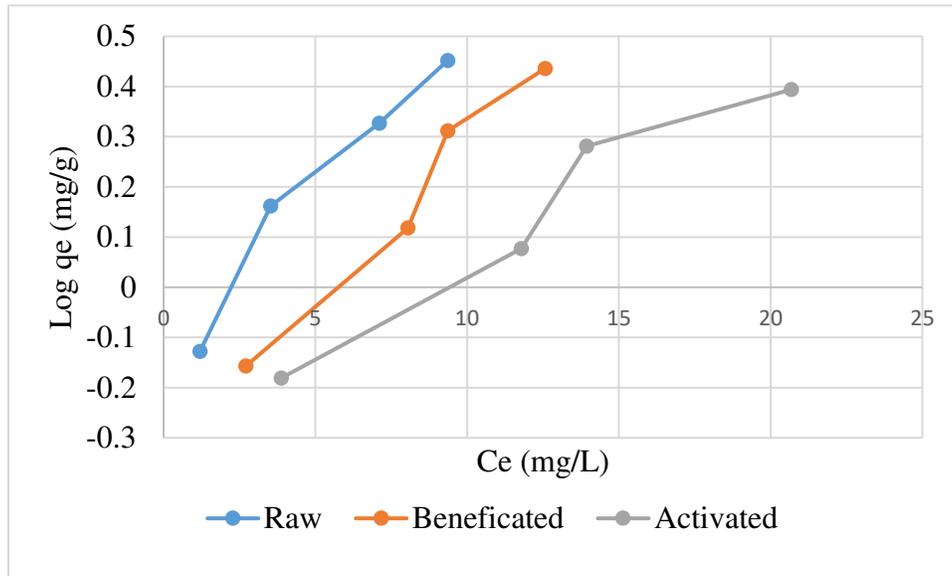


Figure 12. Freundlich isotherm model for different adsorbents (raw, beneficiated and activated ash) at constant dosage (25 mg/l), pH optimum (8 for raw and 12 for beneficiate and activated), contact time 100 min, shaker speed 100 rpm, room temperature and concentration 25-100 mg/l within 25 mg/l intervals.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L given by following relation in **Equation 13** that can be used to determine the feasibility of adsorption in a given concentration range over adsorbent [40, 44, 45].

$$R_L = \frac{1}{1 + bC_0} \dots \dots \dots 13$$

Where b is Langmuir constant related to the energy of adsorption ($L \text{ mg}^{-1}$) and C_0 is initial concentration (mg/l). The calculated R_L values at different initial dye concentration were written in the **Table 4** below. R_L value indicates the adsorption nature to be either unfavorable if $R_L > 1$), linear if $R_L = 1$, favorable if $0 < R_L < 1$ and irreversible if $R_L = 0$ [45]. For this study all the values were lies between 0 and 1 which confirming that the adsorption of dye over the adsorbent was favorable.

Table 3. Dimensionless constant separation factor (R_L) value for different adsorbent at different initial concentration

Adsorbent type	RL values			
	Concentration (mg/L)			
	25	50	75	100
Raw	0.22	0.12	0.09	0.07
Beneficiated	0.09	0.53	0.43	0.36
Activated	0.66	0.49	0.39	0.32

All isotherm parameters for both isotherms were presented in table 4 below and the R^2 values of Freundlich isotherm is greater than Langmuir models for all adsorbents confirms that Freundlich isotherm is suitable for describing the adsorption equilibrium of MB onto these adsorbents.

Table 4. Isotherm parameters obtained from isotherm graphs for all adsorbents

Adsorbent type	Isotherm	R^2	Estimated parameters	isotherm
Raw	Langmuir	0.907	b= 0.142	$Q_m=4.62$
	Freundlich	0.9483	n =14.903	$K_f=0.704$
Beneficiated	Langmuir	0.1014	b= 0.018	$Q_m=13.51$
	Freundlich	0.9667	n= 16.181	$K_f=0.47$
Activated	Langmuir	0.2954	b= 0.021	$Q_m=7.616$
	Freundlich	0.9421	n= 28.25	$K_f=0.50$

Conclusion

In summary, this experimental study showed that the removal of methylene blue through adsorption on raw, beneficiated and activated waste ash adsorbents is effective economical alternative and eco-friendly safe. The adsorption potential obtained using raw waste ash are higher than those using the same dose of beneficiated and activated bio-adsorbents. In fact that water and sulfuric acid treatment causes a significant reduction in the total surface area, enhancement of ash

content, reduction of fixed carbon and promotes the formation of acidic surface groups via protonation. The adsorption kinetics was in good agreement with pseudo second order kinetic model and the adsorption isotherm showed good fitting to Freundlich isotherm model. This study clearly shows that, adsorption strongly depends on solution pH, adsorbents dose, dye concentration and contact time of the experimental parameters.

Abbreviation

FTIR: Fourier transform infrared spectroscopy, Uv/Vis: ultraviolet visible spectroscopy, PZC: point of zero charge, AC: ash content, MC: moisture content, VM: volatile matter, FC: fixed carbon.

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The authors declare that they have no known conflicts of interest.

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