



Treatment of Red Mud with Distilled Water to Improve Its Efficiency to Remove Methylene Blue from Aqueous Solution

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Authors' contributions

This work was carried out in collaboration between all the authors. The author CT conceived coordinated the laboratory work, writing and editing of the text. Authors DJHT and DSM executed the laboratory test and related calculations, participated in the literature review and organization of the article. All authors read through and approved the final manuscript.

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ABSTRACT

In this work, raw red mud was treated with distilled water and its methylene blue (MB) removal efficiency from aqueous solution evaluated and compared to that of raw red mud. The pH, surface charge, particle size distribution, chemical composition, infrared spectrometry and morphology analyses were used to characterize the adsorbents. Batch experiments without agitation and filtration were conducted to determine the influence of contact time, solution pH, temperature, initial dye concentration, adsorbent dose and presence of Cl^- , SO_4^{2-} , HPO_4^{2-} and HCO_3^- on dye removal. Distilled water treated red mud (RMW) had improved adsorbent properties than raw red mud (RM). For all the parameters tested, RMW showed higher removals of MB compared to RM. The fitting order for tested isotherm models was: Langmuir > Dubinin–Radushkevich > Freundlich for RMW and Freundlich > Dubinin–Radushkevich > Langmuir for RM. Monolayer adsorption capacities of RMW and RM were found to be 17.123 and 4.221 mg/L respectively. Pseudo-second-order kinetic model suited well than other tested kinetic models. Equilibrium was attained in 24 hours, and the

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order of shifting of equilibrium to the right as well as the rate of uptake is: MB on RMW > MB on RM. MB removal was found to be more endothermic, more spontaneous and more favourable on RMW than on RM. Desorption experiments using acetone gave good results up to four cycles. These findings revealed that treating red mud with distilled water significantly enhanced its ability to easily remove MB from aqueous solutions.

Keywords: Activation; adsorption; dyes; isotherm modeling; kinetics modeling; red mud.

1. INTRODUCTION

Dye removal from wastewater is becoming a topic of great interest in water pollution due to their adverse effects to many forms of life. Their presence in water even in very small amounts of less than 1 ppm for some dyes is highly visible and undesirable [1]. Color is the most visible form in which pollution is noticed, and the main contributing factor to this type of pollution is the discharge of dyes into water from various industries such as textile, electroplating, paper, food, plastic and tanneries [2] as they consume a lot of water. It is estimated that there are more than 100,000 commercially available dyes with over 7×10^5 tons of dyestuff produced annually [1].

Methylene blue (MB) is soluble dye in water and generally used for printing, dyeing cotton, wood and silk, antiseptic and medical purposes [1,3]. It can cause eye burns which may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion, methemoglobinemia, cyanosis, convulsions and tachycardia [1,3].

Therefore, there is the need for the removal of this dye from the wastewater. At present, coloured wastewater is treated by physical, chemical, and biological methods [4] which present different technological and economic limitations. Of these methods, adsorption is one that sees increasing interest due to its potential efficiency, low energy consumption, high selectivity at molecular level, easy operation, and ability to separate various chemical compounds [3]. One of the important parameters in the adsorption process is the cost of the adsorbent. For this reason, it is important to use low cost adsorbents especially those which are industrial by-products such as red mud. It is a waste product of alumina production. Globally, about 150 million tons are produced annually as approximately, 1.0–2.0 tons of toxic red mud (pH

10-13) are generated per ton of alumina produced [5]. Current estimates show that only about 2-4.5 tons are used annually in some way including its use as adsorbent [5]. Encouraging more red mud utilization as adsorbent will provide an alternative to disposal with its environmental consequences.

In recent years, a great deal of research has been undertaken to utilise red mud for wastewater treatment, such as removal of metal ions, dyes, phenolic compounds and inorganic anions as presented in a number of reviews on red mud utilization as adsorbent [6-9]. These reviews and other literature review report only a few studies on the use of red mud (raw, acid activated, heat activated and combined acid heat activated red muds) for removing dyes and particularly methylene blue [10-12]. These studies show the low ability of red mud in removing methylene blue from waste effluents. The authors of the review [7] concluded that red mud shows very little effectiveness for dye removal and is therefore necessary to continue more research on the removal of different classes of dyes using red mud as adsorbent. The present paper focuses on the possibility of utilization of distilled water treated red mud (RMW) as adsorbent to improve the removal of methylene blue (MB), a cationic dye, from aqueous solution in a batch process without agitation and without filtration as studies on the use of distilled water treated red mud as adsorbent are scarce in literature. Adsorption kinetics, isotherms and thermodynamics of MB removal on raw red mud (RM) and RMW was studied.

2. MATERIALS AND METHODS

2.1 Adsorbent Material

We produced the red mud used for this study in our laboratory from bauxite collected at Minim-Martap deposit as described in my previous work [13]. Then, 2 g of water-washed and dried red mud obtained was equilibrated with 150 mL of distilled water in a stoppered 250 ml Erlenmeyer flask for 10 days. The Erlenmeyer and its

contents were gently turned end-over-end once a day. At the end of the process, the mixture was filtered on a Whatman filter paper N° 1 and dried at 40°C (to avoid degradation of structure) for 1 hour. Distilled water treatment increases settling rates of the red mud, reduces the pH (or solubilises the sodium), improves particle size, reduce surface charge and makes it easier to handle red mud, thus, improving its adsorbent properties [14]. This water modified red mud was designated as RMW while the raw sample was designated RM. They were used for MB removal studies without further treatment.

2.2 Adsorbent Characterization

The pH and surface charge were measured using a METTLER TOLEDO Education line pH meter with two decimal places. A master sizer 2000 was used to study the particle size distribution of the adsorbents. The quantitative elemental composition (expressed as oxide) was determined by X-Ray Fluorescence (XRF) while surface morphology was determined by Scanning Electron Microscopy (SEM). Infrared spectroscopy using an Alpha-P IR spectrophotometer model of Brucker Company was used to identify surface functional groups before and after adsorption to study mechanism of attachment on adsorbent surface. The resulting absorption bands were attributed respective functional groups by comparing them with those of red mud samples and other functional groups reported in literature.

2.3 Preparation of Methylene Blue Stock Solution

A 1000 mg/L synthetic stock solution of methylene blue was prepared by dissolving 1000 mg of MB (AR grade, C₁₆H₁₈ClN₃S, molecular weight = 319.85, λ_{max} = 664 nm) in 1 liter of distilled water. The stock solution was then diluted with distilled water to obtain desired concentrations.

2.4 Adsorption Experiments

Batch adsorption experiments were carried out in 20-mL assay tubes containing the aqueous dye solution of the desired concentration and amount of RM or RMW. Initial pH was adjusted to the desired level with 1N NaOH or 1N HCl solutions. The assay tubes containing the solutions were gently turned end-over-end thrice a day as these experiments were carried without agitation and without filtration. The dye solution was then separated from the adsorbent by decantation and

the dye concentration in the supernatant was determined using UV-Visible spectrophotometer, Spectro 23 RS, LaboMed.inc. Batch experiments were performed at different times 20 min, 40 min, 60 min, 80 min, 120 min and 24 hours (1440 min), adsorbent dosages in the range of 0.1 to 0.5 g/L, initial dye concentration in the range of 5 to 50 mg/L (for RM) and 20 to 100 mg/L (for RMW), pH 2, 4, 7, 8 and 10, temperature 298 K, 303 K, 313 and 333 K and influence of anions (Cl⁻, SO₄²⁻, HPO₄²⁻ and HCO₃⁻).

The amount of MB adsorbed at time 't' was computed according to the expression [10-12]:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where q_t is the adsorption capacity at time 't' (mg/g), C_0 is the initial dye concentration (mg/L), C_t is the dye concentration (mg/L) at time t , 'm' is the adsorbent weight (g) and V is the volume of the dye solution (L).

Percentage removal of MB was calculated using equation [10-12]:

$$\% \text{ Removal} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

2.5 Regeneration Studies

The regeneration study on RM and RMW adsorption capacity after the treatment with MB dye was done by washing the spent adsorbents with acetone as regenerating solution because author [10] demonstrated that the desorption of dyes occurred easily with acetone. After each adsorption experiments, the adsorbents were collected from the solution by filtration and dried under laboratory temperature for 48 hours. Each sample was then agitated with 20 ml of acetone for 30 minutes and the percentage of MB removed evaluated according to Eq. 2. The experiment was carried out until the fourth cycle.

3. RESULTS AND DISCUSSION

3.1 Characteristics of Adsorbents

A pH value of 10.77 was obtained for RM and 8.69 for RMW, with a corresponding surface charge of -202 mV and -73 mV respectively. A pH of 8.9 was obtained by [14] when they neutralized red mud with mine water. In red mud, inter- and intra-particle behaviour in the presence of water (and the inherent dissolved salts) is critically dependent on the surface charge of the constituent particles. This affects not only gross macroscopic physical behaviour such as

rheology, aggregation and coagulation, but also the entire range of particle chemistry including surface hydration, ion-exchange, and redox behaviour. Also, charge development in pH-sensitive mineral–solution phases regulates ion exchange and adsorption/desorption reactions at the mineral–water interface [15]. Consequently, a reduction of surface charge in RMW creates more space on its surface and improves its adsorbent properties.

The particle size distribution curves of RM and RMW are shown in Figs. 1a and b respectively, and the composition of the distributions presented in Table 1. It can be seen that RM has about 76% of its particles below 120 μm while RMW has 72% of its particles above 200 μm and 0% from 0 to 17 μm . In general, red mud is a very fine material in terms of particle size distribution, having an average particle size <10 μm . Typical values would account for 90% volume below 75 μm [6]. The improvement in particle size of RMW also increases its settling rate and makes it easier to handle than raw red mud (RM), thus, improving its adsorbent properties [14].

The results of elemental analyses for both RM and RMW are also shown in Table 1. The major oxides present are those of Fe, Al, Ti and Si. While the Al_2O_3 , TiO_2 and SiO_2 shows little changed with water treatment, Fe_2O_3 had an increase of about 4% and practically complete elimination of Na_2O . The elimination of Na_2O is in accordance with pH results presented above and shows the red mud treatment with distilled water solubilises the sodium content. The oxides of red mud are potential adsorption sites. They are more improved on RMW than RM. This improvement is mainly due to the elimination of other minor elements and impurities, thus

increasing the purity of the material as shown by loss on ignition values of 18% for RM and 16% for RMW.

The IR spectra of RM and RMW each before and after adsorption are shown in Figs. 3a and b, and Figs. 4a and b respectively with their corresponding absorption bands and differences in absorption bands with adsorption presented in Table 1. The bands before adsorption; 3617.16 - 3104.96 cm^{-1} for RM and 3617.25 - 3163.05 cm^{-1} in RMW are hydroxyl stretching region due to the presence of H_2O [16]. The 1680.53 cm^{-1} in RM and 1632.18 cm^{-1} bands in RMW are attributed to the water molecules occluded inside the alumino-silicate structure while bands, 1452.12 and 1394.44 cm^{-1} in RM are C=O [17] and S-O [18] groups respectively. The C = O confirms the presence of carbonate groups due to the presence of chemisorbed CO_2 in RM. Chemical composition of our RM results showed 4 % of SO_3 . These bands were however absent in RMW due to treatment. The bands 1011.14 cm^{-1} in both samples, 963.41 cm^{-1} in RM, 965.23-913.65 cm^{-1} in RMW are Si-O groups. Also, the bands 847.39-795.10 cm^{-1} in RM, 797.21 - 738.16 cm^{-1} in RMW are the Si(Al)-O groups while bands 525.07 cm^{-1} for RM and 518.69 cm^{-1} for RMW confirms O-Si-O functional groups [16,17]. The 439.61 cm^{-1} band in RM and 440.91 cm^{-1} in RMW are the Fe-O groups. After adsorption it can be seen that almost all the groups participated in adsorption as indicated in (+) and (-) values of the differences. There are also the creation of new adsorption bands like 3367.43 cm^{-1} in RMW, 632.29 cm^{-1} in RM, 658.99 cm^{-1} in RMW, 467.17 cm^{-1} in RM and 466.47 cm^{-1} in RMW. These bands probably represent bonds between MB and components of red mud as well as probable deposition of MB groups on red mud.

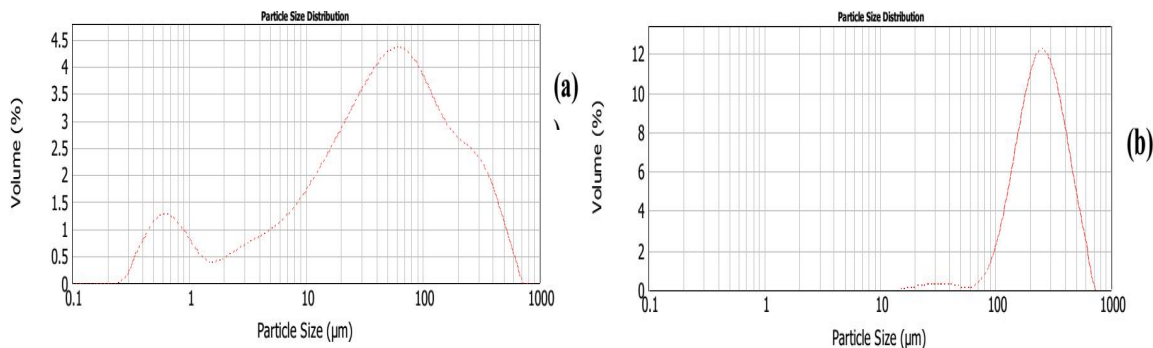


Fig. 1. Particle size distribution of (a) RM and (b) RMW

Scanning Electron Microscopy (SEM) images of RM and RMW are also shown in Figs. 2a and b respectively. These images show that distilled water treatment of red mud improves its porosity.

The RMW SEM image shows more cavities than that of RM, thus giving it better adsorbent properties.

Table 1. Physicochemical characteristics of RM and RMW adsorbents

1.1 Particle size distribution												
Range particle size (μm)		Volume in %										
		RM					RMW					
0.275 \leq d \leq 17.378		27.97					0					
17.378 < d \leq 120		47.82					8.24					
120 < d \leq 200		8.41					19.42					
200 < d \leq 630.957		15.78					72.35					
1.2 - Chemical composition												
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	Mn ₂ O ₃	LOI
RM	0.8	19.44	52.57	0	0	4	1.97	0.02	5.98	0.09	0.03	18.95
RMW	0.88	19.48	56.48	0	0	0.34	0.06	0.02	5.89	0.1	0.03	16.69
1.3 - IR bands of RM and RMW before and after adsorption (cm^{-1})												
RM			RMW									
Before adsorption	After adsorption	Differences	Before adsorption	After adsorption	Differences							
3617.16	3618.50	+1.34	3617.25	3616.64	-0.61							
3519.55	3521.51	+1.96	3520.23	3522.33	+ 2.1							
3429.93	3435.32	+5.39	3426.77	3433.15	+6.38							
3104.96	3164.17	+59.21		3367.43	+3367.43							
1680.53	1400.52	-280.01	3163.05	3118.70	- 44.35							
1452.12		-1452.12	1632.18	1631.82	- 0.36							
1394.44		-1394.44	1011.09	1012.79	+ 1.7							
1011.14	1011.41	+0.27	965.23	965.88	+ 0.65							
963.41	964.12	+0.71	913.65	914.49	+ 0.84							
847.39	794.49	-52.9	797.21	793.91	- 3.3							
795.10	737.10	-58	738.16	744.67	+ 6.51							
	632.29	+632.29		658.99	+658.99							
525.07	514.56	-10.51	518.69	518.03	+ 0.66							
	467.17	+467.17		466.47	+466.47							
439.61	441.90	+2.29	440.91	443.14	+ 2.23							

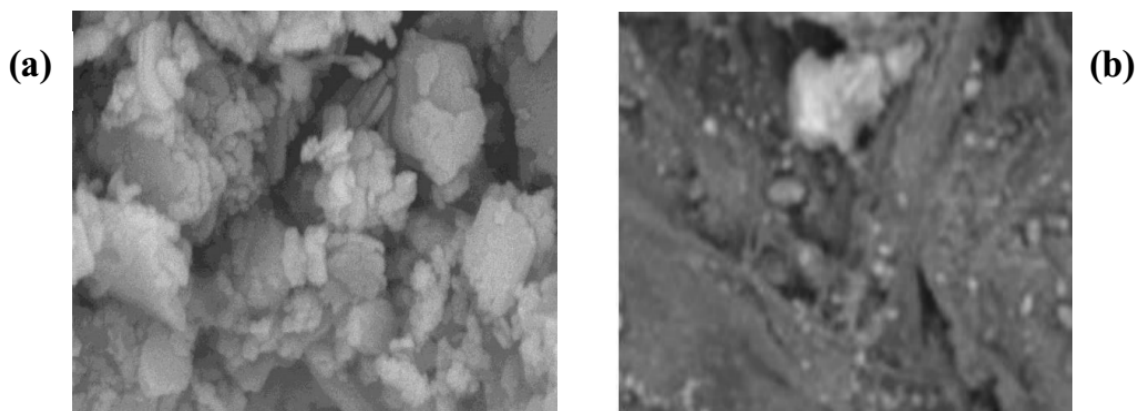


Fig. 2. SEM images of (a) RM (300 nm) and (b) RMW (250 μm)

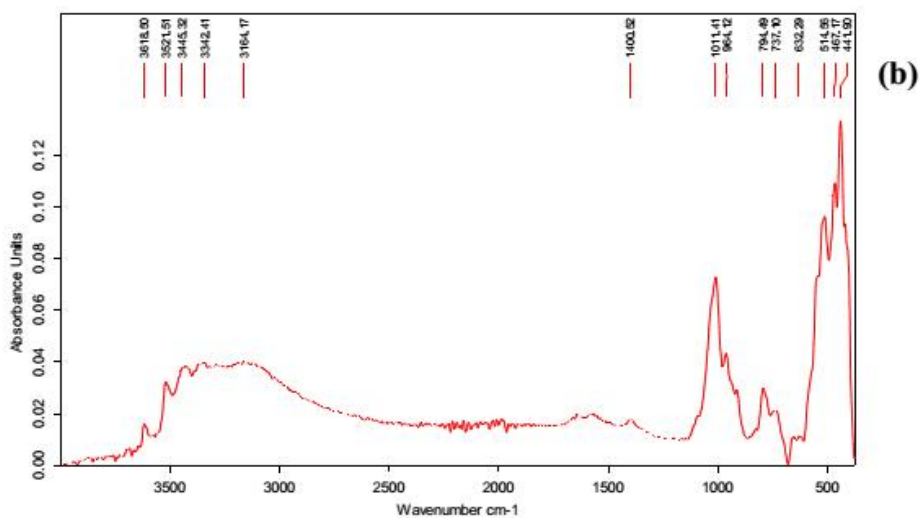
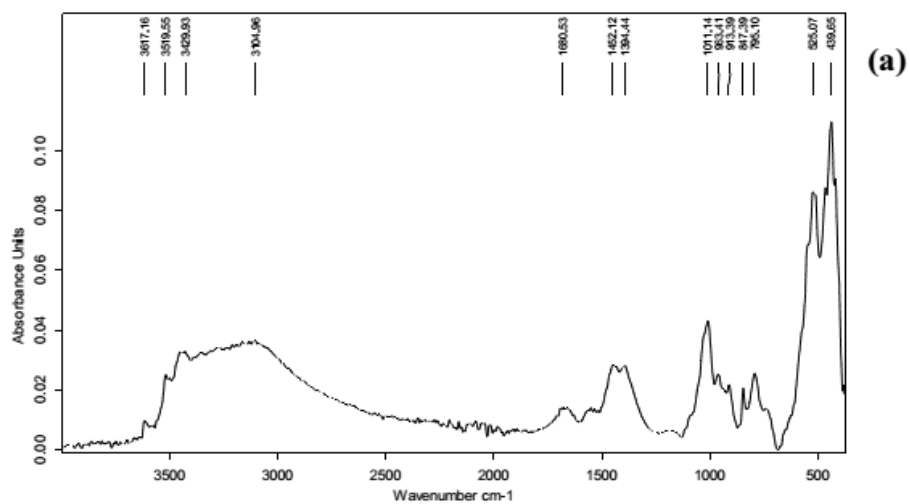
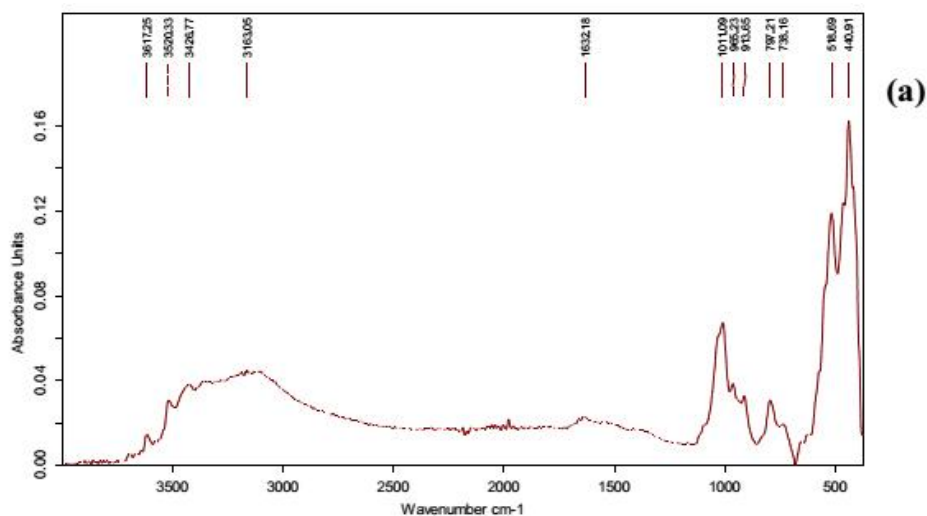


Fig. 3. IR spectra of RM (a) before and (b) after adsorption



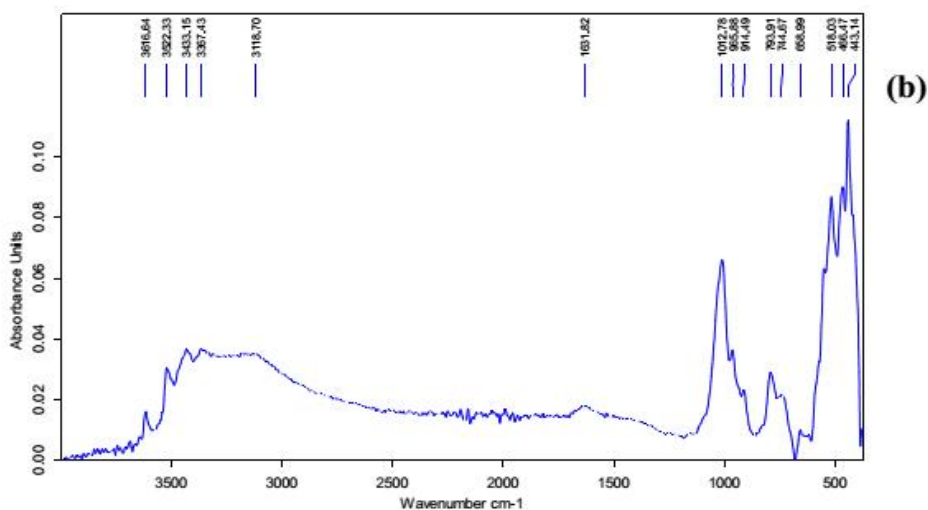


Fig. 4. IR spectra of RMW (a) before and (b) after adsorption

3.2 Effect of Contact Time on Removal of MB by RM and RMW

Results of the effect of contact time for MB removal on RM and RMW are shown in Fig. 5a. For the two adsorbents, there is rapid adsorption in the first 20 minutes attaining 66% for RMW and 18% for RM. After which there is a gradual but steadily increase up to 24 hours (94% for RMW and 64% for RM). Arias et al. [6] also observed two kinetic processes in their study on methylene blue adsorption on red mud using both batch and column techniques: first a rapid process followed by a slow kinetic reaction. At the start of adsorption, there are many adsorption sites but as the process continues there is a reduction in the number of vacant sites thus slowing down the amount adsorbed. However, the fact that there was a steady increase in percentage removal with increase time of contact indicate that long equilibrium time was necessary, so for this process we consider that equilibrium was attained in 24 hours. The equilibrium amounts obtained were 0.946 mg/g for RMW and 0.642 for RM. These were far better than 0.74 mg/g obtained by Arias et al. [6] in 192 hours on RM. The variations in equilibrium amounts removed between RM and RMW shows that distilled water treatment of red mud enhanced its MB removal potentials.

3.3 Effect of pH on Removal of MB by RM and RMW

The results of influence of pH on MB removal by RM and RMW are shown in Fig. 5b. Highest

removal of MB occurs at pH of 4, 8 and 10 for RMW (94.45, 92.27 and 92.79% respectively) and pH of 4 and 8 for RM (72.74 and 72.80% respectively). The zero point charge (ZPC) of red has been reported to be 3.2 [10]. Thus, below pH 3.2, the surface has a high positive charge density, and under these conditions, the uptake of positively charged methylene blue would be low. With increasing pH, i.e., beyond the ZPC, the negative charge density on the surface of the adsorbent increases, resulting in an enhancement in the removal of methylene blue. This explains the low removal at pH of 2 for both RM and RMW. Wang et al. [11] also obtained more significant enhancement in the adsorption of MB at pH=10 than at pH=8 while Gupta et al. [10] obtained highest MB removal at pH of 8, both using RM. The reduction of removal at pH = 10 for RM is to be expected as it has a surface charge of -202 mV thus reducing the space available for further deposition of adsorbed MB. This is contrary to RMW with a surface charge of -73 mV. Except at pH = 2, the percentage removals at all the pH studied for RMW were significantly higher than for RM, indicating the improvement of adsorbent properties of red mud for MB removal by distilled water treatment.

3.4 Effect of RM and RMW Dose on MB Removal

To find out the effect of adsorbent dose for the removal of MB from aqueous solution, adsorption studies were carried out by varying the amount of adsorbents (0.1 – 0.5 g) while keeping MB solution pH of 6.8 for both RM and RMW, initial

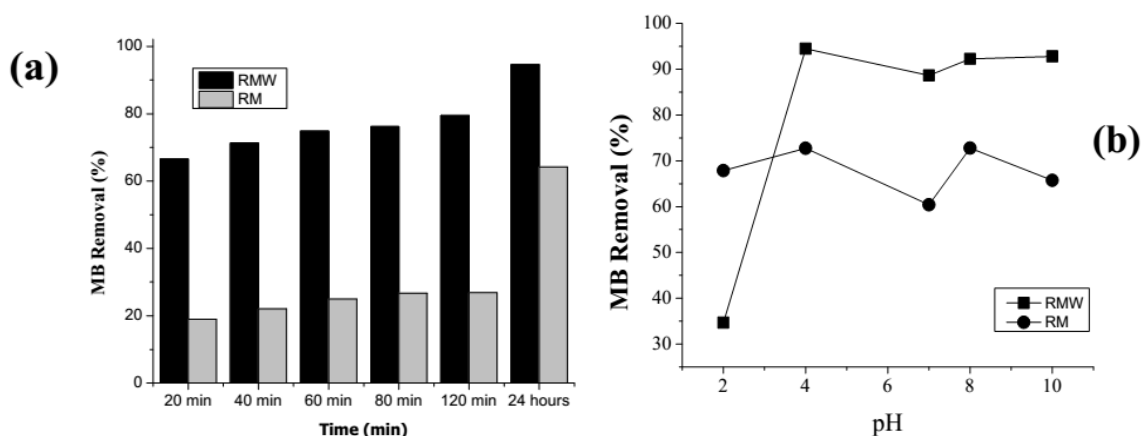


Fig. 5. Effects of (a) contact time (C_0 , 10 mg/L; temperature, 298 K; adsorbent, 0.2 g/L; solution pH, 6.8) and (b) pH on removal of MB on RMW and RM (C_0 , 10 mg/L; temperature, 298 K; adsorbent, 0.2 g/L; contact time, 24 hours)

MB concentration (10 mg/L) and at room temperature. The percentage of adsorption increases for an increase in adsorbent dose as shown in Fig. 6a. At higher adsorbent dosage there is a very fast adsorption onto the adsorbent surface, reducing adsorbate concentration in the solution. But, the adsorption sites of the adsorbent surface are unsaturated with a decreased in the adsorbate concentration in the solution [19]. It can be seen from Figure 6a that RMW dose of 0.1 g/20 mL was able to remove 77.51% of MB in 24 hours and increasing to 98.07% for 0.5 g/20mL RMW dose. However, corresponding removal percentages for RM were 57.63 to 73.37%. The results thus, show that RMW was found to be superior adsorbent for MB removal than RM.

3.5 Effect of Initial MB Concentration on RM and RMW Removal Efficiencies

The effect of increased methylene blue initial concentration on its removal on RM and RMW is shown in Fig. 6b. For RM, the percentage removal increased with increase initial MB concentration from 72.25% (for 5 mg/L) to 85.97% (for 30 mg/L) and drops to 84% for 50 mg/L. similarly, for RMW, percentage removal increased from 97.14% (for 20 mg/L) to 97.17% (for 30 mg/L) and reduced to 96.95% (for 50 mg/L), 96.66% (for 70 mg/L) and 94.70% (for 100 mg/L). The ratio of the initial number of MB to the available sorption sites at lower concentration is low and amount adsorbed becomes independent of initial concentration. However, the available sites of adsorption become fewer or there is saturation of the available active sites on the surface functional

groups at higher concentrations and thus preventing further MB uptake. These results also highlight the superiority of RMW over RM in MB removal. This is also supported by the fact that RMW was able to remove MB at higher initial concentrations, reason why for RM the initial concentration was only varied from 5 to 50 mg/L.

3.6 Effect of Temperature on Removal of MB on RMW and RM

The temperature has two major effects on the adsorption process. Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution. In addition, changing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate [11]. The effect of temperature on the removal of MB on RM and RMW was studied at 298 K, 303 K, 313 K and 333K using 10 mg/L of MB and the results are presented in Fig. 7. RM and RMW showed similar behaviour with temperature. For RM at 298 k, 64.24% was adsorbed in 24 hours and this percentage reduced to 62.17% when the temperature increased to 303 k. Thereafter, at 313 K the percentage adsorbed increased again to 62.68% and to 64.81 at 333 K. The trend was the same with RMW, decreasing from 94.62 at 298 K to 93.83% at 303 K and increasing again to 93.99% at 313 K and 94.91% at 333 K. Increasing the temperature favours MB adsorption on RM and RMW, this was also the conclusion of Wang et al. [11] for their study on MB adsorption on RM. Adsorption reactions are

normally exothermic in nature and the extent and rate of adsorption in most cases decreases with increasing temperature of the system. The decrease in adsorption with increase in temperature may be explained on the basis of rapid increases in the rate of desorption of the adsorbed species from the surface of adsorbent. This may also be due to the fact that the solubility of almost all compounds decreases with increasing solution temperature, thereby

decreasing the adsorption capacity. Meanwhile, the increase in adsorption with increase temperature is mainly due to an increase in the number of adsorption sites caused by the breaking of some of the internal bonds near the edge of the active surface sites of the adsorbent [20]. RMW average removal percentage is 93% while that of RM is 63% over the temperatures studied, confirming the enhanced potentials of RMW than RM in MB adsorption.

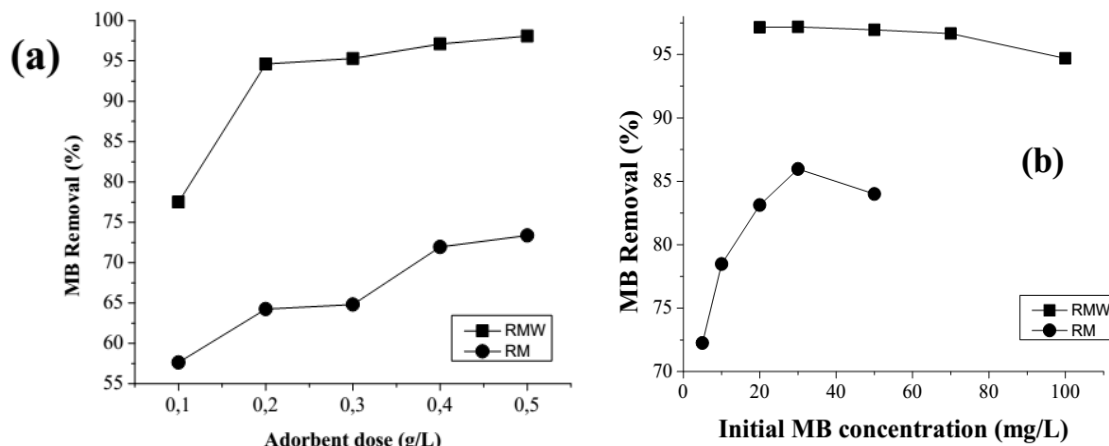


Fig. 6. Effect of (a) RMW and RM dose (C_0 , 10 mg/L; temperature, 298 K; pH, 6.8; contact time, 24 hours) and (b) MB initial concentration on its removal by RMW and RM (adsorbent dose, 0.2 g; temperature, 298K; pH, 6.8; contact time, 72 hours)

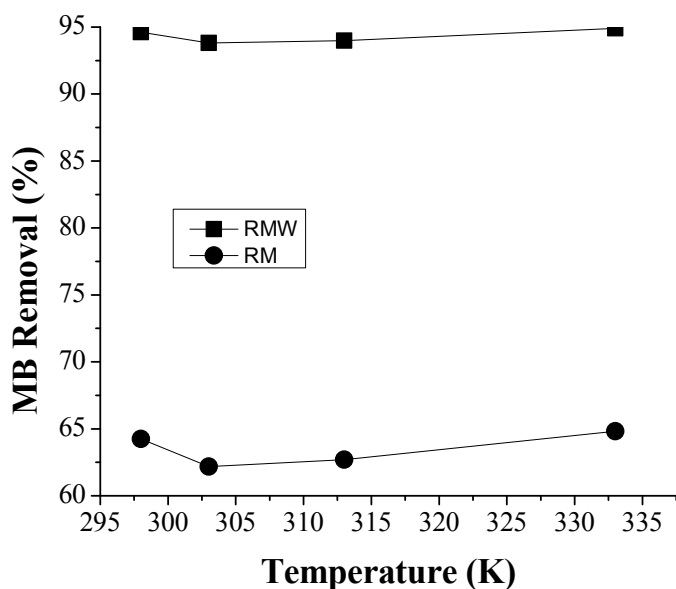


Fig. 7. Effect of temperature on removal of MB on RMW and RM (C_0 , 10 mg/L; pH, 6.8; adsorbent, 0.2 g/L; contact time, 24 hours)

3.7 The Effect of Anions Presence on MB Removal by RM and RMW

The performance of adsorbent for aqueous contaminant transformation and/or removal is dependent upon a range of factors including the concentration of common groundwater cations and anions [21]. In this paper we studied the influence of Cl^- , SO_4^{2-} , HPO_4^{2-} and HCO_3^- all of concentration 0.02 mol/L on the removal of MB (10 mg/L) by RM and RMW for 1, 2, 3 and 10 days (to appreciate their effects on long term performance of adsorbents). The results are presented in Figs. 8a and b. The addition of the respective anions decrease adsorption efficiency in the 1st day for RMW with the order of decrease being: Cl^- (86.70%) < HCO_3^- (84.11%) < SO_4^{2-} (83.71%) < HPO_4^{2-} (83.60 %), Figure 8a. Conversely, the removal starts increasing again from day 2 to day 10 for the anions with the order of increase being: Cl^- (100 %) > HPO_4^{2-} (100 %) > HCO_3^- (98.87% > SO_4^{2-} (98.47), Figure 8a. A contrary behaviour was however observed for RM sample where there was an increase of adsorption from the first day of addition of anions to the tenth day, Figure 8b. The RM system without anion had removal percentage of 87.44% on the 10th day while chloride had 97.55%, sulphate 100%, phosphate 99.97% and bicarbonate ion 99.74%. These results show that anions addition to raw red mud (RM) significantly enhanced its potentials to remove Methylene blue. The presence of anion improves the ionic strength of raw red mud, thus reducing the charge density on its surface and increasing its surface area available for adsorption. Although presence of anions equilibrated the performances of RM and RMW, in the absence

of anions RMW had removal efficiency of 100% in three days (Figure 8a) compared to 87% for RM in 10 days (Fig. 8b).

3.8 Adsorption Isotherms

Equilibrium adsorption isotherms are of fundamental importance in the design of adsorption systems since they are used in the determination of adsorption capacity and the nature of adsorbate-adsorbent interactions. The data of sorption equilibrium in this work was tested with Langmuir, Freundlich and Dubinin–Radushkevich isotherms. The experimental data on the effect of MB initial concentration on the RM and RMW of the test medium were fitted to the isotherm models, Figs. 9a, b and c and all of the constants are presented in Table 2.

The Langmuir isotherm is meant for monolayer adsorption taking place over an even homogeneous adsorbent surface [22]. The linearized form of this model is given by the formula:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \left(\frac{1}{q_m}\right)C_e \quad (3)$$

Where C_e is equilibrium concentration of the ionic species (mg/L), q_e is the equilibrium adsorption capacity (mg/g), q_m represents the monolayer adsorption capacity (mg/g), and b is the Langmuir isotherm constant (L/mg). Separation factor, R_L , which is considered as a more reliable indicator of the adsorption is defined by:

$$R_L = \frac{1}{1+bC_0} \quad (4)$$

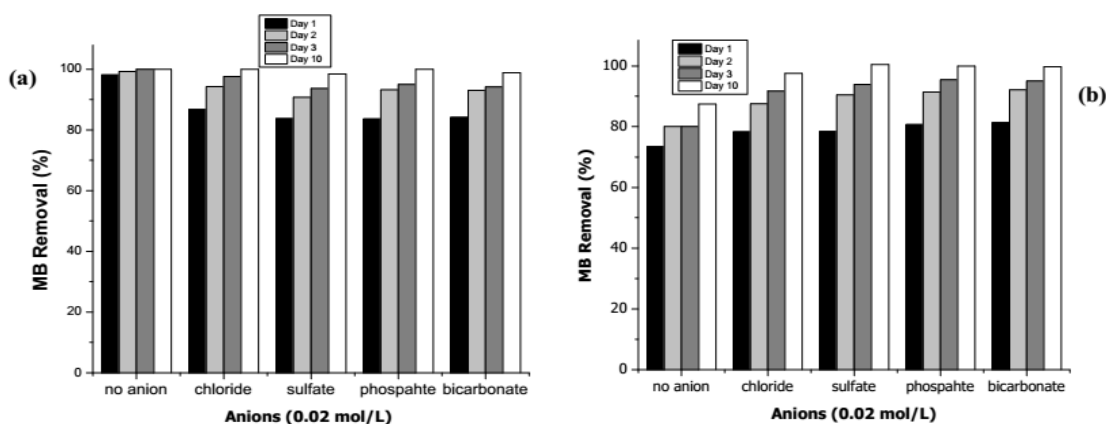


Fig. 8. Effect of some anions on removal of MB on (a) RMW and (b) RM (C_0 , 10 mg/L; pH, 6.8; adsorbent, 0.5 g/L; contact time: 1, 2, 3 and 10 days)

Where, b (L/mg) is the Langmuir constant and C_0 (mg/L) the initial concentration of solute. For favorable adsorption, $0 < R_L < 1$; while $R_L > 1$, $R_L = 1$ and $R_L = 0$, respectively, describe unfavorable, linear and irreversible adsorption.

Linearization of equilibrium data for MB removal on RM and RMW was performed by plotting C_e/q_e versus C_e , Fig. 9a, and Langmuir parameters are presented in Table 2. It can be seen from this table that the coefficient of determination of RM is 0.471 and is 0.968 for RMW, indicating that MB adsorption on RMW followed Langmuir isotherm model contrary to adsorption on RM which does not follow Langmuir isotherm. This is probably due to the fact that raw red mud (RM) contains many impurities and consequently a non-homogeneous surface. However, distilled water treatment eliminates most of these impurities making the surface more homogeneous. The Langmuir equilibrium coefficient, b , had values of 0.246 Lmg^{-1} for MB adsorption on RMW and 0.071 Lmg^{-1} on RM. The relatively large value of b on RMW than on RM shows the more favourable formation of the MB–RMW complex than MB–RM complex, thus equilibrium is more shifted to the right for MB removal on RMW than on RM. Similarly, the Langmuir monolayer capacity, q_m , for MB adsorption on RM and RMW shows a significant difference, 17.123 mg/g on RMW and 4.221 mg/g on RM. This indicates that distilled water treatment has significant influence on the monolayer capacity of red mud and also that adsorption of MB on RM and RMW do not take place by the same mechanism. Other authors have reported monolayer adsorption capacity for methylene blue adsorption on different forms of red mud: Gupta et al. [10] obtained monolayer capacity of 16.72 mg/g when they modified red mud with oxygenated water, Arias et al. [6] obtained q_m of 0.74 mg/g on raw red mud and Wang et al. [11] obtained q_m values of 2.49, 0.48 and 1.02 mg/g on raw red mud, heat treated red mud and HNO_3 modified red mud respectively [6]. The low value of the separation factor, R_L (0.169–0.039) for RMW indicate a more favourable adsorption of MB on RMW than on RM with high R_L (0.738–0.220) values. Thus, modification of red mud with distilled water improves its adsorption capacity for MB than does red mud modification with acid, heat and oxygenated water.

The Freundlich model describes multilayer adsorption process which takes place on

heterogeneous surface [22]. Freundlich isotherm model can be written as:

$$q_e = K_F C_e^{1/n} \quad (5)$$

Where K_F is the Freundlich constant $(\text{mg/g})(\text{L/mg})^{1/n}$ and n is the Freundlich exponent (dimensionless) which defines extent of linearity of the adsorption. Equation 5 was linearized, Fig. 9b and constants K_F and n were determined. From Table 2, R^2 values indicated that Freundlich isotherm represents a good fit to the equilibrium data for RM and RMW. By definition, the adsorption intensity, n , is less than unity [23]. However, the fact that $n > 1$ for MB adsorption on RMW indicate that this model does not describe the adsorption of MB on RMW.

The Dubinin–Radushkevich isotherm [22], which assumes a heterogeneous surface, is expressed as:

$$q_e = X_m \exp(-K\varepsilon^2) \quad (6)$$

where ε (the Polanyi potential) = $RT \ln(1 + 1/C_e)$, q_e is the amount of MB adsorbed per unit weight of adsorbent (mg g^{-1}), X_m the adsorption capacity of the sorbent (mg g^{-1}), C_e the equilibrium concentration of MB in solution (mg L^{-1}), K is a constant related to the adsorption energy ($\text{mol}^2 \text{kJ}^{-2}$), R the gas constant ($\text{kJ K}^{-1} \text{mol}^{-1}$), and T is the temperature (K). The significance of applying Dubinin–Radushkevich model is to determine apparent adsorption energy, E (kJ/mol) which is given by the equation [22]:

$$E = 1/\sqrt{2K} \quad (7)$$

Plot of $\ln q_e$ versus ε^2 , Fig. 9c, gives X_m and K values. If the value of E is between 8 and 16 kJ/mol, ion exchange is the main sorption process in the system. If the value is lower than 8 kJ/mol, physical sorption is the main sorption mechanism and if the value is greater than 16 kJ/mol, it may be chemisorption [22,24]. The Dubinin–Radushkevich constants were calculated and are shown in Table 2. However, the value of E for RMW and RM was found to be 1.420 and 0.605 kJ/mol, respectively. These values are all less than 8 kJ/mol, suggesting that physical forces dominated the sorption process. The good fit of the Dubinin–Radushkevich isotherm, with all R^2 values greater than 0.9, suggests that adsorption on RM surface was principally heterogeneous (good fit Freundlich and Dubinin–

Radushkevich isotherms) while that on RMW surface was mix homogeneous-heterogeneous (good fit Langmuir and Dubinin–Radushkevich isotherms). Under industrial conditions, mixing of the adsorbent and the wastewater solution would be imperfect, thus the adsorbent surface is less likely to be homogeneous and the assumptions required by the Langmuir isotherm would be less likely to be correct [24]. The good fit of the Dubinin–Radushkevich isotherm for RM and RMW suggest that these isotherms could be more appropriate under industrial conditions.

The Lanmuir, Freundlich and Dubinin–Radushkevich adsorption capacities for RMW were all higher than those for RM, confirming the enhancement of distilled water treated red mud for MB removal.

A comparison of the sorbent capacities of RM and RMW for methylene blue with those of other available adsorbents is summarized in Table 3. Although RMW is relatively favourable over most

other industrial waste and natural materials than bio adsorbents, its greater availability and hence lower cost means it will provide a comparable adsorption capacity per unit cost. Out of the 150 million tons of red mud produced annually, current estimates shows that only about 2-4.5 tons are used annually in some way including its use as adsorbent [5]. Thus, encouraging more red mud reuse will reduce its environmental impacts resulting from disposal.

3.9 Adsorption Kinetics

Kinetic analysis is required to get an insight of the rate of adsorption and the rate-limiting step of the transport mechanism, which are primarily used in the modelling, and design of the process [28]. Pseudo-first-order, pseudo-second-order and intraparticle diffusion models have been widely used to study the rate-limiting step of the adsorption process. The plots of these models are shown in Figs. 10a, b and c respectively and their calculated parameters are presented in Table 4.

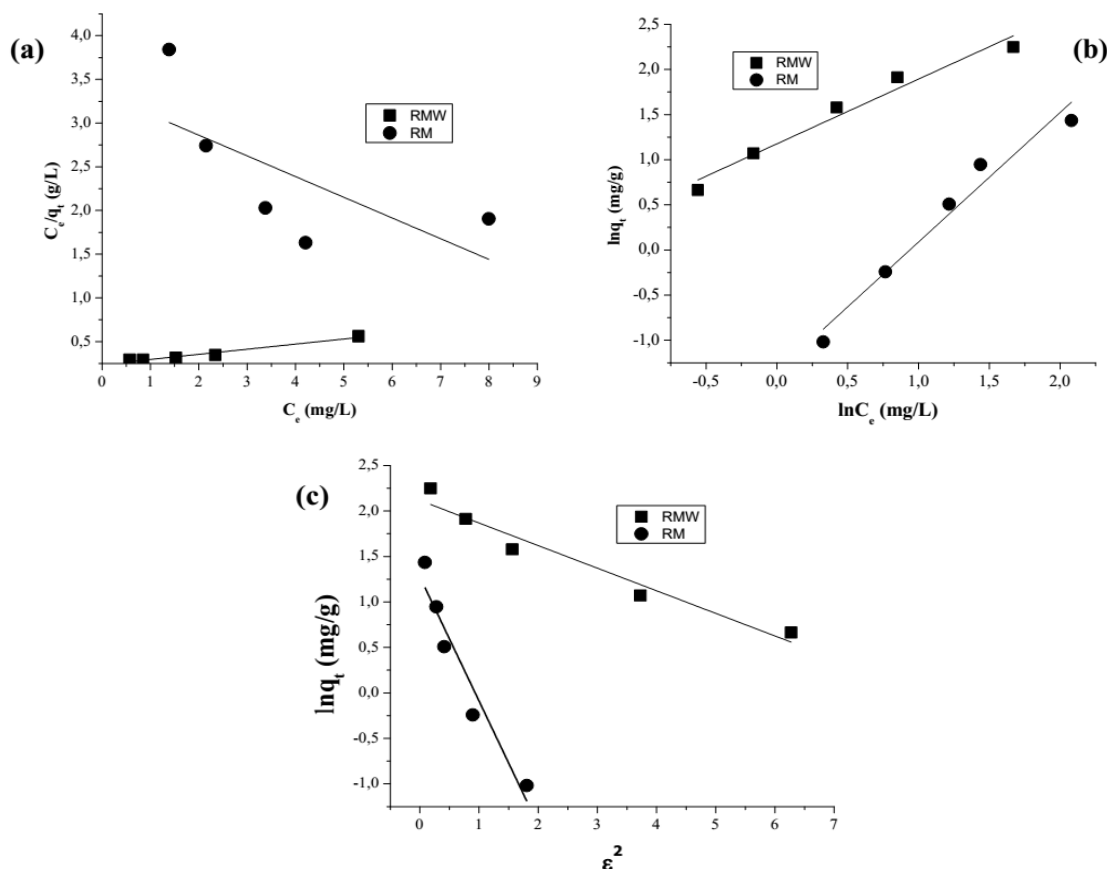


Fig. 9. (a) Langmuir, (b) Freundlich and (c) Dubinin Radushkevich isotherms plots for MB removal on RMW and RM

Table 2. Isotherm parameters for MB removal by RMW and RM

Models	Parameters	RMW	RM
Langmuir	q_m (mg/g)	17.123	4.221
	b (L/mg)	0.246	0.071
	R^2	0.968	0.471
	R_L		
	5 mg/L	-	0.738
	10 mg/L	-	0.585
	20 mg/L	0.169	0.413
	30 mg/L	0.119	0.319
	50 mg/L	0.075	0.220
	70 mg/L	0.055	-
Freundlich	100 mg/L	0.039	-
	K_F (mg/g)(L/mg) ^{1/n}	3.232	0.260
	n	1.394	0.697
	R^2	0.967	0.967
Dubinin Radushkevich	X_m (mg/g)	8.300	3.581
	K (mol ² /KJ ²)	0.248	1.364
	E (kJ/mol)	1.420	0.605
	R^2	0.951	0.937

Table 3. Comparison of monolayer capacities for methylene blue on some adsorbents

Adsorbent	Adsorption capacity (mg/g)	
Pearl millet husk carbon	82.37	
Sagaun saw dust	2.0-3.0	[25]
Banana peel	15.9	
Orange peel	13.9	
Chrome sludge	0.51	
Neem leaf powder	8.76	
Rice husk	40.58	
jute fibre carbon	22.5	
Rice husk (Cair pith carbon)	5.87	[26]
Wheat Bran	3.08	
Guava seed	0.1	
Activated carbon	8.77	
Palm-Tree Waste	39.47	
Activated carbon (olive stones)	303	
Date pits	80	
Pyrophyllite	70.42	
Fly ash	53.84	[27]
Activated carbon (coconut shell fibbers)	19.59	
Perlite	5.6 – 9.08	
Perlite (EP)	17.4 – 31.7	
Walnut shell-activated carbon 750°C	3.53	
Fire wood based activated carbon	1.21	
Clay	6.3	
Pure kaolin	15.55	
Zeolite	10.82	[1]
Fly ash	2.85	
Coal fly ash (0.01 NaCl)	16.6	
RMW	17.123	This work
RM	4.221	

The pseudo-first-order kinetic model in its linearized form is given by the Lagergren equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

Where q_t is adsorption capacity (mg/g) at time t (min), q_e is the equilibrium adsorption capacity (mg/g) and K_1 is the pseudo-first-order equilibrium rate constant (min^{-1}). Due to boundary layer limitations, pseudo-first-order model had a least fit to the equilibrium data, Fig. 10a, Table 4. Though R^2 values ranging from 0.966 to 0.818 were obtained for RMW and RM respectively, calculated q_e values did not match with the experimental values thus, indicating the unsuitability of this model compared to other models.

The pseudo-second-order kinetic model expression is given by [29]:

$$\frac{1}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right) t \quad (9)$$

Where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the pseudo-second-order constant. If the second-order kinetics is applicable, then the plot of t/q_t versus t should be a linear relationship. The initial adsorption rate, h ($\text{mg/g}\cdot\text{min}$), as $t \rightarrow 0$ can be defined as $h = k_2 q_e^2$. The initial adsorption rate (h), the equilibrium adsorption capacity (q_e), and the second-order constant (k_2) can be determined experimentally from the slope and intercept of plot t/q_t versus t , Fig. 10b and values of the parameters are shown in Table 4. The experimental and calculated q_e values were well correlated and R^2 values were above 99%. However, R^2 value was at unity for RMW with higher k_2 value indicating more rapid adsorption on RMW than RM. This is also supported by the fact that the correlation was stronger for RMW, with higher initial sorption rate than RM.

The half adsorption time of dye, $t_{1/2}$, that is the time required for RMW and RM to uptake half the amount adsorbed at equilibrium is often considered as a measure of rate of adsorption and for the second-order process is given by [30]:

$$t_{1/2} = 1/K_2 q_e^2 \quad (10)$$

The determined values for $t_{1/2}$ are given in Table 4. While this value is 16.568 min^{-1} for RMW, it is 111.644 min^{-1} for RM, indicating faster adsorption on RMW than RM.

When there is a possibility of diffusion of adsorbate species into the interior of the pores of the adsorbent, the intraparticle diffusion rate constant (k_{id}) is obtained from intraparticle diffusion model equation [27]:

$$q_t = k_{id} t^{0.5} + C \quad (11)$$

Where q_t (mg g^{-1}) is the amount of adsorption at time t (min), k_{id} ($\text{mg g}^{-1} \text{min}^{1/2}$) is the rate constant of intraparticle diffusion and C is intercept. The intercept of the plot, Fig. 10c, reflects the boundary layer effect. Larger the intercept, greater is the contribution of the surface sorption in the rate controlling step. The calculated diffusion coefficient K_{id} values are listed in Table 4. For the process to be completely controlled by the intraparticle diffusion model, the plot of q_t versus $t^{0.5}$ yields a straight line passing through the origin with the slope giving the rate constant, k_{id} . But the plots did not pass through the origin on any of the samples. This deviation from the origin is due to the difference in the rate of mass transfer in the initial and final stages of the sorption [27]. This indicated the existence of some boundary layer effect (0.678 for RMW and 0.137 mg/g for RM) and further showed that Intraparticle diffusion was not the only rate-limiting step.

Pseudo-second-order model represents a best fit for all the samples, than the other models examined with a higher R^2 and correlated equilibrium values; hence, it is clear that the uptake was a two-step process; migration of adsorbate to red mud surface followed by attachment.

3.10 Adsorption Thermodynamics

The main thermodynamic parameters such as Gibbs free energy (G), enthalpy (H), and entropy (S) for the adsorption process were obtained using the equations [31]:

$$\Delta G = -RT \ln K \quad (12)$$

$$\ln K = (\Delta S/R) - (\Delta H/RT) \quad (13)$$

Where R is the ideal gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$) and T is the temperature (K). The enthalpy change (H) and the entropy change (S) are calculated from a plot of $\ln K$ versus $1/T$.

$$K \text{ was calculated from } K = C_{\text{ads}}/C_e \quad (14)$$

$$C_{\text{ads}} = C_o - C_e$$

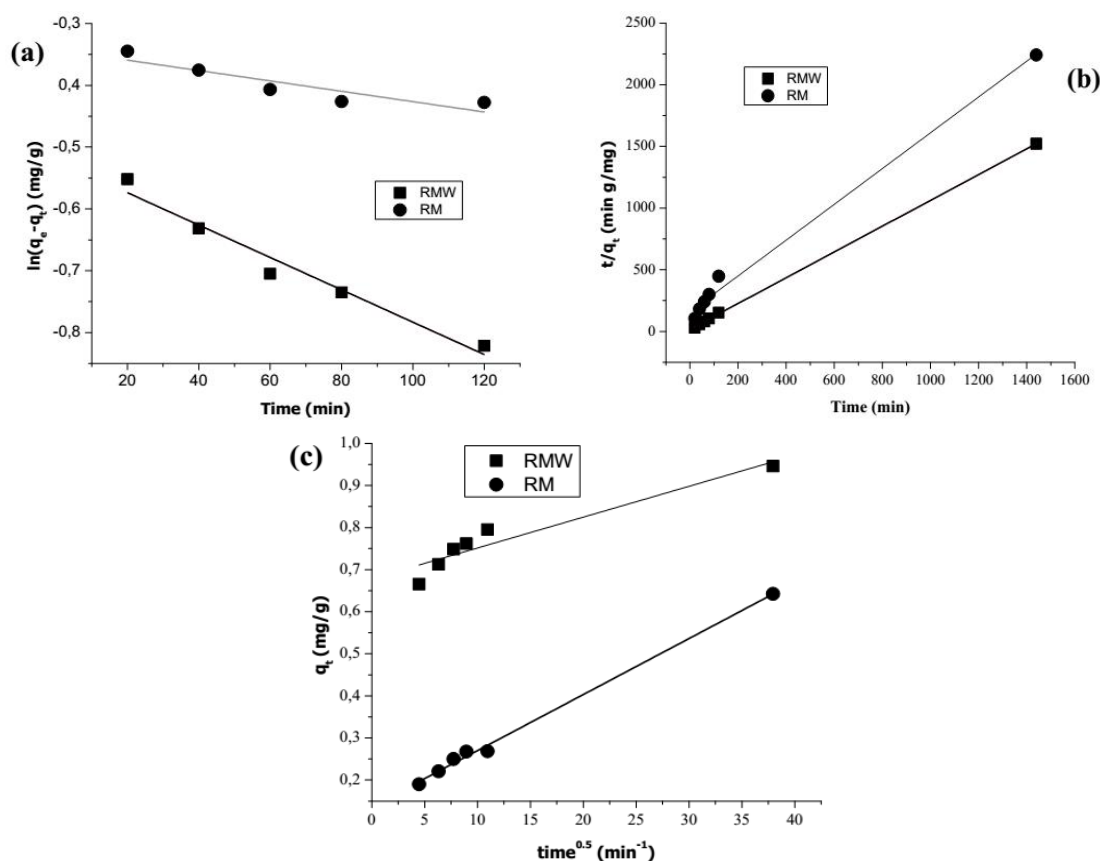


Fig. 10. (a) Pseudo-first order, (b) pseudo-second order and (c) intraparticle diffusion models kinetic plots for MB removal on RMW and RM

Table 4. Kinetic parameters for MB removal by RMW and RM

Models	Parameters	RMW	RM
Pseudo-first-order	k_1 (min)	0.003	0.001
	q_e, cal (mg/g)	0.595	0.710
	q_e, exp^t (mg/g)	0.946	0.642
	R^2	0.966	0.818
Pseudo-second-order	k_2 (g/mg/min)	0.063	0.013
	q_e, cal (mg/g)	0.957	0.689
	q_e, exp^t (mg/g)	0.946	0.642
	R^2	1.000	0.994
	h (mg/g·min)	0.058	0.006
Intraparticle diffusion	$t_{1/2}$ (min)	16.586	111.644
	k_{id} (mg/g/min ^{1/2})	0.007	0.013
	C (mg/g)	0.678	0.137
	q_e, exp^t (mg/g)	0.946	0.642
	R^2	0.910	0.997

q_e, cal and q_e, exp^t are respectively, calculated and experimental equilibrium amounts adsorbed

Where K is the equilibrium constant, C_e is the concentration of MB in solution at equilibrium (mg/L) at temperature T , C_o is the initial MB concentration (mg/L), C_{ads} is the concentration of MB in the adsorbent at equilibrium (mg/L) at temperature T .

The results of these thermodynamic calculations are shown in Table 5. The negative value for the Gibbs free energy shows that the adsorption process is spontaneous and that the degree of spontaneity of the reaction increases with increasing temperature. However, the more

negative values for RMW than for RM indicate a more spontaneous adsorption on RMW than RM. The overall adsorption process seems to be endothermic ($\Delta H^\circ = 2.623$ on RMW and 1.350 on RM kJ mol^{-1}). This result also supports the suggestion that the adsorption capacities of RMW and RM for all MB increases with increasing temperature. Results in Table 5 also show that the ΔS values were positive (i.e., that entropy increases as a result of adsorption). This shows the increased randomness at solid liquid interphase during the sorption processes of MB dye on RMW and RM. This is a direct consequence of (i) opening up of structure of adsorbent beads (ii) enhancing the mobility and extent of penetration within the adsorbent beads and (iii) overcoming the activation energy barrier and enhancing the rate of intra-particle diffusion [31]. Thus, adsorption is thus likely to occur spontaneously at normal and high temperatures because $\Delta H > 0$ and $\Delta S > 0$ as evident from K and ΔG values in Table 5.

3.11 Regeneration Studies

Although red mud is available in large quantities, regeneration of its removal capabilities is important not only because of reducing disposal problems and saving cost from using fresh adsorbents but also for selective recovery of desired species from selected medium. The results are presented in Fig. 11. The percentage of desorption of MB from RMW was 71.88, 67.97, 51.49 and 39.77% while for RM, it was 90.37, 79.00, 53.32 and 40.85% for the 1st, 2nd, 3rd and 4th cycles, respectively. The high removal is probably due to the polar relation between MB and acetone and physical nature of MB adsorption on these samples as revealed by energies calculated from Dubinin–Radushkevich isotherm. However, desorption values from RM were higher than in RMW as we earlier showed that MB adsorption on RMW involved stronger interactions (as evident from Langmuir equilibrium constant, b) than on RM. The

Table 5. Thermodynamic parameters of RMW and RM for the removal of MB

	C_0 (mg/L)	Temperature (K)	Equilibrium constant	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (KJ/mol K)
RMW	$C_0 = 10$	298	17.600	-7.105	2.623	0.032
		303	15.180	-6.852		
		313	15.644	-7.157		
		333	18.650	-8.100		
RM	$C_0 = 10$	298	1.796	-1.451	1.350	0.009
		303	1.643	-1.252		
		313	1.680	-1.350		
		333	1.842	-1.691		

C_0 = initial methylene blue concentration

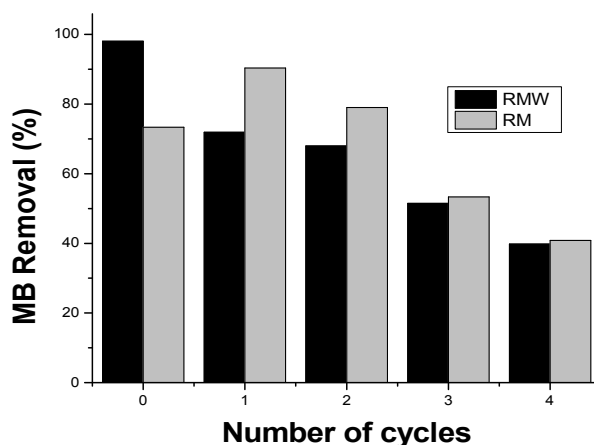


Fig. 11. Regeneration studies of MB on RMW and RM (C_0 , 10 mg/L; pH, 6.8; adsorbent, 0.5 g; contact time, 24 hours)

decrease in the desorption percentages might be due to the heterogeneity of the surface after being repeatedly encountered by MB molecules [22].

4. CONCLUSION

The removal of methylene blue dye onto raw and distilled water modified red muds has been studied in detail. Determined physicochemical properties such as pH and surface charge, chemical composition (XRF), surface groups (IR) and morphology (SEM), showed distilled water treated red mud to be a better adsorbent than the raw red mud. The distilled water treated red mud was able to remove over 98% of 10 mg/L of MB in 24 hours against 73% for raw red mud with adsorbent dose of 0.5 g/L from aqueous solution. In general, for all the parameters studied, RMW showed higher MB removal than RM, the difference averaging about 30%. Nevertheless, the two samples showed similar adsorption behaviour with the tested parameters. For example, there is increase in removal efficiency with increase contact time, pH 4 to 10, temperature 298 K to 333 K, adsorbent dose 0.1g/L to 0.5 g/L, and increasing initial MB concentration. At high concentrations, a decrease in efficiency is observed for both samples. However, RMW can remove higher MB concentrations than RM.

The Langmuir, Freundlich and Dubinin–Radushkevich isotherms models were used to explain the adsorption phenomenon. The order of fit in relation to coefficient of correlation was Langmuir > Dubinin–Radushkevich > Freundlich for RMW and Freundlich > Dubinin–Radushkevich > Langmuir for RM. Monolayer adsorption capacity was calculated as 17.123 and 4.221 mg/g for RMW and RM respectively. Thus, water treatment has significant influence on the monolayer capacity of red mud. Pseudo second-order kinetics fitted well adsorption on the two samples with RMW having high initial sorption rate and low half adsorption time than RM. The order of shifting of equilibrium to the right as well as the rate of uptake is: methylene blue on RMW > methylene blue on RM. The process was found to be more endothermic, more spontaneous and more favourable on RMW than on RM. Desorption experiments using acetone as desorbing agent produced considerable results up to four cycles depicting that RMW and RM are reusable.

Water modified red mud is relatively efficient as other used materials for MB removal (Table 5), so it was concluded that red mud modified with distilled water can be used for industrial applications in removing methylene blue from various real effluents released from various types of industries such as chrome plating, textile dyeing, leather tanning and photolithographic industries. Also modification of red mud with water is a cheaper process with no risk of introducing other chemicals on to it as opposed to other neutralization methods that use mineral acid, heat and other chemicals. Using cheaper neutralization methods and encouraging more red mud use will reduce the over 140 million tons disposed worldwide and thus reducing the risk of red mud disasters with corresponding environmental consequences.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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