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A chief, industrial waste, activated red mud for subtraction of methylene blue dye from environment

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ABSTRACT

Dyes are used as a colored compound and considered as a highly toxic to biological species in water medium. Adsorption is most comprehensively used technology because of simple, low cost and effective for pollutant removal. Red mud activated by acid followed by heat treatments (ARM) was used as an adsorbent. 80% dye removal within 75 min observed when adsorbent dose was 100 mg and initial dye concentration 10 ppm having solution pH 10. The R^2 value was to be 0.991 at temperature 308 K which fits with Langmuir isotherm model. The process is exothermic in nature was confirmed by thermodynamic parameters.

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1. Introduction

The heavy toxic metal ions, various types of dyes, drugs, various phenolic compounds, pest and insect controlling chemicals, house hold products and wide spectrum of aromatics are a common pollutants present in a water [1–2]. The presence of pollutants in water makes water highly toxic to the aquatic life and changing the water potable to the non potable. A number of processes are available for the treatment of water to make water potable having some advantages and disadvantages [3]. Adsorption of various pollutants from the water and waste water is more superior process among the different treatment processes. It is well known that solid waste materials (byproducts) generated from various industrial activities poses one of most vexing problems of society. Cities of developing countries have no adequate treatments for solid waste generated by houses and industries and are a major challenge to solve. Solid waste generated form houses and industries were used as adsorbents for the treatment of water and waste water is an interesting and beneficial alternative. If it is, reduces the volume of solid waste and reduces the pollution at reasonable cost.

Adsorption of different types of pollutants from solution is a superior choice and many advantages over the other processes. For the adsorption process, adsorbents material with specific properties was essential. Oxides and hydroxides of metal, biomaterial, synthetic resins, polymer, porous materials and industrial waste were reported as adsorbents for the elimination of pollutants from solution [4–7]. Industrial waste from thermal power station, metallurgical processes and others industrial waste can be a smart choice over the others due to advantages was reported [8]. In aluminum metallurgical processes, the bauxite ores was leach with alkali and red mud, an industrial waste product was generated. Globally 90 millions tones red mud was produced each year [9–10]. Size and worth of red mud generated in alumina process obtained from one location was not similar from other location.

Red mud is a highly alkaline waste material due to use of sodium hydroxide solution during metallurgical process. Fine particles of red mud containing oxides and hydroxides of aluminum, iron, silicon and titanium metal mainly. Red mud containing 60% mass of oxidized iron and hence the color becomes red. High alkali content, chemical species and a noteworthy impact on environment make red mud problematic and hence its dumping is a big challenge where alumina industries are installed. Alkaline nature of red mud makes is harmful material and is big hurdle using this material as an adsorbent [11–13].

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Dyes are used as a colored compound and considered as a highly toxic to biological species in water medium in a different ways. Due to presence of dyes in water several common problem was observed in human such as allergic symptoms, skin related problem, leads to cancer and mutation in genetic material [14–15].

The elimination of chemicals having serious impact on environment using different industrial waste reported in the literature. The removal of dyes from water using red mud was also reported [16]. The procion orange dye removal from water by red mud was reported in a literature. It is observed that it is act as an adsorbent and its efficiency was not only affected by initial dye concentrations but also by agitation time, adsorbent dosage and pH [17]. Acid violet dye, can be eliminated from the environment using red mud was reported [18]. Red mud for the elimination of dyes from the environment has less effectiveness been reported as an adsorbent. Hence in order to explore more applicability and excellent effectiveness on the removal of different classes of dyes using red mud as adsorbent more emphasis is required.

2. Experimental

Red mud used in the present experiments was supplied from (Jawaharlal Nehru Aluminum Research Design and Development Centre) JNARDDC, Nagpur, Maharashtra. It has the following average chemical composition (%): Al_2O_3, 19.88; Fe_2O_3, 36.47; CaO, 2.33; SiO_2, 15.95; Na_2O, 10.03; TiO_2, 4.97; CO_2, 2.48; S, 0.09; V_2O_5, 0.074; P_2O_5, 0.041 and loss on ignition is 8.04%. Red mud was first air dried and sieved by 200 mesh steal sieve. Sieved red-mud was stored in a laboratory under atmospheric conditions before activation processes. 10 g of red mud and 190 mL of Millipore water was introduced in a beaker and stirred to form slurry. Further 18 mL of 31% HCl was introduced in a beaker and resulting solution was heated at 60 °C for 20 min and diluted with water to make total volume of 800 cm^3 with constant stirring. Liquor ammonia was added drop wise with constant stirring till the pH of solution become 8. The precipitate obtained was further heated at 50 °C for 10 min with constant stirring. The whole solution was cooled and precipitate has been separated using Whatmann filter paper. After filtration, precipitate wash with Millipore water several times and dried in oven at 110 °C and finally calcined at 700 °C for 2 h. The resultant material place in a desiccators and finally grind in a fine powder and here after is called as an activated red mud (ARM)**.** 0.1–1.0 mm diameter red mud particles were used for all characterization and dye adsorption study.

X-ray diffraction (XRD) patterns were collected on a Philips PANalytical Diffractometer with standard protocol. Fourier transform infrared spectroscopy (FT-IR) spectra were measured on a Bruker alpha model. SEM images was recorded by JEOL Model JSM – 6390 LV field-emission instrument, Nitrogen adsorption–desorption isotherms were determined on a Micromeritics ASAP 2420 analyzer and data analyse by software.

100 ppm methylene blue (s.d fine Chemicals) stock solution was used. Methylene blue solution having concentrations ranging between 5 ppm and 50 ppm of MB were prepared using stock solution. All experiments were measured at room temperature (25 °C) and the initial pH of the solution was adjusted by NH_4OH (0.1 M) and HCl (0.1 M) solution. The amount of MB dye was calculated spectrophotometrically (Shimadzu UV-1800 model) using wavelength of maximum 663 nm.

3. Results and discussion

The X-ray diffraction pattern of red mud and activated red mud is represented in Fig. 1.

Fig. 1 shows that, the raw red mud having calcite phase had been disappears after acid treatment. This is may be due to decomposition of goethite phase and formation of new magnetite phase after acid-thermal treatment. The dominant phase in activated red mud is hematite and its peak intensity significantly enhance. SEM pictures provide morphology of surface of red mud before activation of sample at micro-scale and after activation was represented in a Fig. 2. Fig. 2 shows that there is a mark difference in a surface morphology of red mud before acid activation and red mud after acid activation. SEM images of red mud after acid activation shows illustrative proof for the enhancement of surface area by acid followed by thermal treatment. The red mud after acid treatments has many cavities probably due to removal of some acid-soluble salts. After heat treatment, Activated Red Mud exhibits flake like morphology with additional porosity.

The EDS spectrum of Activated Red Mud clearly provides the obvious highest content of aluminum as shown in Fig. 3(A). The presence of iron with traces of oxygen and silicon content was also observed. These may be attributed towards reactive component as a result of activation of red mud with Acid treatment.

Fig. 3 (B & C) represented the FT-IR spectra of red mud before activation (B) and after activation(C). Both the samples show two peaks at 3450 cm^{-1} which one is very broad and another one at 1643 cm^{-1} corresponding to the stretching vibration of hydroxyl. The presence of water molecule or hydroxyl group in the samples was confirmed by these two peaks. The peak at 1470 cm^{-1} and 1400 cm^{-1} was observed in the red mud sample before the activation corresponding to the presence of CO_3^{2-} indicating the presence of a large amount of carbonate in the sample. However, these two bands was not observed in red mud after activation, owing to the fact that the carbonates are reacted with HCl and decomposed after thermal treatments. The peaks at 591 cm^{-1} and 546 cm^{-1} in both the sample were attributed to the stretching vibration of Fe–O, indicating the existence of Fe compounds. The peak at 1002 cm^{-1} corresponding to Si–O stretching vibrations was observed for the red mud before activation which was noticeably absent in the red mud after activation. This indicated that that the silicate groups may be remove during the activation process. The peak at 617 cm^{-1} correspond to Al–O band was observed in both the sample. The results observed are well match with reported literature [19].

The surface areas of red mud before activation and red mud after activation were evaluated by BET method and results are represented in Table 1. The surface area of red mud before activation is low than red mud after activation. This change of specific surface area will be an advantage to use red mud as an adsorbent after activation. During the activation process the metal ions present in red mud may react with acid molecules and assemble in such a manner so the diameter of internal pore increases which leads to increase of surface area.

Activated red mud (ARM) was use as a adsorbent for the removal of methylene blue. To analyse the efficiency of ARM as a adsorbent the influence factors including adsorbent dosage, contact time, pH, and initial concentration was studied and result are represented in Fig. 4. The amount of ARM dose was investigated to analyze the maximum dose of ARM for MB dye removal. To analyze it, 10 ppm initial concentration and 100 mL volume of MB dye solution was used for all experiments. The results are depicted in Fig. 4(A), show that as an amount of ARM was increases the subtraction efficiency of MB dye also increases. It shows that removal efficiency was 50% when the amount was 40 mg. For 50 mg, it was 60% and 85% for 100 mg. The increase of removal efficiency with increase of ARM amount is may be due to increase of number of sites available for adsorption. Therefore, removal efficiency reached in equilibrium with the amount of 100 mg of ARM and is sufficient for 85% MB dye removal from 10 ppm solu-

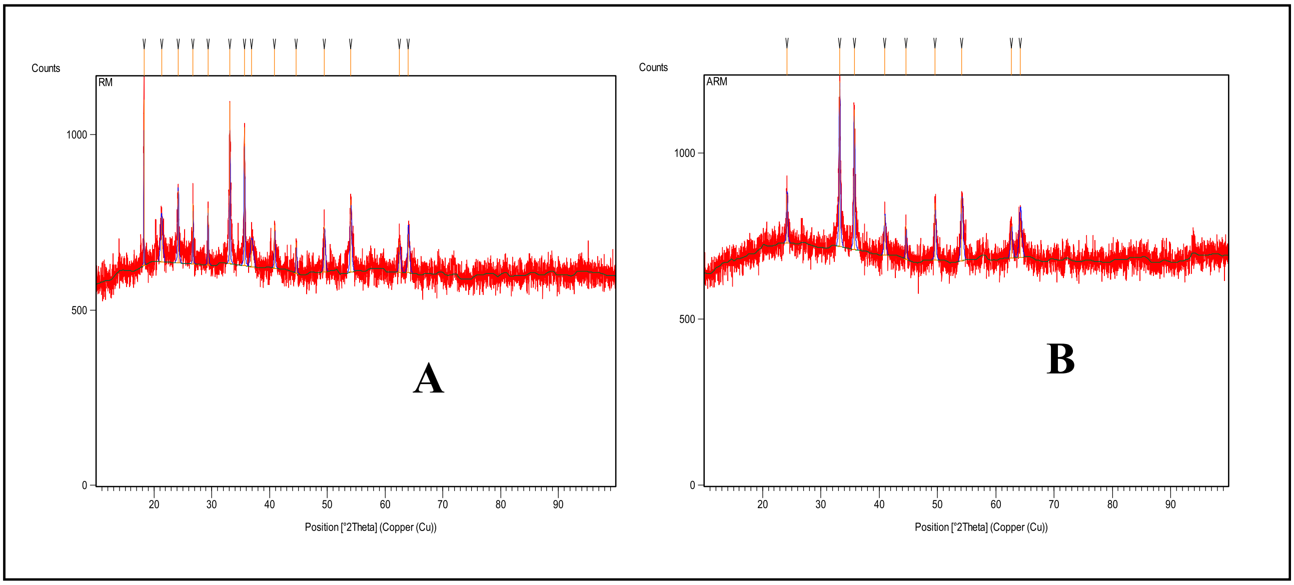

Fig. 1. X-ray diffraction spectra for (A) Red Mud and (B) Activated Red Mud. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

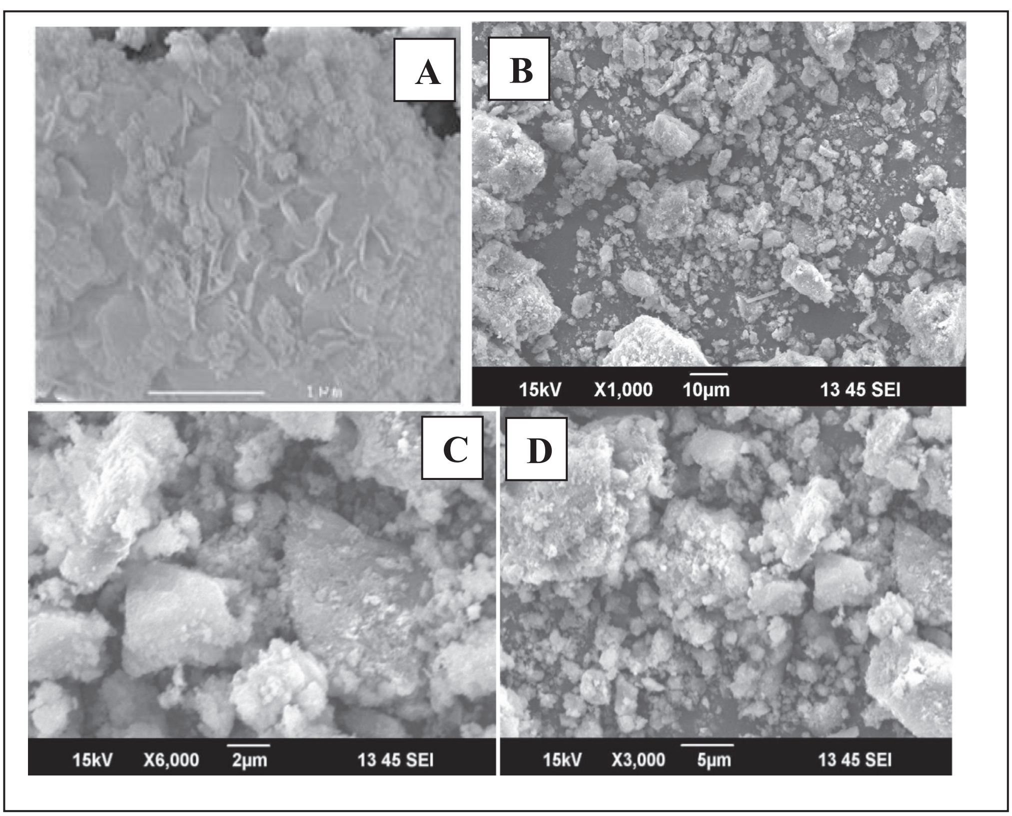

Fig. 2. SEM images of Red Mud before activation (A) and Activated Red Mud (B, C, D).

tion. The higher dose of adsorbent seems not to be required in all concentration ranges suggesting the effective use of ARM for efficient MB dye removal from water. The highly competent adsorption property may be ascribed due to the porous and crystalline layered structure formation of ARM.

The pH of solution is critical factor and to analyze the pH of solution on the subtraction efficiency of MB dye was studied in a solution pH of 2–12 using volume of solution 100 mL with 10 ppm MB concentrations. Fig. 4(B) indicates the outcome of pH on the removal of MB dye in the presence of ARM. When initial pH of the dye solution was increased from 3 to 11, the percentage removal increased from lower to higher. The subtraction tendency of methylene blue increases with increasing the solution pH is dependent on the environment of the adsorbent. At lower pH, the percentage of the removal of MB dye was 40%. Interestingly, at higher pH, the trend of the removal was increased. Fig. 4(B) sug-

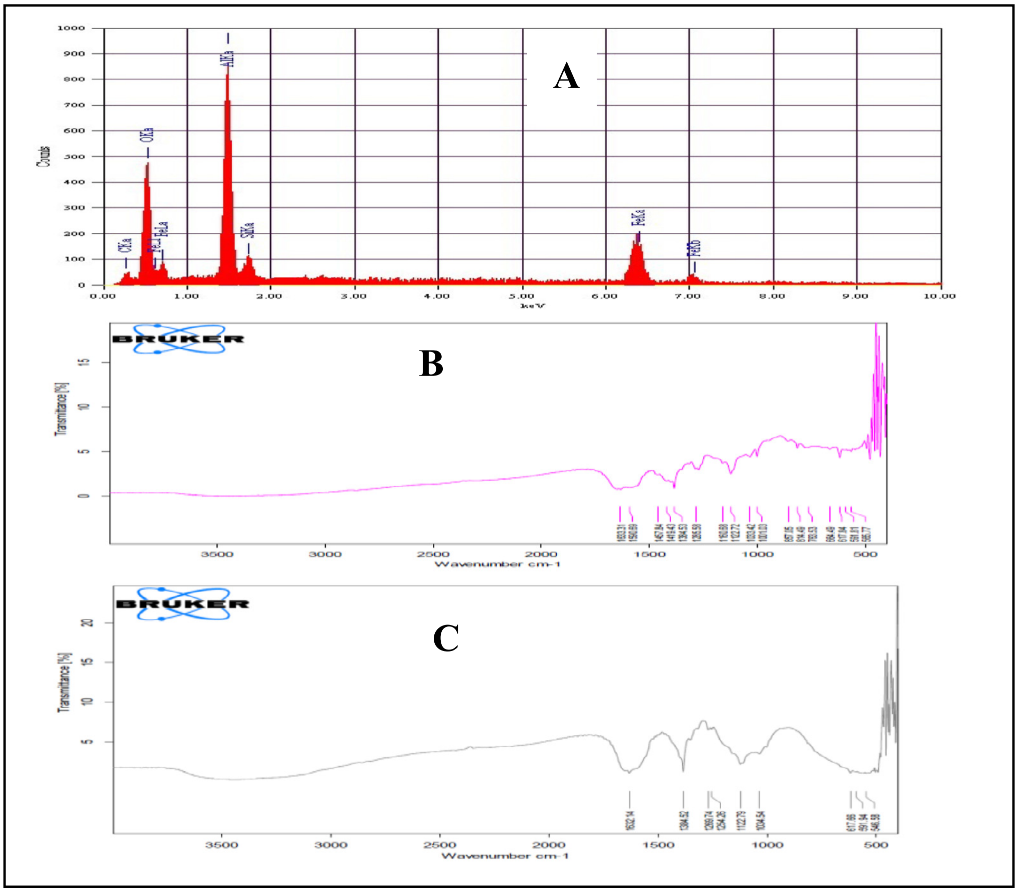

Fig. 3. EDS spectra of Activated Red Mud (A); FTIR image of Red Mud before activation (B) and FTIR image of Activated Red Mud(C). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Comparison of specific surface area.

Sample	Specific surface area (m^2g^{-1})
Red Mud before activation	67,92
Activated red mud (ARM)	241,989

gests the efficient removal performance of ARM in basic pH. Red mud is a mixture of oxides having surface hydroxyl groups, while MB is a cationic dye molecule. AT low pH, the adsorbent surface will be positively charged and hence may be repulsion take place. At higher pH, the surface of adsorbent will be negatively charged and hence MB molecule is easily adsorbed. On the basis of observation, the adsorption mechanism can be attributed to the ionic interactions between the dyes and the adsorbent surface [20–21].

The relation between subtraction efficiency of MB dye and contact time is a critical factor to analyze more about adsorption study. The results of subtraction efficiency of MB dye with change of contact time using ARM are presented in Fig. 4(D). It was found that the 80% removal of MB dye concentration occurred within 75 min and after 75 min of time the subtraction efficiency of MB using ARM was slow. The equilibrium was attained at 80 min when the maximum MB dye adsorption onto activated red mud was reached.

Preliminary concentration of dye molecule greatly affects the adsorption process on the adsorbent. To analyze the preliminary concentration of MB dye molecule, 100 mL volume of solution with different preliminary concentration of MB dye was exposed with ARM adsorbent. 10 to 100 ppm MB dye concentration was used for the analysis of effect and results were represented in Fig. 4 (C). It shows that subtraction efficiency was decreased with increasing of preliminary concentrations. 85% methylene blue was removed at initial concentration 10 ppm. At low concentration, most of methylene blue in the sample solution might contact with active sites of adsorbent and when the concentration is increased all methylene blue species will not be available to contact with the active surface due to active sites are already filled up.

Thermodynamic parameter such as Gibb's free energy ($\Delta G°$), enthalpy change ($\Delta H°$) can be determine by well known thermodynamic equation. The chemical thermodynamics relates the change in a chemical equilibrium constant (K_{eq}) to the change in temperature, T, given the standard enthalpy change, ΔH^0 for the process shown in Fig. 4(E). The increase of temperature decreases the adsorption indicate the process is exothermic. Data obtained by various experiment were analyzed using well known adsorption isotherm models. The straight line plot of C_e/q_e versus C_e with correlation coefficient R^2 was found to be 0.991, 0.995, 0.996 for temperature 308, 318 and 328 K, indicates the accuracy of Langmuir isotherm. This indicates a monolayer adsorption of MB onto the adsorbent surface. The Freundlich isotherm is employed to describe heterogeneous system. Where C_e is the how much dye was absorbed by ARM and n is the empirical parameter. The values of R^2 are 0.982, 0.965, and 0.961 respectively. Higher value of correlation coefficient of Langmuir isotherm indicates that adsorption data fits better with Langmuir equation than the Freundlich's isotherm.

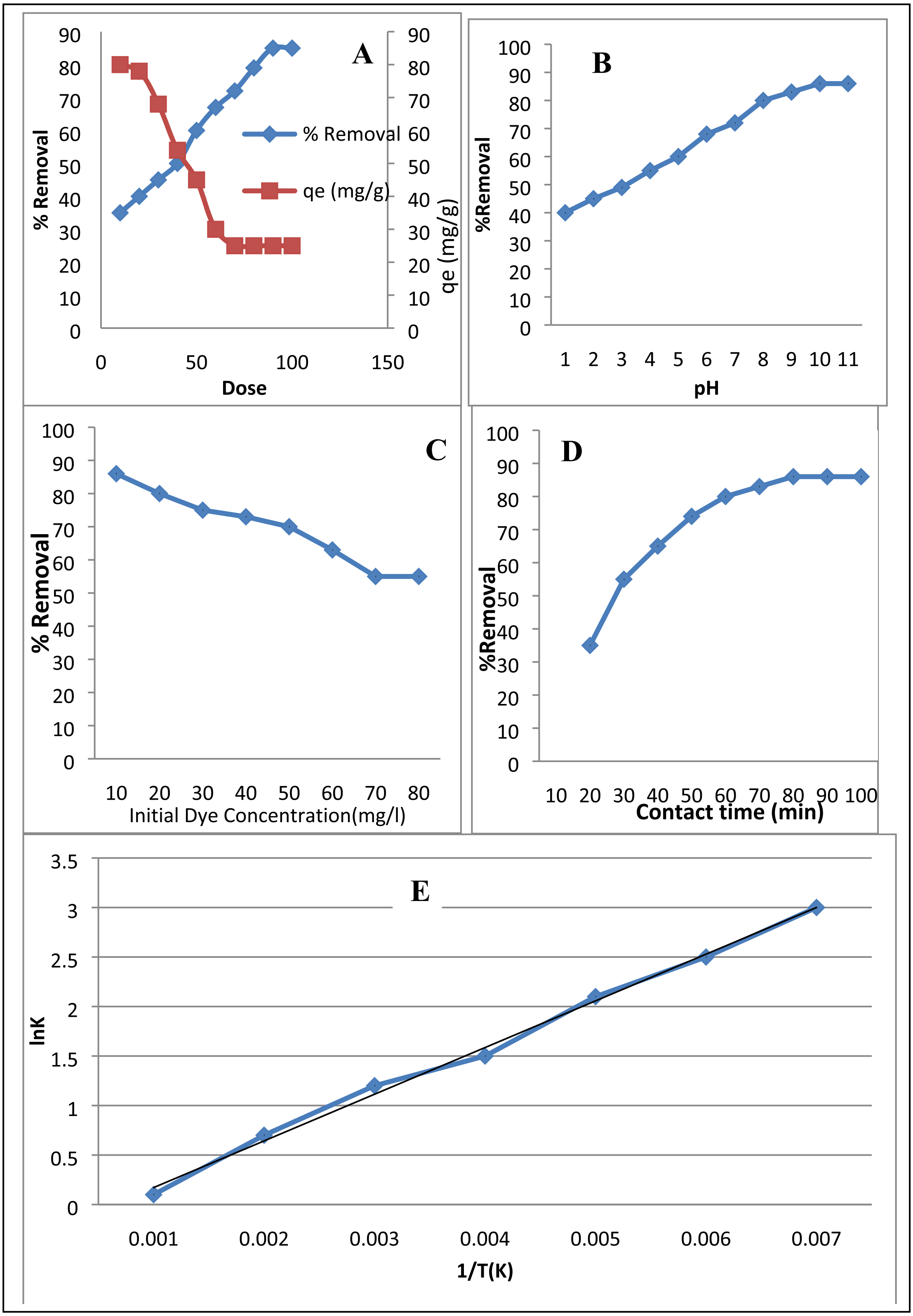

Fig. 4. Removal efficiency of MB Dye by activated red mud A-Dose of ARM; B-pH effect; C-Dye concentration; D-Contact time; E- Van't Hoff plot. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4. Conclusion

Activation of red mud is a important tool for using this industrial waste as a adsorbent for environmental purification. Activation of red mud induced the formation of new magnetite phase and decomposition of calcite and goethite phase was confirmed by XRD analysis.

Surface morphology of ARM is porous while red mud before activation is not porous was confirmed by SEM analysis. It is assume that during the activation process the carbonate and silicate are removed from the material induces the porosity. This was confirmed by FTIR analysis. The inducement of porosity to the material may be a reason of increase of surface area of red mud after activation than red mud before activation. From the result it was concluded that red mud which is a waste was successfully utilized for the removal of methylene blue from water.

Authors contributions

All authors are equally contributed for materials Synthesis, characterizations, experimental and writing of manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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