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EFFECT OF PH ON THE ADSORPTION OF METHYLENE BLUE ON CLAY MATERIAL

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ABSTRACT
The paper reports the effect of PH on the adsorption of a dye (methylene blue) from aqueous solution by laboratory-made clay material prepared from magnesium sulphate and aluminium sulphate.The effect of pH on the adsorption of the dye on the clay material was found to be quite distinct; the change of adsorption is regular with increase of pH. The results have revealed that both physical and chemisorption are occurring here.

INTRODUCTION
In the last couple of decades, a myriad of technologies have been developed to remove metals from waters: precipitation, ion exchange, membrane separation, and adsorption. Of these, adsorption processes are relatively preferable for eliminating metals from waters, especially at very low metal concentrations.In this purpose, different adsorbents can be used but activated carbons are the most widely used, either as powders or grains, because of their versatile physical and chemical properties [1]. Activated carbon fibers and clothes have recently drawn attention as better adsorbents than granular activated carbons [2–5]. Because of their well-developed microporosity and easy accessibility, the former normally have much higher adsorption kinetics and adsorption capacity. Zinc is a common pollutant in different industrial effluents. The adsorption of Zn species from aqueous solutions by activated carbons has been explored by various authors [1,5–9]. The aim of this work was to study the effect of surface oxidation, solution pH, and ionic strength on the static adsorption of Zn(II) ions using commercial granular activated carbon and activated carbon cloth. In addition, the effect of surface oxidation and dissolved natural organic matter on the dynamic adsorption of Zn(II) ions was studied by using column beds of the activated carbon cloth.

It has been widely recognized that heavy metal ions in aqueous systems have wider adverse effect on humans, animals, and plants. These ions are often found in wastewaters from various industrial processes. Due to its deleterious effect on environment, it is indispensable to remove these ions from the aquatic system. For this purpose, various processes can be applied for their removal from aqueous industrial effluents. Adsorption processes are very often used for this purpose and, in that case, they are influenced by some factors such as the nature and the size of adsorbents, the pH value, temperature, ionic strength, and buffer capability of aqueous solutions. Among them, the pH value and temperature are considered the most crucial factors. Therefore, effects of these two parameters are reported very often in the literature.[1 – 11] Temperature is a very important parameter in industrial wastewater treatments and in self-purification of natural water systems.

Industrial wastewaters often contain two or more kinds of metal ions. The interaction among these ions and the competition for the active sites of adsorbents will influence adsorption equilibrium. There are two approaches for investigating the competitive adsorption of metal ions on adsorbents. One approach is based on the measurement of the uptake of metal ions with the pH change at a constant initial total metal ion concentration, and it provides the adsorption edge curves.[12,13] The other approach is based on monitoring the uptake of metal ions with various initial total metal ion concentrations at an initial pH value, and it results in the adsorption isotherms.[14 – 17]

Textile industry plays an important role in the economic development in non-oil and gas sector of many developing countries. Apart from its significant role, however, textile industry also creates serious problems to environment, particularly disposal of colored dye wastewater. Dye contaminated wastewater contains colored compound from residues of dyes and various chemical additives. Reactive dyes are extensively used in dyeing processes for colouring yarn or fabric due to their high reactivity and good colour resilience.

Clays have a high adsorption capacity due to their lamellar structure which provides high specific surface areas and possibility to adsorb ions and polar organic molecules on particle external site and in interlayer positions. Adsorption and desorption of organic molecules in the clays are primarily controlled by surface properties of the clay and the chemical properties of the molecules. Natural clay exhibits a negative charge of structure which allows it to adsorb positively charged dyes but induces a low adsorption capacity for anionic dyes. Recently a number of worker have studied adsorption of methylene blue on a clay surface [18] as well as adsorption on silica gel [19],peat [20,21],etc. In this study, an attempt has been made to understand theeffect of pH on the adsorption of methylene blue on the laboratory-made clay surface.

EXPERIMENTAL

Materials and Methods

Preparation of Clay material

In a beaker, 39.9gm (300mmol) Aluminium chloride and 60.9gm (647mmol) Magnesium chloride are allowed to mix and thereafter a little amount of water is added to the mixture in order to bring equilibrium. To the mixture sodium hydroxide was added drop wise with constant stirring. The product formed is filtered ,then washed several times with water .The remaining precipitate was dried at room temperature .Then precipitate is heated in a silica crucible up to 600^{o}C in Muffle furnace. The product was finally grinded and sieved .The fine product was the clay material and was stored in polypropylene bottle.

Preparation of methylene blue solution (Stock dye)

Methylene blue Solution (Stock dye) was prepared by pouring by 0.636 ml of methylene blue in 1000ml of water and was stirred thoroughly with glass rod. The resultant solution was stock dye solution for preparing different concentrations (100, 200, 300, 400, 500 and 600 mg/litre) of the solution.

Determination of Maximum absorption

To determine the maximum absorbance, a solution containing 10mg per litre of methylene blue was prepared. The solution was examined at different wavelength using UV specrephotometer. Absorbance was plotted against wavelength.The wavelength corresponding to the maximum absorbance (max= 665 nm) as determined from the plot, was noted and this wavelength was used for measuring the absorbance of residual concentration of methylene blue.

A graph was drawn by plotting concentration of methylene blue against absorbance. The wavelength corresponding to maximum absorbance was determined from the plot.The maximum adsorption was found at 665 nm.

Determination of methylene blue concentration

For the determination of methylene blue concentration various concentration of
Methylene blue solution was examined in aa UV-visible spectrometer. Maximum absorbance at 665 nm was considered for preparation of standard curve. The actual adsorbed concentration of methylene blue was calculated as follows:

Adsorbed methylene blue = Initial concentration – unadsorbed mtthylene blue.

Method of adsorption

Various methylene blue solution with different initial concentrations in the range of 100-600 mg/L were prepared by diluting stock dye solution (1 g/L). The ionic strength was adjusted in 1.0 X 10^{-2} M with KNO_3. Equilibrium experiments are conducted using a centrifuge tube where 0.1 g of clay and 50 ml of the above dye solution were added and shaken for two hours at room temperature. The p^Hs were adjusted at 3.0, 7.0 and 8.0 using 1M HCl and 1M NaOH solutions.

Specific amount of adsorbent were shaken in 50 ml aqueous solutions of dye of varying concentration for different time period at certain p^H and room temperature. At the end of pre-determined time intervals adsorbent was removed by centrifugation and supernatant was analysed spectromaterically for residual concentration of

methylene blue at maximum wavelength. The value of amount of dye adsorbed was calculated using the following relationship.

Amount adsorbed =(Ci – Cf)m/v
where,
Ci= initial concentration Cf = final concentration m =mass of adsorbent
v = volume of dye solution

RESULT AND DISCUSSION

Adsorption of methylene blue has been undertaken at three pH i.e. 3.0, 7.0 & 8.0. The nature of adsorption of methylene blue on the clay surface is different for different pH. For each pH, adsorbed methylene blue is plotted against time has been presented in Figures 2-4

Figure 2 shows the adsorption of methylene blue at different times on the clay surface at pH 3.0. It has been observed that the adsorption of methylene blue increases sharply almost to 15 minutes, and beyond that time, it increases.

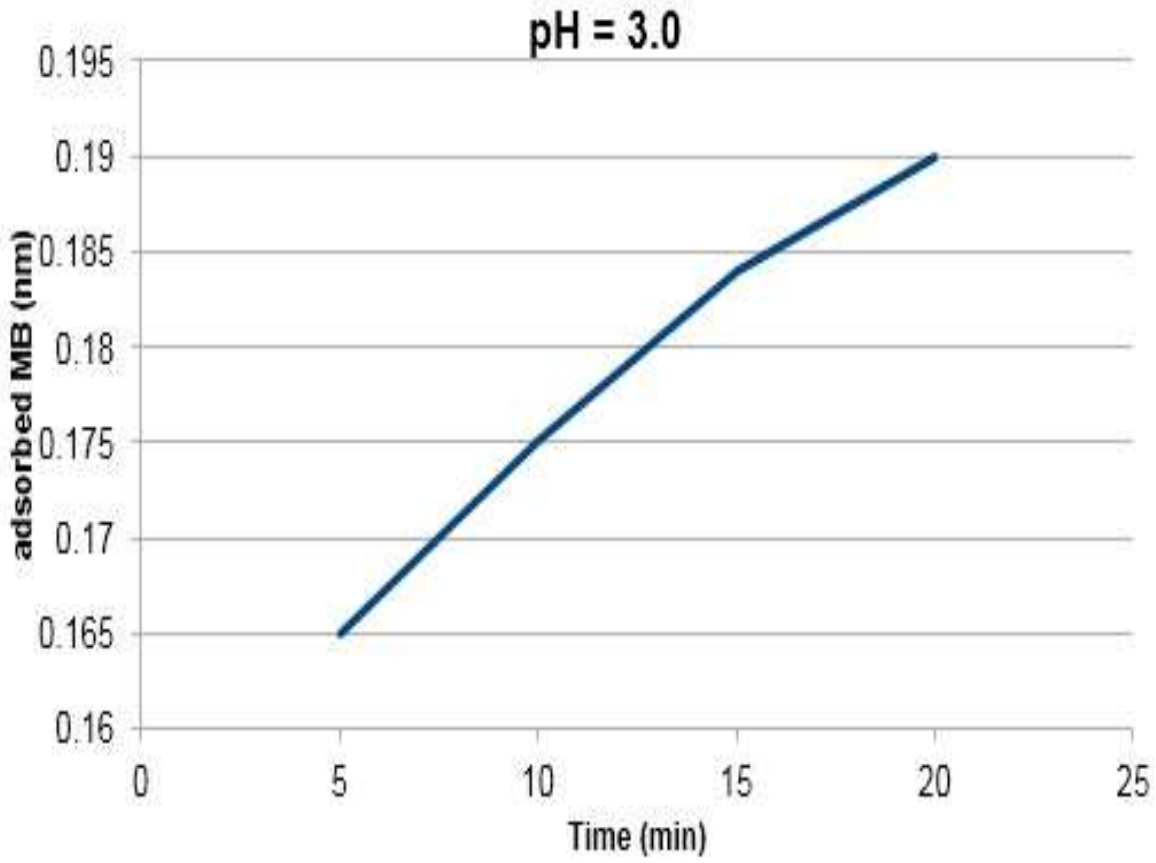

Figure 2. Adsorption of methylene blue at different times on clay surface at pH 3.0.

The adsorption nature of methylene blue at neutral pH (7.0) is shown in Figure 3. It has been found that up to 10 minutes, the adsorption of methylene blue increases sharply; however, beyond 10 minutes, the adsorption of the dye remained constant.

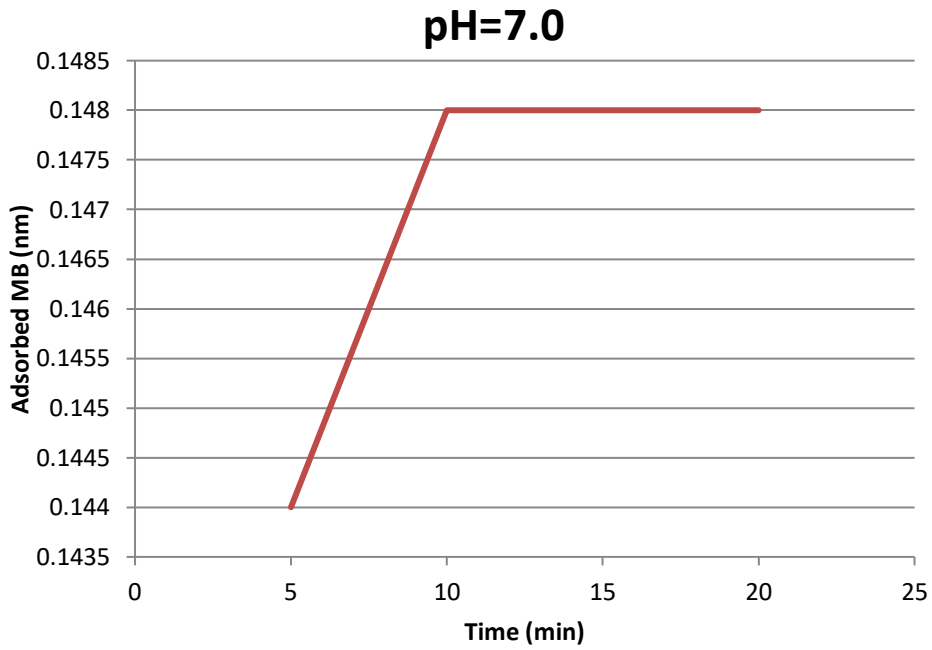

Figure 3. Adsorption of methylene blue at different times on clay surface at pH 7.0

Figure 4 represents the adsorption of methylene blue at different times on the clay surface at pH 8.0. It appears that the adsorption of methylene blue initially increases gradually almost to 15 minutes, and then increases sharply thereafter.

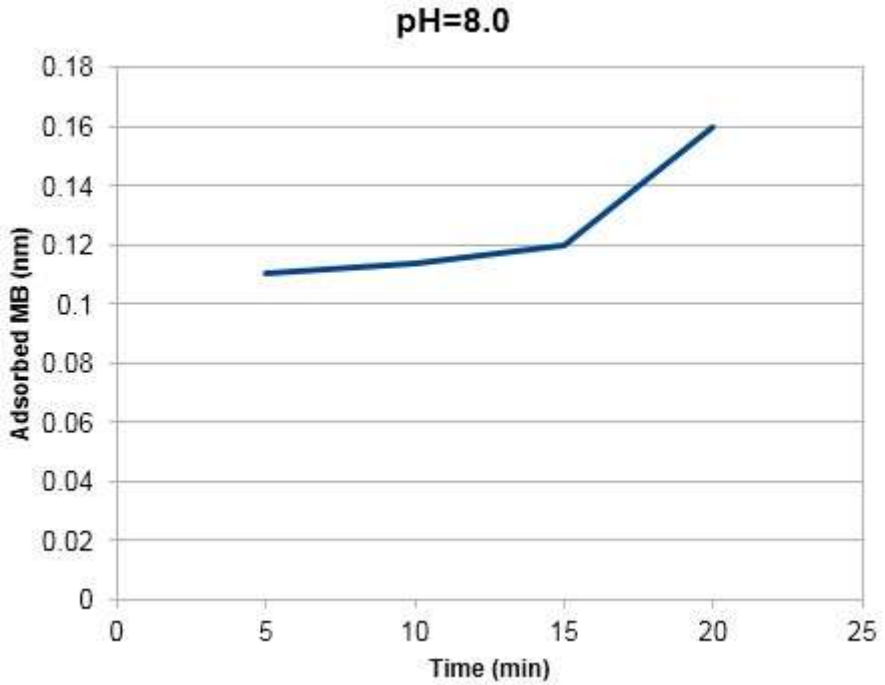

Figure 4. Adsorption of methylene blue at different times on clay surface at pH 8.0

The equilibrium adsorption of methylene blue was performed and the equilibrium time showed that the adsorption reaction was completed in 24 hours. Figure 5 represents the equilibrium adsorption of methylene blue on the clay surface at different pHs. It has been found that the highest adsorption of methylene blue occurred at pH 3.0 followed by pH 8.0. It is interesting that equilibrium adsorption of methylene blue is higher at acidic and basic solution.

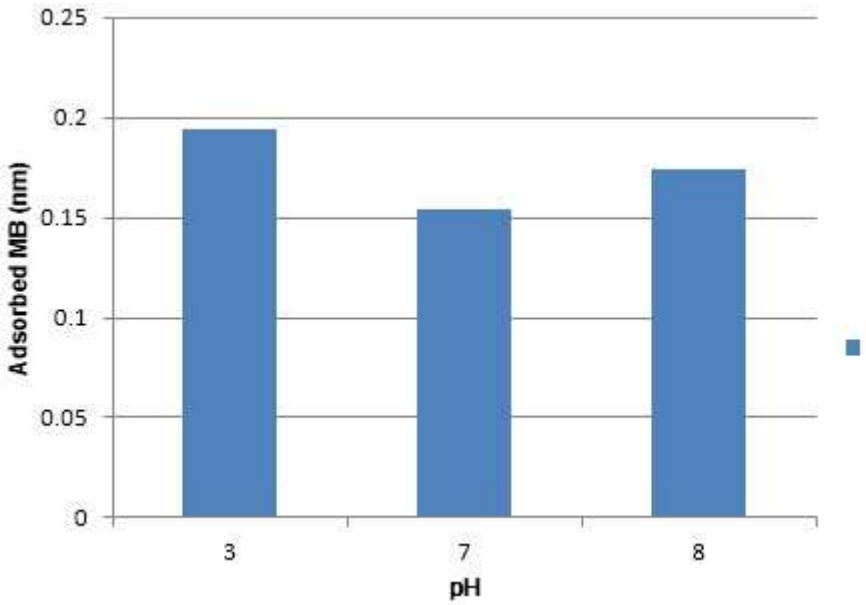

Figure 5. Equilibrium adsorption of methylene blue on clay surface at different pHs.

The curves observed in Figures 2-4 characterized by increase of the amount of dye sorbed during the initial sometime of contact solution – sorbent followed by different patterns of increase until to reach a state of equilibrium. The favourable adsorption occurred at acidic medium. Since methylene blue is a cationic dye, due to electrostatic force of attraction, the methylene blue molecules were adsorbed on the surface of clay. Moreover, surface pore and cavities of clay material are also responsible for the uptake of methylene blue. The formation of aggregates after adsorption of dye on clay surface cannot be ruled out. According to Zaker et al [21], adsorption on adsorbents involves the adsorbent and adsorbate as equal partners of the adsorption process.

CONCLUSION

The present study shows that clay material can be efficiently used as a sorbent material for the removal of methylene blue from aqueous solution. Acidic medium of the solution is more preferred for the higher amounts of methylene blue sorbed on clay. Even similar result has been found where amount of dye sorbed at equilibrium at any pH (3.0. 7.0 or 8.0 pH), no continuous increase of methylene blue has been found; however, adsorption of the dye on the clay surface has been recorded. Under the investigated experimental conditions, the laboratory-made inexpensive clay material was shown to be promising sorbent material for the removal of methylene blue from aqueous solution. This work has some technological importance.

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