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Adsorption study of various dyes on Activated Carbon Fe_3O_4 Magnetic Nano Composite

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Abstract

This article gives adsorption study of dyes which is a mixture of three dye solutions (methylene blue, malachite green and cango red) using Cajanus cajan stem Activated Carbon-Fe_3O_4 Magnetic Nano composites. Removal of these dyes from aqueous solution using Activated Carbon Fe_3O_4 Magnetic Nano Composite has been prepared and adsorption experiment studies were conducted. Batch adsorption studies are carried out by observing the effect of experimental parameters like pH, amount of adsorbents, contact time and temperature. Adsorption capacity of Fe_3O_4 Cajanus cajan stem activated carbon magnetic nano composite is determined for various adsorption of mixture of dyes. The conditions for dye removal are studied like pH value, contact time required, amount of adsorbent, temp, etc. The results generated by this work can be used for determination of optimum conditions for adsorption of mixture of dyes in aqueous solutions. Dyes are present in mixture form in various Industrial effluents like Textile Industries, Sewage water, Water treatment plants. This work can have use in Design of adsorption columns for dyes removal.

Keywords: activated carbon; adsorption; nanoparticle; pores; cracks

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I. INTRODUCTION

In olden days peoples are used carbonized wood as a medical adsorbent and purifying agent. Activated carbon from agricultural waste material was introduced industrially in the first part of the 20th century, and used in sugar refining. In the US activated carbon from black ash was found very effective in decolorizing liquids [1]. The treatment of industrial effluents is a challenging topic in environmental science, as control of water pollution has become of increasing importance in recent years. Synthetic dyes are widely used in a number of industrial processes, such as the textile industry, paper printing, etc. Although dyes not particularly hazardous, it can cause some harmful effects like increasing heart beat rate, shock, Heinz body formation, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans [2]. Recently, textile, printing, and other related industries are facing problems of treatment and disposal of dye wastewater. Many countries discharge the effluent to surface water without any treatment because of technological and economical limitations [3]. There are currently numerous treatment processes for effluent discharged from industrial processes containing dyes, the important and economic method is adsorption process [4]. The use of nanoparticles for separation and treatment of waste water is a new methodology that is faster and simpler. Nanoparticles have been widely studied because of structural and functional elements have various applications [5]. Among the treatment methods, adsorption on agricultural waste activated carbon nano material is a very effective removal technique which produces effluents containing dissolved organic compounds. However, the expensive price of the commercial activated carbon had encouraged many researchers to investigate the use of cheap and efficient alternative substitutes to remove dyes from wastewater [3].The magnetic nanoparticles have many uses such as magnetic drug target, magnetic resonance imaging forclinical diagnosis, recording material and catalyst, environment, etc., [5,6]. Iron oxides nanoparticles play a major role in many areas of chemistry, physics and materials science. Fe_3O_4 (magnetite) is one of the important magnetic nanoparticle. There are many various ways to prepare Fe_3O_4 nanoparticles, which have been reported in other papers. Furthermore, the presence of magnetic iron oxide (Fe_3O_4) leads to chemical stability, low toxicity, and excellent re-cyclability of adsorbent and these have caused to use this method widely for removal of toxic ions and organic contaminants from water and wastewater [7]. Use of the magnetic particles in the nano scale have attracted by many authors. Extremely fine size of nano-particles yields favorable characteristics with a reduction in size, more atoms located on the surface of a particle results to a remarkable increase in surface area of nanopowders [8]. In this study, Cajanuscajan stem activated carbon- Fe_3O_4 magnetic nano composite were prepared by a hydrothermal method and characterized by X-ray diffraction study (XRD), Fourier Transformation Infrared Spectroscopy (FTIR) and Scanning Electronic Microscopy (SEM) [9]. In this study we have to see some different adsorption studies of methylene blue, malachite green and cango red dyes on cajanuscajan stem activated carbon Fe_3O_4 magnetic nano composite [9,10]. The present research investigates the obtained cajanuscajan stem activated carbon Fe_3O_4 magnetic nano composite is confirmed as a cheap and effective adsorbent of dyes [11].

II. MATERIALS AND METHODS

A. *Materials*

Agricultural waste cajanuscajan stem was collected from fallow lands in and around Erode District, Tamil Nadu, India and washed with tap water followed by washing with distilled water [12]. The material was cut into pieces of 2-4 cm size sun dried for one week. The dried mass was used for the preparation of adsorbent as per the following procedure [13].

B. *Preparation of Activated Carbon by Physical method*

A dried sample of cajanuscajan stem placed in a muffle furnace and heated at 800^0C for two hours. This was allowed to cool and washed with distilled water to a pH of 7, oven dried at 105^0C for four hours and grounded. It was sieved with a 53µ mesh to obtain a fine powdered cajanuscajan stem activated carbon and it was kept in an air tight container and used for various experiments [14].

C. Synthesis of nano composite by Hydrothermal synthesis

Hydrothermal synthesis is a typical solution based approach, which is usually employed under high temperature and pressure. Unlike the thermal decomposition method, which can only use an organic compound as a solvent, hydrothermal synthesis can occur in a water-based system and at a lower reaction temperature (160–220 °C) in a relatively environment friendly approach. It is an effective and convenient process in preparing nono composite materials [15]. The Fe_3O_4/ACMNCS were prepared by hydrothermal method. In typical experiment 50 mg of cajanuscajan stem AC were suspended in 50ml of di-ionized water to form stable black color solutions. Subsequently, 30ml of FeCl2·4H2O and 80ml of $FeCl_3·6H_2O$ were dissolved in to the above solution and pH value was adjusted 10-11 by adding 30% of ammonium hydroxide solution (NH_4OH). After that, the final solution was transferred into the 75 ml Teflon-lined stainless steel autoclave were placed in an oven at 180^0C for 12 hours. After hydrothermal reaction, the autoclave was cooled down to room temperature and black color precipitate was washed with double distilled water and ethanol several times. Finally, the prepared Fe_3O_4/cajanuscajan stem AC MNCS sample was dried in vacuum oven at 70^0C for overnight [16].

D. Characterization

Cajanuscajan stem activated carbon Fe_3O_4 Magnetic nanocomposites were successfully synthesized using low-cost, renewable, eco-friendly biotemplates. The activated carbon and nanoparticles were characterized using X-ray diffraction technique, Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR) spectroscopy. From XRD analysis we obtain the characteristics of activated carbon (002) peak is observed diffraction is almost at around 26^o reveals to amorphous nature of carbon. The characteristics of Fe_3O_4/Activated carbon nano particles in X-ray diffraction technique various peaks corresponding to planes (220), (311), (400), (422), (511) and (440) are observed so the crystal structure is found to be

face centered cubic with lattice constant and the average particle size is 30 nm. So the Fe_3O_4/Activated carbon nano particles are confirmed as nano particles [17]. From the results of Fourier Transform Infrared Spectroscopy (FTIR) the bands 1706, 1619, 1477,891 and 579 cm^{-1} show that the different functional groups such as surface hydroxyl, carbonyl, methylene and alcohol etc were responsible for the adsorption process and it should be very effective in adsorption of dyes compare to normal activated carbon [18]. The Scanning electron microscopy (SEM) result of Fe_3O_4/Activated Carbon Nano composite confirms the formation of spherical shape Fe_3O_4/Activated Carbon magnetic nano composite with large number of pores, cracks and peaks were responsible for the adsorption process and it should be very effective in adsorption of dyes compare to normal activated carbon [19].

III. EXPERIMENTAL ADSORPTION STUDIES

A. Effect of contact time

100 ml of methylene blue, malachite green and cango red dye solution is prepared with dye concentration (50mg/L) and taken in a conical flask with Cajanus cajan stem activated carbon magnetic nano composite adsorbent concentration (0.5g/100ml) and placed in the shaker. From the corresponding λmax value obtained from spectrophotometrically concentration of dye can be calculated. The samples to be taken from the orbital shaker at equal time intervals and the dye solution should be separated from the adsorbent. The absorbance of dye solution is then measured. The dye concentration is to be measured after 10, 20, 30,40, 50 mins until equilibrium reaches. A graph is to be plotted with qe vs time. The qe is

$$qe = (C0 - Ce)/X$$

Where,

qe = Amount of dye adsorbed per unit mass of adsorbent (mg/g).

C0= Initial dye concentration (mg/L).

Ce= Final dye concentration (mg/L).

X = Dose of adsorbent (g/L).

B. Effect of initial pH:

100ml of dye solution with dye conc. 50mg/L is prepared in a conical flask and adsorbent conc.(1g/100ml) and the conical flask initial pH value is to be measured. The pH of the dye solutions was adjusted with dilute HCl (0.05N) or NaOH (0.05N) solution by using a pH meter.100 ml of dye solution was already prepared and the pH of solution is changed from 2 to 10. All the conical flasks were placed in the shaker (100 rpm fixed through out the study) maintained at 300K and the final concentration of dye was measured using UV spectrophotometer with the calibration plot of the dye after 2 hours. A graph is drawn with qe vs initial pH.

C. Effect of adsorbent dose:

100ml of dye solution was prepared in different flasks with dye concentration (50mg/L) and adsorbent concentration 1,2,3,4,5 g/100ml. The flasks are kept in side the shaker for two hours and get the final dye concentration readings. A plot of qe vs adsorbent dose is taken.

D. Effect of temperature:

100 ml of dye solution was prepared in conical flask with dye concentration 50mg/L and

adsorbent dose (1g/L) and placed in the thermo control shaker. The temperature was maintained at 20°C. The final dye concentration readings were taken at 10, 20, 30, 40,50 mins. The same procedure was followed for temperatures 30°C and 40° C. A plot of qe vs time at different temperatures is obtained.

IV. RESULT AND DISCUSSION

A. Effect of Contact time:

The Fig.1. gives the details of effect of contact time for the dyes. From this fig.1. we can clearly know that the extent of adsorption is fast in initial stages and becomes slow in latter stages till saturation allowed for all three dyes [20]. The final dye concentration did not vary significantly after two hours from the beginning of adsorption process. It explains that equilibrium can be reached after two hours of the starting adsorption process. It is basically due to saturation of the active site which do not allow further adsorption to take place [21].

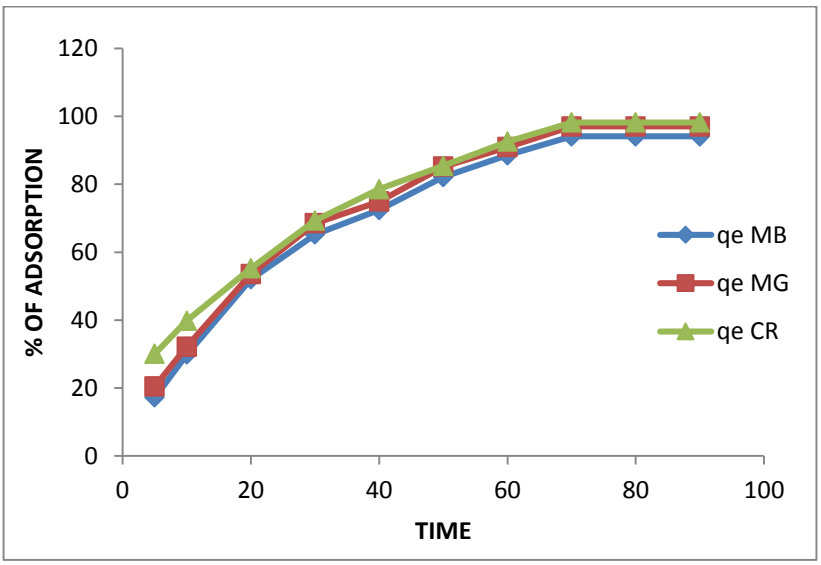

Fig.1. Effect of contact time

B. Effect of initial pH of the solution:

The effects of initial pH on dye solution of two dyes removal were obtained by varying the pH from 2 to 10. At pH 2 the removal was minimum but it increased with increasing initial pH of dye solution. For malachite green it was maximum at pH = 9 as we see in the fig.2. In case of methylene blue higher the pH, greater is removal by adsorption. For cango red there is no considerable change in amount adsorbed after pH 7. Infact adsorption found to decrease with increase in pH of solution [22]. The adsorption of these positively charged dye groups on the adsorbent surface is primarily influenced by the surface charge on the adsorbent which in turn is influenced by the solution pH. The result showed that availability of negatively charged groups at the adsorbent surface is necessary for the adsorption of basic dyes to proceed which we see at pH 2. Thus as the pH increased, more negatively charged surface was available for greater dye removal [23]. We see that the trend is increasing with increasing pH.

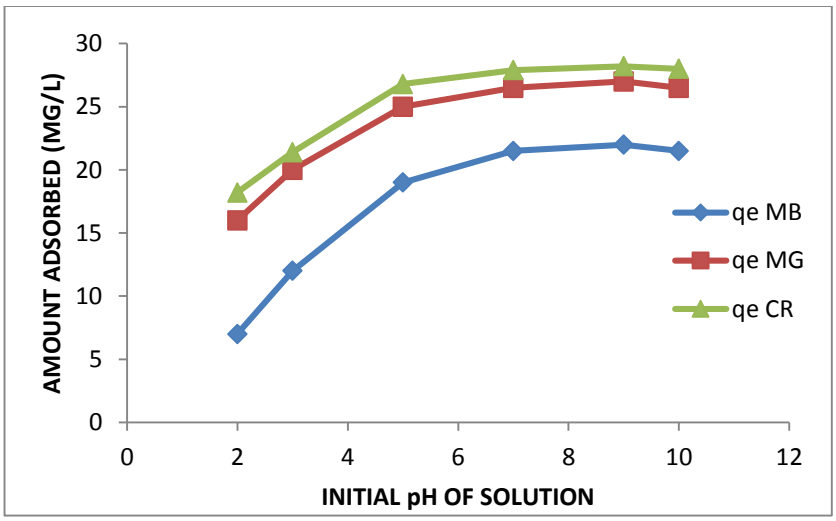

Fig.2. Effect of initial pH of the solution

C. Effect of adsorbent dosage:

From fig.3. we see that the optimum dose for the dye is 6g/100ml. Though at 8g/100ml, there is slight increase in qe value but if we get nearly the same result as we get at adsorbent dosage of 5g/100ml then going for 8g/100ml will be expensive and loss of adsorbent. It is obvious as with increasing amount the active sites for adsorption of mixture of dyes increases which results in an increase in removal efficiency [24]. The decrease in adsorption capacity with an increase in the adsorbent concentration could be ascribed to the fact that some of the adsorption sites remained unsaturated during the process.

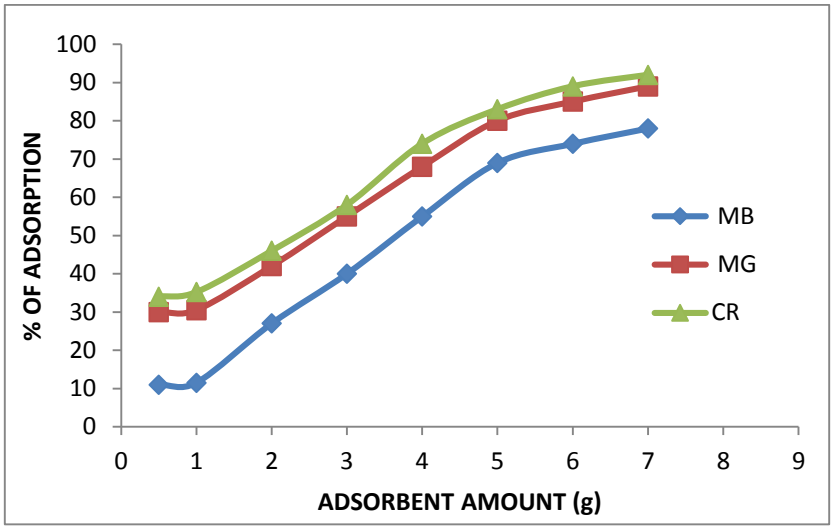

Fig.3. Effect of adsorbent dosage

D. Effect of temperature

The effect of temperature on adsorption of dye solution with initial concentration of 50mg/L at temperatures 20, 30 and 40°C on has been determined. The result of time rate studies for the adsorption of the dyes malachite green, methylene blue and cango red at different temperature has been shown in the fig.4, fig.5 and fig.6 is given below.

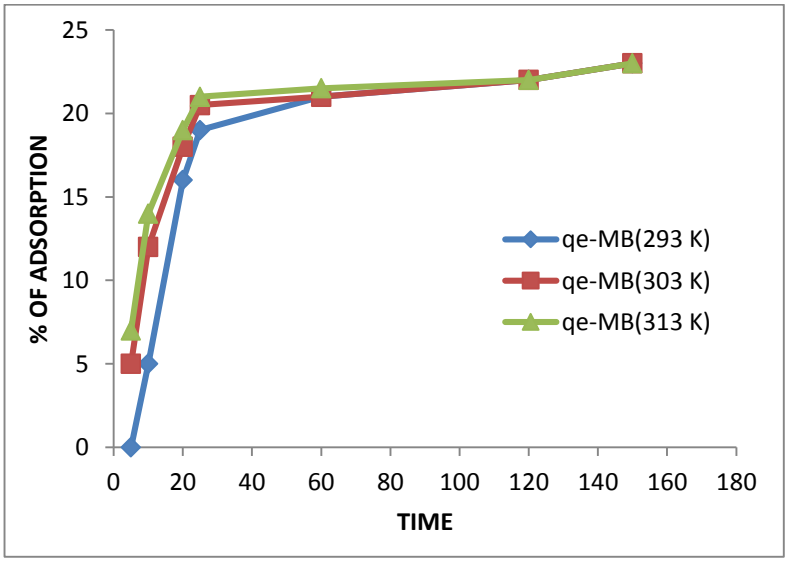

Fig.4. Effect of temperature (Methylene blue)

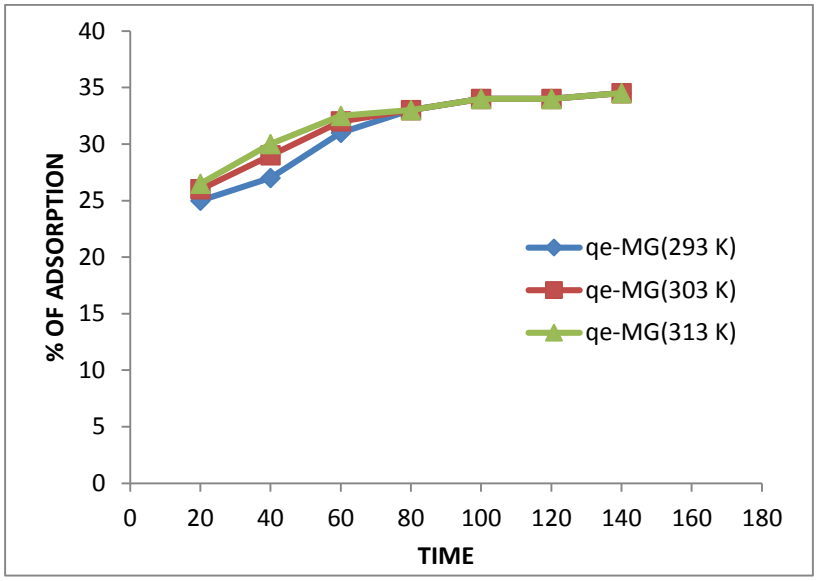

Fig.5. Effect of temperature (Malachite green)

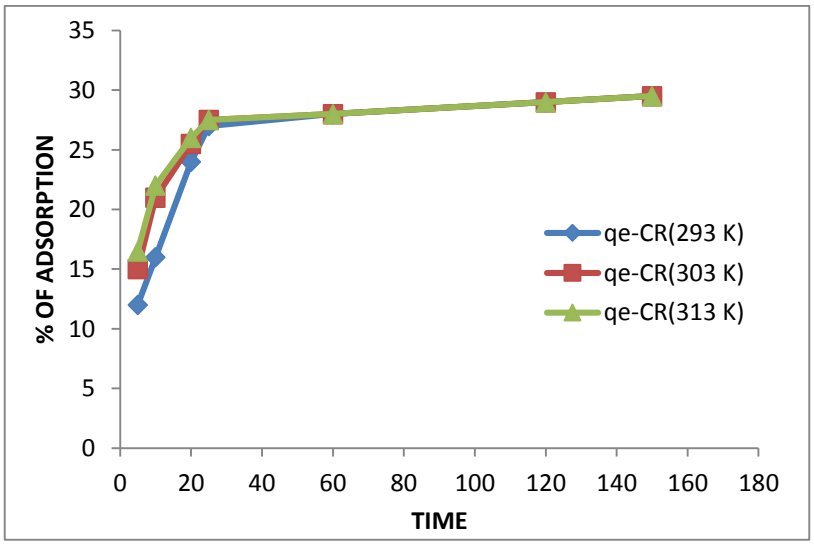

Fig.6. Effect of temperature (Cango red)

Results indicate that the adsorption capacity of activated carbon for two dyes (methylene blue and malachite green) increased with temperature. This may be a result of increase in the mobility of the large dye ion with temperature [25]. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface. Furthermore, increasing temperature may produce a swelling effect within the internal structure of the activated carbon enabling large dyes to penetrate further [26].

V. CONCLUSION

Removal of dyes from aqueous solutions by adsorption with Cajanus cajan stem Activated Carbon Fe_3O_4 Magnetic Nano materials has been experimentally determined from this data we can easily explain the adsorption process . The percentage of colour removed increase with increasing adsorbent dosage, increase with increasing contact time and varied with dye solution pH. The adsorption rates increases with increasing temperatures. Optimum contact time for equilibrium to be achieved is found to be 2 hours. It is basically due to saturation of the active site which do not allow further adsorption to take place. For malachite green maximum adsorption found to be at pH = 9. In case of methylene blue higher the pH, greater is removal by adsorption. Infact adsorption found to decrease with increase in pH of solution. The adsorption of these positively charged dye groups on the adsorbent surface is primarily influenced by the surface charge on the adsorbent which in turn is influenced by the solution pH. Optimum adsorbent dose for the dye is 6g/100ml. It is obvious as with increasing amount the active sites for adsorption of mixture of two dyes increases which results in an increase in removal efficiency. The decrease in adsorption capacity with an increase in the adsorbent concentration could be ascribed to the fact that some of the adsorption sites remained unsaturated during the process and agglomeration of activated carbons as a result all the surface area is not available for adsorption process. Optimum temperature is 30^oC. The adsorption capacity of activated carbon for the dyes increased with temperature. This may be a result of increase in the mobility of the large dye ion with temperature. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface. Furthermore, increasing temperature may produce a swelling effect within the internal structure of the activated carbon enabling large dyes to penetrate further.

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