ADSORPTION OF METHYL RED AND METHYL ORANGE USING DIFFERENT TREE BARK POWDER

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ABSTRACT

An experimental study has been conducted on the comparative adsorption of dyes using Neem tree bark powder (NBP), Mango tree bark powder (MBP) and Locust bean tree bark powder (LBP). The effects of initial dye concentration, adsorbent dosage, temperature and pH of the medium were investigated. Moisture content, bulk density and ash contents are some of the proximate analysis carried out on the bark of trees powder produced. The adsorption capabilities of the adsorbents were tested by adsorbing a known concentration of methyl orange and methyl red at the same operating conditions. Adsorption of the dyes were found to increase as the adsorbent dosage increases but decreases as initial concentration of the adsorbate (dyes) increases, this due to the fact that the active site of the adsorbent can adsorb a certain concentration of the dye. It was also found that the pH of the solution determines the concentration of the adsorbate that would be adsorbed on to a given adsorbent. Neem tree bark, Mango tree bark and Locust bean bark are promising adsorbent which can be used to clean up textile wastes. The adsorption isotherm was also studied and the data obtained fits in well into Langmiur isotherm.

Keywords: Adsorption, Methyl red, Methyl orange, NBP, MBP, LBP.

INTRODUCTION

Environmental pollution due to industrial effluents is of major concern because of their toxicity and threat for human life and the environment. The discharge of textile effluents to the water bodies has raised much concern because of potential health hazards associated with the entry of toxic components into the food chains of humans and animals. Synthetic dyes are extensively used for dyeing and printing in a variety of industries (Sandeep, 2010). The removal of colour from textile effluents has targeted attention over the last few years, not only because of its toxicity, but mainly due to its visibility. Conventional treatment facilities are often unable to remove certain forms of colour, particularly those arising from reactive dyes as a result of their high solubility and low biodegradability; thus, methods for decolourizing textile effluents are on the horizon (Vijayaraghavan et al., 2009). Over 10, 000 dyes with an annual production over 7x105 metric tonnes worldwide are commercially available and 5-10% of the dye stuff is lost in the industrial effluents. Therefore, there is a need to remove dyes before effluent is discharged into receiving water bodies. The most popular treatment methods for textile wastewater are combinations of biological treatment, chemical coagulation and activated carbon adsorption. Discharging of dyes into water sources even in a small amount can affect the aquatic life and food web. Dyes can also cause allergic dermatitis and skin irritation. Some of them have been reported to be carcinogenic and mutagenic for aquatic organisms (Lorenc-Grabowska et al., 2007). Annual production of textile dyes is estimated to be over 8×10 tonnes of which 10% are discharged as effluents

(Zollinger, 1987). Release of these dyes in water stream is aesthetically undesirable and has serious environmental impact. Due to intense colour they reduce sunlight transmission into water hence affecting aquatic plants, which ultimately disturb aquatic ecosystem (Jeremias et al., 2006). Dyes can be classified as follows (Yuzhu & Vijayaraghavan, 2002) anionic: direct, acid, and reactive dyes; cationic: basic dyes; and non-ionic: disperse dyes. Adsorption process has been proven one of the best water treatment technologies around the world and activated carbon is undoubtedly considered as universal adsorbent for the removal of diverse types of pollutants from water. However, in view of the high cost and associated problems of regeneration, there is a constant search for alternate low cost adsorbents. Previously several researchers had proved several low cost materials such as clay (Tsai et al., 2005), narrow-leaved cat tail (Inthorn et al., 2004), fly ash (Janos et al., 2003), wood dust (Garg et al., 2004), alunite (Ozacar & Sengil, 2004). This present study is aimed at removing methyl orange and methyl red dye from their aqueous solution using adsorbents prepared from bark of mango tree, locust-beans tree and neem tree.

MATERIALS AND METHODS

The materials employed in this work include among others, pH meter (LP115), spectrophotometer(Model 722, Shanghai), Water bath ,Electronics weighing balance (Ohaus, USA), Dryer/ Oven, Sieve, Conical flasks, Stop watch, Thermometer, Centrifuge, Bark of trees, Dyes, Crusher, Methyl red(Rosi Chemical Co. Ltd.), methyl orange(Beijing Chemical Co.). All chemicals used were of analytical grade.

Adsorbent Preparation

The trees bark (Neem tree, Mango tree and Locust-beans tree) were collected from the forest. The collected barks were washed with water several times to remove dirt particles and water soluble materials. The washing process was continued till the wash water contained no colour. The washed materials were then completely dried in an air oven at 105-110^{0}C for 24hrs till the barks could be grinded into fine powder by the local mixer grinder. The particle sizes such as 150-212µm. Finally, the product was stored in vacuum desiccators until required. The developed powders are designated as Mango bark powder (MBP), Neem bark powder (NBP) and Locust-beans powder (LBP).

Adsorption Procedure

Adsorption studies were performed by the batch technique to obtain rate and equilibrium data. Batch adsorption studies were performed at different temperatures dyes initial concentrations and adsorbent doses to obtain equilibrium isotherms. For isotherm studies, a series of 100 mL conical flasks were employed. Each conical flask was filled 50 mL of dye solution of varying concentrations (1x10^{-3} -5x10^{-3} M) separately and adjusted to the pH and temperature. The effect of pH was observed by studying the adsorption of the dye over a broad pH range of 2-9. The adsorption studies were also carried out at different temperatures, i.e., 303, 308, 313, 318 and 323 K. Adsorption of dye was also studied at different initial concentrations of dyes solution and doses of adsorbents.

Effect of Initial Dye Concentration

A mass of 0.5 g of each adsorbent (NBP, MBP, LBP) was contacted with 50 mL of the dye concentration 1x10 $^{-3}$ – 5x10^{-3} mol.L^{-1} at pH 3 and 8 for the adsorbents respectively, using water-bath maintained at 30^{0}C. The agitation speed was kept constant. At predetermined intervals of time, samples were analysed for the final concentration of dyes by a spectrophotometer.

Effect of Adsorbent Dose

Samples of NBP, MBP and LBP (0.5, 1.0, 1.5, 2.0 and 2.5 g) were added to 50 mL dyes solution. The initial dye concentration was $1x10^{-3}$ mol L^{-1} at pH 5 for the dyes concentration at constant temperature of 30^0C and stirring at the same speed.

Effect of Temperature

The effect of temperature (at 303, 308, 313, 318 and 323 K) on the adsorption of dyes by NBP, MPB and LBP was studied at 0.5 g adsorbent and initial dyes concentration of 10^{-5}mol L^{-1} at pH of 5 for 60 minutes contact time.

Effect of pH

The effect of pH on the amount of colour removal was analysed over the pH range from 2-9. The pH was adjusted using 0.1 M NaOH and 0.1 M HCl solutions. In this study, 50 mL of dye solution was agitated with 0.5 g of NBP, MBP and LBP separately for 60minutes. The samples were then filtered and allowed to settle, the left out concentration in the supernatant solution were analysed using a spectrophotometer by measuring the absorbance changes at a wavelength of maximum absorbance.

RESULTS AND DISCUSSION

The physicochemical properties of the adsorbents as obtained in this work after their characterization are shown in Table 1.

Table 1. Characterization of Adsorbents

Parameters	*Values* *NPB*	*MPB*	*LPB*
Bulk density	0.424	0.408	0.521
Moisture content (%)	8.00	9.00	7.00
Ash content (%)	10.65	13.34	10.09
pH	6.85	6.09	6.52
Pore Volume	1.5	1.8	1.6

Effects of Initial Dye Concentration/Dosage

From the results obtained, an increase in initial dye concentration or dosage from $1x10^{-3}$ mol/dm^3 to 5 x 10^{-3} mol/dm^3 leads to a decrease in the percentage of the dyes removed (methyl orange and methyl red) respectively.

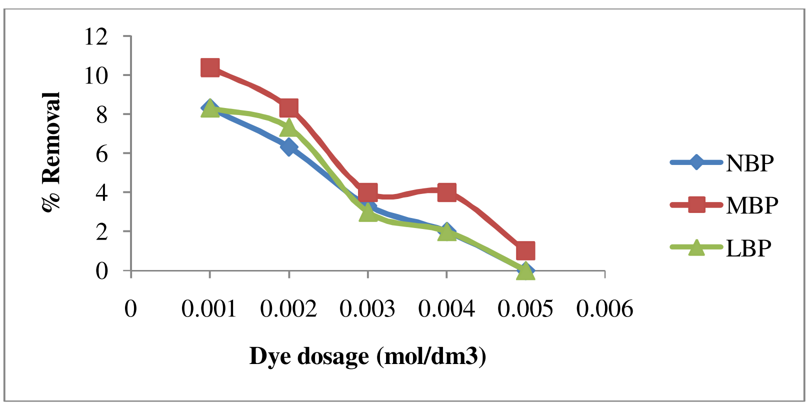

Figure1. Effect of initial concentrations for the removal of methyl red over NBP, MBP and LBP

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Figure 1 and 2 shows the plot of the effect of initial dye concentration on the percentage of the dyes removed.

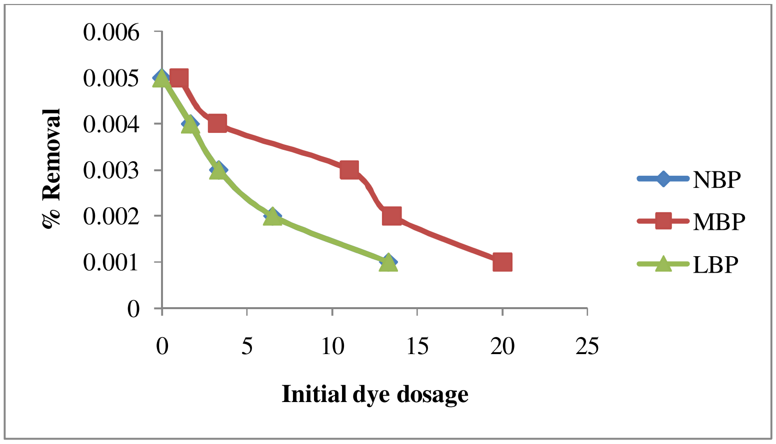

Figure 2. Effect of initial concentrations for the removal of methyl orange over NBP, MBP and LBP

The negative slope of the plot deduce that the percentage of the dyes removed by the powder decrease with an increasing concentration of the dye in an aqueous solution. This is because at low dye/sorbent ratios, there are number of sorption sites in the powders structure but as the ratio increases the sorption sites are saturated, resulting to decrease in the sorption efficiency (Srivastava & Rupainwar, 2011). At high initial concentration, the gradient between the solution sample and the centre of particle enhances dye diffusion through the film surrounding the particle and in the porous network of the tree barks (Ahmad et al., 2005).

Effect of Adsorbent Dose

An increase in the adsorbent dose (NBP, MBP and LBP) from 0.5 to 2.5 g/50 mL increases the percentage of the dyes removed. This may be attributed to increased sorbents surface area and availability of more sorption sites resulting from increased dose of the sorbent. The increase in adsorbent dose at constant dye concentration and volume results to increased availability of sorption sites and result to unsaturation of the sites. Greater adsorption rate was observed when the adsorbent/dye concentration ratio is greater than when the ratio is lower. Figure 3 and 4 shows the plot of adsorbent dosage versus percentage of the dye removed for methyl orange and methyl red respectively.

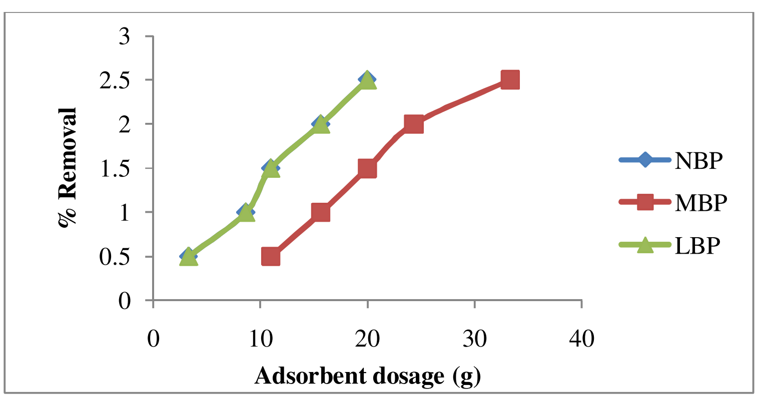

Figure 3. Effect of adsorbent dosage for the removal of methyl orange over NBP, MBP

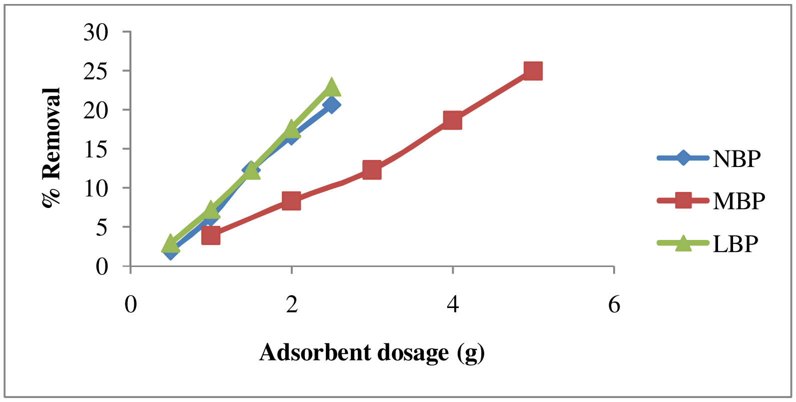

Figure 4. Effect of adsorbent dosage for the removal of methyl red over NBP, MBP and LBP

From the plot, the slope is positive indicating that adsorption increases with an increase in the adsorbent dose. It can be deduced that a fixed mass of the adsorbent is needed to adsorb certain amount of the dye, this then means the higher the adsorbent dose, the larger the volume of effluent can purify (Ahmad et al., 2005). The increase in sorbent dose at constant dye concentration and volume will lead to unsaturation of sorption sites through the sorption process. The higher the sorbent dosage, the larger the volume of effluent that a fixed mass of neem tree bark powder, mango tree bark powder (Srivastava &Rupainswar, 2011; Garg et al., 2004) and locust bean tree bark can absorb or purify.

Effect of Temperature

Adsorption of dyes (methyl orange and methyl red) increased with an increase in temperature for the adsorbents (NBP, MBP and LBP) respectively. This indicates that adsorption is endothermic. The solubility of the dyes increases with an increasing temperature, thus at high temperature the dyes solution reaches an equilibrium where they can be adsorbed out by the adsorbent particle. In addition, at higher temperature the adsorbents active sites are activated thereby increasing the concentration of the dye removed. The enhancement of the adsorption might also be due to enhancement of the adsorptive interaction between the active sites and the adsorbate ion. Figure 5 and 6 shows the plot of temperature variation versus percentage of dyes (methyl orange and methyl red) removed respectively.

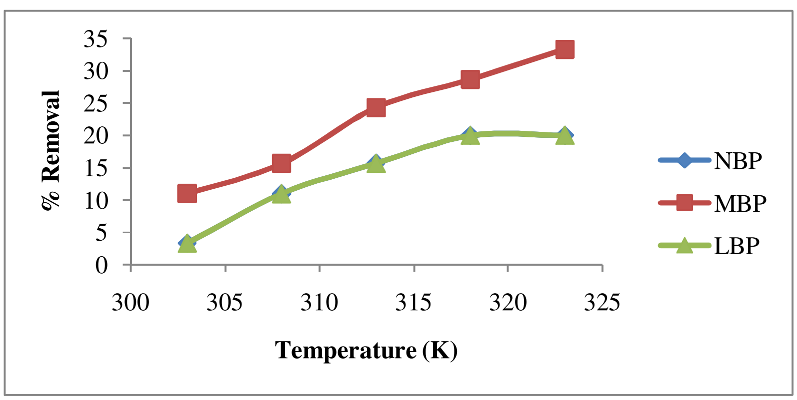

Figure 5. Effect of Temperature variation on the removal of methyl orange over NBP, MBP and LBP

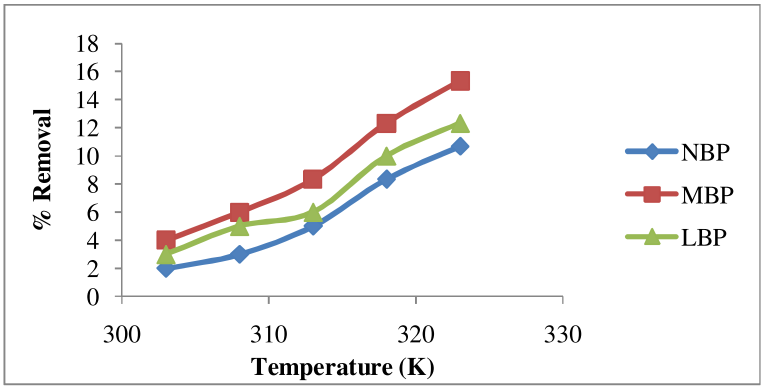

Figure 6. Effect of Temperature variation on the removal of methyl red over NBP, MBP and LBP

It can also be said that increasing temperature may also produce a swelling effect within the internal structure of the powders enabling more dye molecules diffusion into the adsorbents (Srivastava &Rupainswar, 2011; Inthorn et al., 2004).

Effect of pH

The result of the experiments done at different pH values, which were conducted to determine the optimum pH range for the dyes adsorption on Neem tree bark powder, Mango tree bark powder and Locust bean tree bark powder are shown in figure 7 and 8 for methyl orange and methyl red respectively. The percentage removal of methyl orange and methyl red by Neem tree bark powder was optimum at 6.5 and 4 respectively, while that of mango tree bark powder was optimum at pH 2 and 6 respectively and the optimum pH for methyl orange and methyl red on Locust bean tree bark powder was 9 and 4 respectively. The variation in concentration of the dyes adsorbed at different pH may be due to different reasons. It could be as a result of the degree of ionization of the species at the different pH. More methyl orange was absorbed by Mango tree bark powder in an acid medium while Neem tree bark powder adsorbed more in a fairly neutral medium and Locust bean tree bark powder adsorbed more in a basic medium. Likewise for methyl red, high concentration was absorbed by the three adsorbent in an acidic medium although it range from highly acidic for Locust bean tree bark to slightly acidic for Mango tree bark powder. pH of the medium affect the quantity of the adsorbent adsorbed by a given adsorbent.

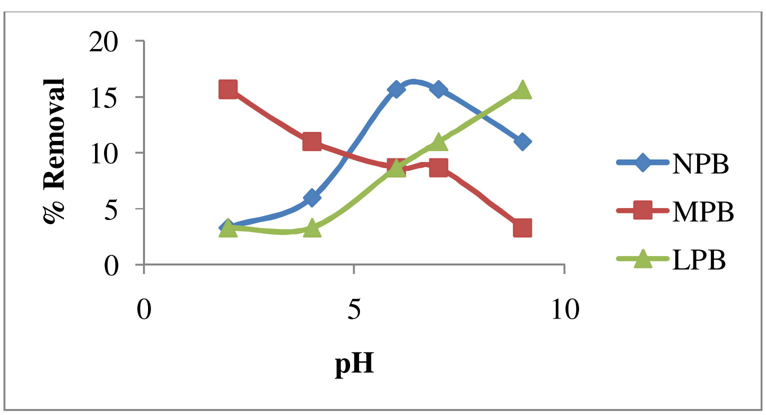

Figure 7. Effect of pH on the removal of methyl orange over NBP, MBP and LBP

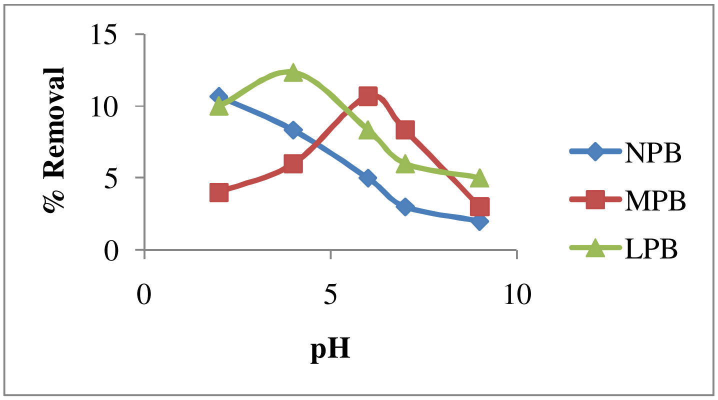

Figure 8. Effect of pH on the removal of methyl red over NBP, MBP and LBP

The dyes sorption behaviour as exhibited by the three biosorbent relative to solution pH could be attributed to several reasons. The surface of all the bark powder may contain a large number of active sites and the solute (dye ions) uptake can be related to the solute in the solution (Srivastava & Rupainswar, 2011).

ADSORPTION ISOTHERM

Langmuir Isotherm

Adsorption isotherm is important in describing how solutes interrelate with the adsorbent and so is critical in optimizing the use of adsorbents. Correlation of isotherm data by empirical or theoretical equations is thus essential for the operation of adsorption systems and practical design (Ahmad et al., 2005). The Langmuir equation assumes that maximum adsorption occurs when surface is covered by the adsorbate. The distribution of dyes has been described by the linear form of Langmuir equation given as:

$(C_e/q_e) = (1/bQ_0) + (C_e/Q_o)$,

Where Ce is concentration of dye solution (mol L^{-1}) at equilibrium, q_e is amount of dye adsorbed per unit weight of adsorbent (mol g^{-}), b is related to the energy of adsorption (l mol^{-1})

Figure 9 and 10 shows the Langmuir isotherm for the adsorption of methyl orange and methyl red by neem tree bark powder, mango tree bark and locust tree bark powder respectively.

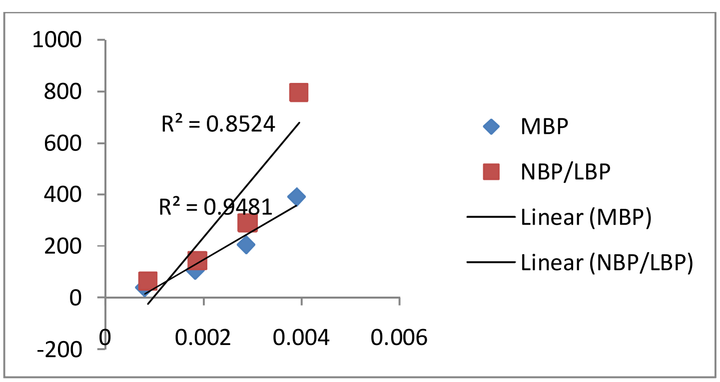

Figure 9. Langmuir isotherm for adsorption of methyl orange over neem tree bark powder, mango tree bark powder and locust bean tree bark powder.

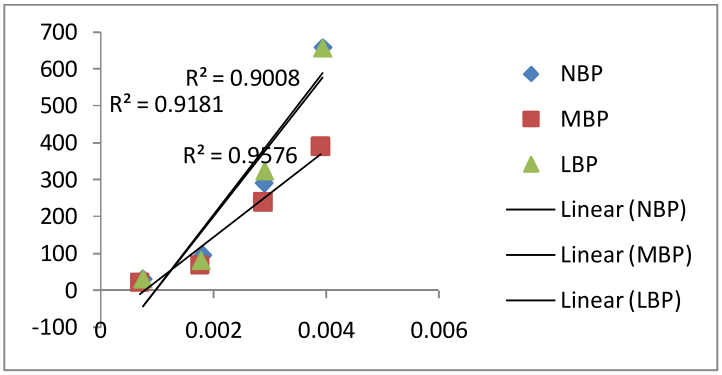

Figure 10. Langmuir isotherm for adsorption of methyl red over neem tree bark powder, mango tree bark powder and locust bean tree bark powder.

The adsorption was found linear over the entire concentration range studied with good regression coefficient (R^2 = 0.9481 and 0.8524) for mango tree bark powder and neem tree bark powder/ locust tree bark powder respectively on methyl orange and also the regression coefficient (R^2 = 0.9576, 0.9181 and 0.9008) for mango tree bark powder, locust bean bark powder and neem tree bark powder respectively. The result shows that the correlations fit in well into the Langmuir isotherm for methyl red than methyl orange, this can then imply that the bark of trees are better used to adsorb methyl red than methyl orange of the same concentration. It was observed to fit in correctly into Langmuir isotherms. The fact that Langmuir isotherms fits the monolayer coverage of dye very well confirms the monolayer coverage of dye on adsorbent particles and also the homogenous distribution of active sites on the material, since Langmuir equation assumes that the surface is homogenous (Srivastava & Rupainwar, 2011).

CONCLUSION

The adsorptive properties of Neem tree bark powder, Mango tree bark powder, Locust bean tree bark powder was studied under the same experimental condition by adsorbing the concentration of methyl orange and methyl red dyes. It was observed that Mango tree bark powder have the best adsorptive power for both methyl orange and methyl red while Locust bean tree bark powder has a better adsorptivity for methyl red than Neem tree bark powder. Moreover, Neem tree bark powder and Locust bean bark powder have the same adsorptivity for methyl orange and they can be used interchangeably. It was also observed the rate of adsorption of methyl orange and methyl red, onto Neem tree bark powder, Mango tree bark powder and Locust bean tree bark powder increased with increasing temperature. This indicates that adsorption is an endothermic process. The adsorption isotherm also reveals that the data obtained from the adsorption of dyes using neem tree bark powder, mango tree bark powder and locust-bean tree bark powder fits in well into the Langmuir isotherm which means that the monolayer coverage of dye onto adsorbent particles and also homogenous distribution of active sites on the material. It can be concluded that bark of trees (Neem, Mango and Locust bean) are promising adsorbent for removal of dyes from textile waste.

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