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Kinetic and Equilibrium Studies of Methyl Orange Removal from Aqueous Solution by Adsorption on Activated Rubber Sawdust

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Abstract: *This work investigates the removal of the methyl orange by adsorption using rubber saw dust activated carbon (RSDAC). The application of the adsorbent for methyl orange removal was observed to be influenced by the variation in these parameters like adsorbent dose, contact time and pH .The equilibrium data were analysed based on the Langmuir and Freundlich isotherms. Kinetic data were analysed using the pseudo –first order and pseudo –second order models. The maximum adsorption capacity is 111.11mg/g.*

Keywords: Adsorption, Low Cost Adsorbents, Aqueous Solution, Isotherm, Saw Dust

I. Introduction

A dye is a coloured substance that chemically bonds to the substrate to which it is being applied. The distinguishes dyes from pigments which do not chemically combine to the substance they colour. The dye is generally applied in an aqueous solution and may need a mordant to develop the fastness of the dye on the fiber.(Nigam et .al, 2000)

Dye,a constituent that is widely used in textile, paper, plastic food and aesthetic industries is an easily predictable pollutant. Decolourizing of textile and industrialized waste water is currently a major difficulty for environmental managers. Dyes may considerably affect photosynthetic activity in aquatic life due to the presence of aromatics, metals ,chlorides and so forth in them . Many of the dyes used in the industries are steady to light and oxidation as well as opposing to aerobic digestion (Arwa et al)

Textile industries lie first in the dye usage. The wastewaters discharged from dyeing processes show a high BOD, high COD, visible pollutants and high amounts of dissolved solids. Effluents discharged from dyeing industries are highly coloured and are toxic to aquatic life. Some dyes are mutagenic, carcinogenic and teratogenic. Therefore, it's a must to treat dye effluents before being discharged into the environment.

Many physical, chemical and biological processes for colour removal have been applied as well as de-colorization methods such as coagulation and flocculation treatment, biodegradation processes, oxidation methods, membrane filtration and adsorption (Robinson et al., 2001). Among the studied methods, removal of dyes from adsorption is found to be the most aggressive one because it does not need a high effective temperature and several colouring materials can be removed simultaneously (Bhanuprakash. & Belagali 2016).

Adsorption is moderately superior because of simplicity of design, low cost, availability and ability to treat dyes more concentrated than other methods (Mahmoode et al., 2011, Yagub et al., 2012). Activated carbons are generally used as adsorbents because they have high adsorption abilities for a huge number of inorganic/organic metal ions. However, the cost of activated carbon is comparatively high which restrictions their usage(Cui et al., 2008). Natural materials that are obtainable in large quantities or certain waste products from industrial or agricultural materials may have the potential to be used as low-cost adsorbents. Agricultural wastes are renewable and available in large quantities at no or low cost.

In the present study, activated carbon prepared from Rubber wood saw dust (RSDAC) have been used as an adsorbent for dye removal of MO. The effects of operating parameters such as pH, contact time, adsorbent dosage were studied. The adsorption isotherm studies were performed using three different isotherm equations (Langmuir, Freundlich, Temkin).

II. Materials and Methods

2.1 Adsorbate

The concentration of MO was analysed by UV-Visible spectrophotometer. A standard MO solution of 1000 mg/l was prepared and absorbance was determined at various wavelengths to obtain a plot of absorbance versus wavelength (Fig 1.1). The plot showed wavelength related to the maximum absorbance of MO at 465 nm.

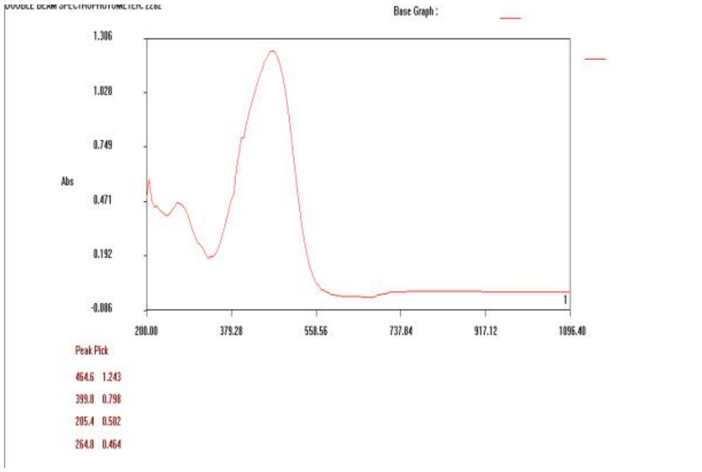

Figure 1.1: UV-Visible spectrum of Methyl Orange

2.2 Adsorbent

The sawdust of rubber wood used in this study was collected from Kanakam sawmill located at Manali, Thuckalay, Kanyakumari. The collected material was washed with distilled water and dried in an oven at 120^0 C. The dried material was cut into small pieces for further chemical modification. The ground material was mixed with equal amount of 1:1 phosphoric acid and heated for 2 hrs at 500^0C in a muffle furnace. The product was cooled, washed several times with distilled water to remove residual acid, finally dried at 110 °C and preserved in a desiccator as adsorbent for further use. The powdered activated carbon materials sieved through a 0.25 mm sieve.

2.3 Batch adsorption experiments

The effects of pH, contact time, adsorbent dosage and initial dye concentration were investigated using 0.1g of each adsorbent except for adsorbent dosage experiments where various amounts were used. In all cases residual concentrations of MO after equilibration were measured at 465 nm wavelength using UV/ Visible spectrophotometer.

2.4 Adsorption isotherms

In order to determine the sorption isotherm 100mg of adsorbents are brought into contact with 50ml of the MO dye solutions of varying concentrations (20-100ppm). The equilibrium concentration is determined at 180 minutes. After the equilibration period, the concentration of the filtrate is measured by using UV-visible spectrophotometer.

III. Results and discussion

3.1. Effect of adsorbent dose on the adsorption of MO - dye

The experiments were conducted with constant dye concentration (20 ppm) and adsorbent dosages ranging from 0.015g to 0.2g (Fig 3.1). The maximum adsorption of RSDAC was found to be 83.9% with carbon dose of 0.1g per 50 ml of 20ppm dye solution. As ordinary, the percentage sorption of the dye increased with increasing adsorbent dosage. The results (Figure 3.1) indicate that adsorption percentage of MO increases with the increasing of adsorbent dose, it increased from 68% for 0.015g to 83.9% for 2g.

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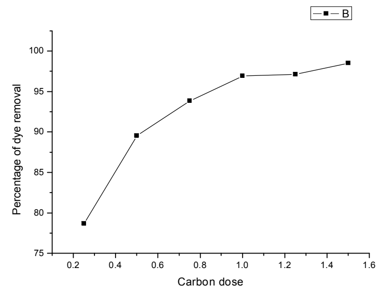

Figure 3.1: Effect of adsorbent dose

3.2. Effect of pH on adsorption of MO dye

The effect of pH on MO dye adsorption has been studied by varying pH on dye solution from 2 to 10 using 0.1N NaOH and 0.1N HCl. 0.1g adsorbents were then added to 50ml of MO dye solution with a concentration of 20 mg/L. The maximum adsorption of MO dye takes place to the extent of 82 - 83% for RSDAC in the range of pH 7-9. As shown in Figure 3. 2., the percentage of dye removal increases in the pH range of 2- 6, then the amount becomes constant within the range of 7-10.

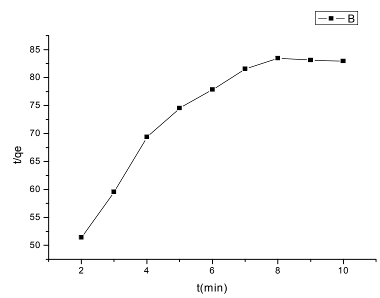

Figure 3.2: Effect of pH

3.3. Effect of Contact Time on the Adsorption of MO Dye

The results showed a rapid increase of dye removal percentage at the initial stage. This is due to the presence of a huge number of vacant sites on the peripheral surface of the adsorbent on which MO dye molecules get adsorbed through boundary layer adsorption. The rapid uptake of methyl orange dye at the initial stage might be due to the accessibility of vacant binding sites on the surface of the sorbent. The equilibrium agitation time required for removing methyl orange using RSDAC was found to be 180 minutes with a dye removal efficiency 89.52%.

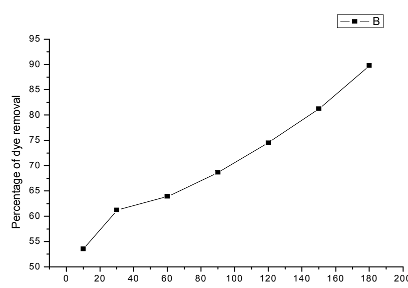

Figure 3.3: Effect of contact time

3.4. Langmuir Isotherm

The Langmuir isotherm assumes that adsorption occurs on a homogeneous monolayer surface containing sites with uniform energy with a finite number of identical sites. It also assumes there is no interaction between the adsorbed molecules (Xing et al.,2010). Langmuir adsorption isotherm equation can be expressed as,

$$\frac{Ce}{Qe} = \frac{1}{Qm} Ce + \frac{1}{Qm k_L}$$

Where Ce is the concentration of the adsorbate at equilibrium (mg/g), Qe is amount of adsorbate adsorbed per gram of adsorbent at equilibrium (mg/g), Qm is Langmuir constants related to adsorption capacity (mg/g), k_L=Langmuir constants associated with energy of adsorption (L/mg),

The validity of Langmuir model can also be proved through a constant, called equilibrium parameter or dimensionless factor, i.e, $R_L = \frac{1}{1+kC_0}$ (Hall et al., 1966) which measures the suitability of the adsorbent for dye adsorption

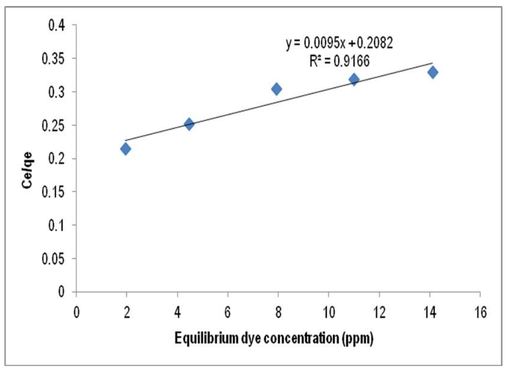

Figure 3.4: Langmuir adsorption plot of MO onto RSDAC adsorbent

R_L values indicate the type of adsorption to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$). The separation factor, R_L, has been calculated from Langmuir plot. It has been found that the calculated R_L values for RSDAC 0.187. These R_L values indicate favourable adsorption as it lies in $0 < R_L < 1$. Maximum adsorption capacity (Qm) 111.11 mg/g was observed in RSDAC.

3.5 Freundlich Isotherm

The Freundlich expression is for a multilayer sorption to occur and it is an empirical equation for adsorption on heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface (Xing et al.,2010). The Freundlich adsorption isotherm equation can be expressed as

$$\text{Log } qe = \log k_f + \frac{1}{n} \log Ce \qquad (3.12)$$

Where, qe=the amount of dye adsorbed at equilibrium time (mg/g), Ce=the equilibrium concentration of dye in the solution (mg/L), k_f=Freundlich constant related to adsorption capacity of adsorbent, n=the intensity of adsorption constant for Freundlich

Linear plot of $\log q_e$ versus $\log C_e$ shows that the adsorption of MO follows the Freundlich isotherm(fig 3.5). The value of K_f and n were calculated from the intercept and slope of the plot . The scale of the exponent (n) gives an indication of the favourability and K_f the capacity of the adsorbent / adsorbate. The value of k_f and n were calculated from the intercept and slope of the plot. The value of n was found as 1.2936 which is large than one which indicated the favorable native of adsorption and a physical process (Meroufel et al., 2013; Ruziwa et al., 2015).

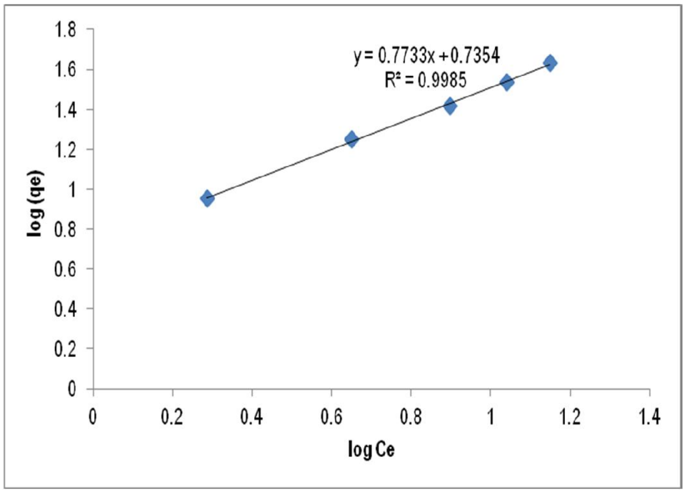

Figure 3.5: Freundlich Isotherm for MO sorption on to RSDAC

Table 1: Langmuir and Freundlich parameters of adsorption isotherms

Langmuir Isotherm			Freundlich Isotherm		
R^2	R_L	K_L(L/m)	R^2	K_F(L/m)	N
0.9166	0.187	0.0432	0.998	2.0854	1.293

3.6 Adsorption kinetic study

The pseudo – first order kinetic model assumes that the rate of occupation of sorption sites is proportional to the number of unoccupied sites. The pseudo-first order equation was expressed in equation.(Ho and Mckay 2004).

$$\log(qe - qt) = \log qe - \frac{K1}{2.303}\,t$$

Where qe is the adsorption capacity of the adsorbent at equilibrium (mg/g), qt is the amount of dye adsorbed at time t(mg/g) and $k_1$is the pseudo first order rate constant(min^{-1}). The pseudo second order kinetics can be expressed in a linear form as integrated second order rate law(Kamal 2014).

$$\frac{t}{qt} = \frac{1}{qe}t + \frac{1}{K2qe^2}$$

Where k_2 is the pseudo second order rate constant (g mg^{-1} min^{-1}).

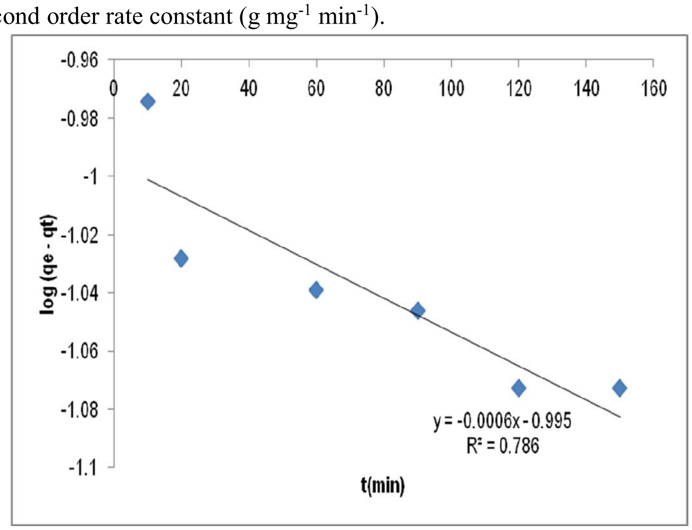

Figure 3.6.1: Pseudo-first-order kinetic for adsorption of the MO dye onto SDC

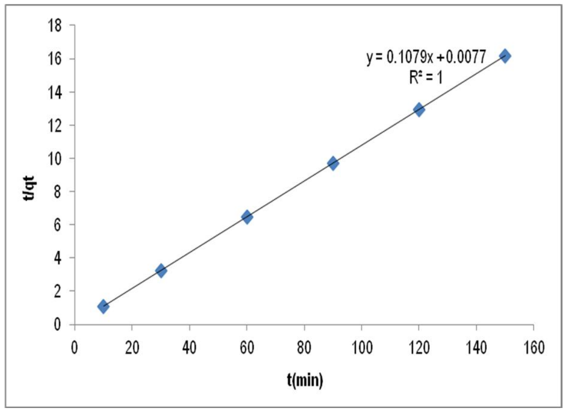

Figure 3.6.2: Pseudo-Second-order kinetic for adsorption of the MO dye onto SDC

Table 2: Pseudo first order and pseudo second order parameters for MO dye adsorption onto RSDC plant

qe(mg/g)	**Pseudo Ist order**			**Pseudo 2nd order**		
	qe(mg/g)	K_1 (min^{-1})	R^2	qe(mg/g)	K_2(mg^{-1}g.min^{-1})	R^2
9.3515	0.3696	0.0013	0.7868	9.2421	0.1282	1

In pseudo first order kinetics, the calculated qe value does not match with the experimental qe value (Table.2). This pointed that the adsorption of MO dye does not obey the first-order kinetics, hence pseudo first order model is not the appropriate one. The results confirmed that the pseudo second order kinetic model perfectly fits the experimental data with linear regression coefficient which equals to, 1.

IV. Conclusion

The present investigation has shown that activated rubber sawdust can be effectively used as a raw material for the removal of methyl orange dye from aqueous solution. Methyl orange is found to adsorb strongly on the surface of activated sawdust. The removal efficiency increased with increasing of adsorbent dosage, contact time and pH removal efficiency. The adsorption data was well described by the Langmuir isotherm equation with a maximum adsorption capacity of 111.11 mg/g. The results confirmed that the pseudo second order kinetic model perfectly fits the experimental data with linear regression coefficient which equals to, 1.

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