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Rhodamine-B and Metanil Yellow Dyes Adsorption on Onion Sheath

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ABSTRACT

Organic dyes are very harmful and toxic in nature. They pollute the soil, water, plants and all living systems in the environment. In this study, how the onion is affected by Rhodamine-B and Metanil Yellow dyes has been verified by the adsorption of both dyes on onion sheath as an adsorbent. Varying the parameters such as contact time, concentration, adsorbent dosage, temperature and pH are optimized to attain equilibrium adsorption. Langmuir and Freundlich methods, pseudo second order kinetics are applied to find out the adsorption capacity and rate of adsorption respectively. The entropy, enthalpy and free energy of adsorption of both dyes have been evaluated by adsorption thermodynamics.

Keywords: Adsorption, Metanil Yellow, Rhodamine-B, Onion Sheath.

INTRODUCTION

Pollution can be made by human activity and by natural forces [1]. Today we can say that we are living in a world of waste; because of population growth with increasing of that makes landfill are becoming more numerous and increasingly degrade the environment. Every day a huge amount of waste, in agricultural areas is produced in villages. Every year, about 10 million tons of oil products and more than 500 billion tons of industrial waste reaching rivers and oceans [2]. The most worried environmental pollution is air pollution and wastewater pollution. Industrial effluent and domestic sewage are the main sources of water pollution. 2.07% of water is consumed by textile industries. The consumption for the textile industry includes various processes such as sizing, dyeing and other end product processes. These chemicals are directly released into water bodies and it causes water pollution. This water pollution not only affects human beings and house hold animals but also aquatic animals to the same extent.

There are 7 x 10^5 tons of synthetic dyes are produced worldwide every twelve months [3-5]. Dyes are extensively used in many industries such as textile, rubber, paper, plastic, cosmetic etc. Out of these a variety of industries, textile posses the first place in usage of dyes for coloration of fiber. In the textile industry, up to 200,000 tons of these dyes are lost to effluents every year during the dyeing and finishing operations [6]. The discharge of the colored effluents into water bodies is objectionable not only from aesthetic considerations but also due to the fact that it reduces penetration of sunlight through the water body thereby retarding biological activity. The presence of dyes and chemicals in waste effluents is harmful to both aquatic and terrestrial life even at very low concentration [7].

So many physico-chemical methods such as coagulation, flocculation, biosorption, Photodecomposition, ultrafiltration and adsorption are reported for dye effluent treatment. Among these methods, adsorption is an efficient method for dye effluent treatment [8-10]. In particular, the use of agricultural waste as adsorption systems has drawn attention because it is abundantly available. A number of low-cost adsorbents are reported in the literature. These include wheat shells, rice husk, garlic peel, raw beech, sawdust, coir pith and peanut hull [11-16].

Onion sheath, an agricultural and easily available waste, could be an alternative for more costly wastewater treatment processes. Due to the high consumption of onion, massive amounts of sheath are disposed off. In the interest of the environment, it is proposed that this agricultural waste be used as a low-cost adsorbent to remove RB and MY from aqueous solution.

MATERIALS AND METHODS

The chemicals used in this present work are analytical grade and used directly without further purification. The cationic dye Rhodamine B and anionic dye Metanil Yellow are used to study the removal of organic pollutants. All dyes are purchased from Loba Chemie Pvt. Ltd. The physical properties of organic dyes are given in table 1. The structures of cationic and anionic dyes are given in figure 1 and 2.

Table 1: Physical property of organic dyes

S.No	Name of the dye	Molecular formula	Maximum absorption λ_{max}
1	Metanil yellow	$C_{18}H_{14}N_3NaO_3S$	434.76
2	Rhodamine B	$C_{28}H_{31}ClN_2O_3$	553.65

Chemical structures of organic dyes

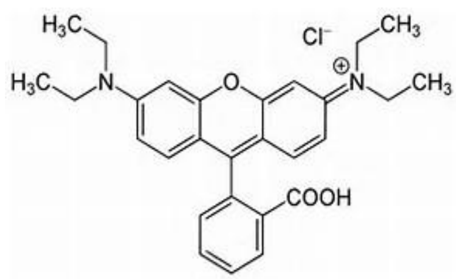


Figure 1: Structure of Rhodamine B

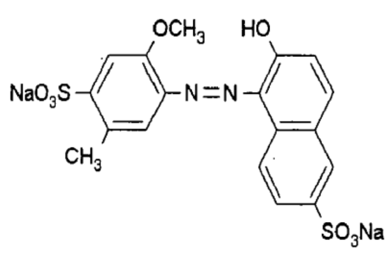


Figure 2: Structure of Metanil Yellow

Preparation of adsorbent: Onion sheath is collected from nearby agriculture land. It is washed to remove the soil and dust particles. It is dried under sunlight for 10 days. Then it is grinded into fine powder.
The powder is washed with distilled water to remove any compounds present in the adsorbent material. After washing, it is dried in an oven for 110 °C and stored in an air tight container.

Preparation of stock solution: Stock solution (1000 mg L^{-1}) of cationic dye Rhodamine B (RB) and anionic dye Metanil Yellow (MY) is prepared by dissolving in distilled water. Experimental solutions of the desired concentrations are then obtained by successive dilutions with distilled water.

Adsorption experiment: 0.5 g of adsorbent is added with 50 mL of cationic dye Rhodamine B and anionic dye Metanil Yellow solutions separately. The solutions are agitated (Kemi agitator) at 150 rpm. The solution concentrations are measured by spectrophotometer. The maximum absorbances are found by spectrophotometer at the respective wavelength. The maximum wavelength of RB and MY are 553.8 nm and 434.76 nm respectively.

To find out the maximum removal of organic dyes over onion sheath, the experimental conditions like, dye concentration, temperature, adsorbent dosage and pH are carried out.

RESULTS AND DISCUSSION

Adsorption Studies: The effect of removal of organic dyes on onion sheath through adsorption at different conditions such as contact time, dye concentration, temperature, adsorbent dosage and pH are analyzed for maximum adsorption.

Effect of contact time: The effect of contact time study has been carried out at room temperature for the adsorption of organic dyes on onion sheath up to 210 min. The maximum adsorption is observed at 180 min for cationic dyes (Figure 3). The rate of dye removal increases slowly and attains equilibrium at 180 min. After that there is no adsorption takes place. The maximum dye removal is 62%. In anionic dyes, the rate of dye removal increases at the beginning and attain maximum at 20 min. This may be due to the saturation of the active sites which is not allowed further adsorption takes place. The maximum dye removal is 35%.

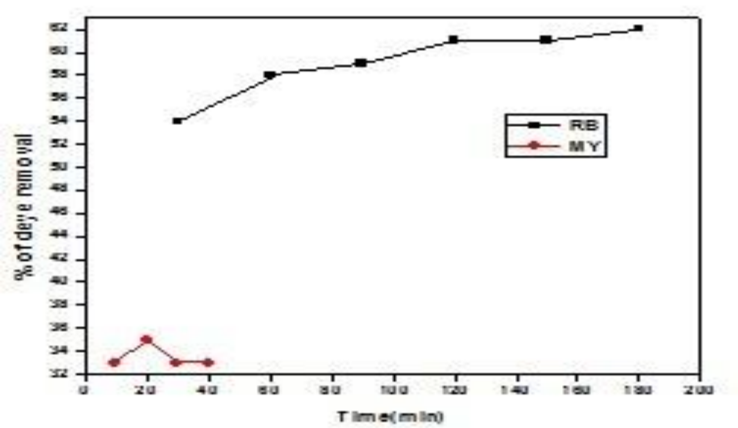


Figure 3: Effect of contact time for adsorption of cationic and anionic dyes on OS
Concentration: 100 mg L^{-1}, Temperature: 30 °C, Adsorbent dosage: 0.5 g

Effect of concentration: The effect of cationic and anionic dyes adsorption on onion sheath is studied at various concentrations between 50 mg L^{-1} to 400 mg L^{-1} at room temperature. The adsorption of cationic and anionic dyes is shown in figure 4. The adsorption percentage of organic dyes (RB and MY) on onion sheath is maximum at 100 mg/L and further increased of concentration decreases the adsorption. This may be due to the saturation of active sites of onion sheath.

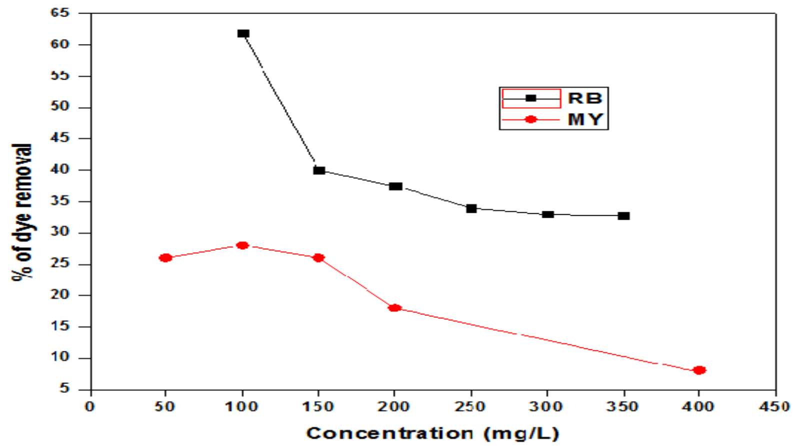


Figure 4: Effect of concentration on adsorption of cationic and anionic dyes on OS
RB: Contact time 180 minutes, Temperature 30^0C, Dosage 0.5g
MY: Contact time 20 minutes, Temperature 30^0C, Dosage 0.5g

Effect of temperature: The effect of temperature for the adsorption of cationic dye (RB) and anionic dye (MY) on onion sheath are studied at various temperatures between 30 °C to 70 °C. The effects of temperature of cationic and anionic dyes are given in figure 5. Temperature increased from 30 °C to 70 °C, the adsorption of dyes on OS decreases. When increases of temperature, dye molecules absorb heat energy and randomness increases too high. Hence adsorption decreases with increased of temperature.

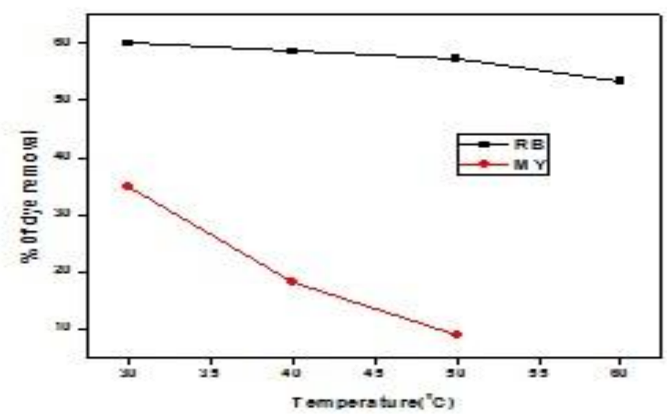


Figure 5: Effect of temperature for adsorption of dyes on OS
RB: Contact time 180 min, Dosage 0.5 g, concentration 150 mg L^{-1}
MY: Contact time 20 min, Dosage 0.5 g, concentration 100 mg L^{-1}

Effect of pH: Effect of cationic and anionic dyes adsorption has been carried out at different pH. RB dye adsorption on OS decreases with increased of pH above 7. This may be due to balancing of positive charge of RB by the OH^- groups at basic medium. The OS also has OH^- group on its surface, so adsorption of RB in basic medium decreases. MY adsorption on OS is pH dependent. At lower pH adsorption is more and further increases of pH decrease of adsorption. MY dye is anionic, at higher pH , adsorbent surface become basic. So adsorption of MY dye decreases with increased of pH (Figure 6).

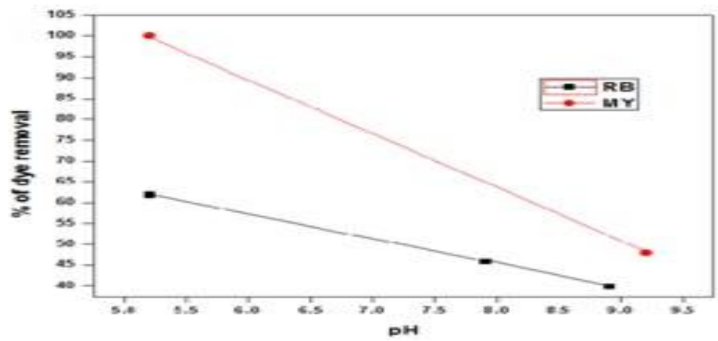


Figure 6: Effect of pH for dyes on OS
RB: Contact time 180 min, Temperature 30 °C, Concentration 150 mg L^{-1}, Dosage 0.5 g.
MY: Contact time 20 min, Temperature 30 °C, Concentration 100 mg L^{-1}, Dosage 0.5 g.

Effect of adsorbent dosage: Effects of dosage on adsorption of cationic dye and anionic have been carried out between 0.5 g to 2 g (Figure 7). Dye removal increases with increased of dosage due to the increase of surface area and active sites.

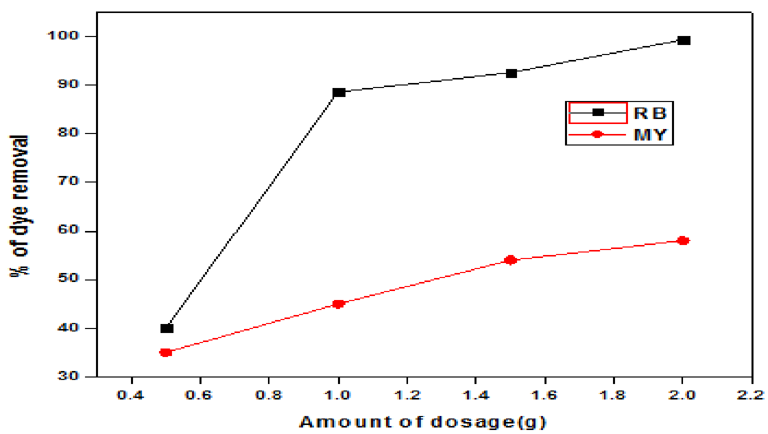


Figure 7: Effect of dosage for adsorption of dyes on OS
RB: Contact time 180 min, Temperature 30 °C, Concentration 150 mg L^{-1}
MY: Contact time 20 min, Temperature 30 °C, Concentration 100 mg L^{-1}

Adsorption Kinetics: The adsorption kinetics of dyes adsorption on onion sheath is studied to find out the rate constant of the adsorption. The adsorptions of organic dyes are studied at regular time interval at room temperature.

Pseudo first order kinetics: The adsorption kinetics of RB, MY have been studied using onion sheath as an adsorbent. The first order kinetics has been evaluated for these dyes on OS adsorbents. RB dyes adsorption has not followed the first order kinetics. The correlation coefficient for the adsorption of MY dye is not equal to 1(R^2 = 0.1922). This result revealed that the adsorption process does not follow the Pseudo first order kinetics model.

Pseudo second order kinetics: The pseudo-second order kinetic model is based on adsorption equilibrium and it is expressed as,

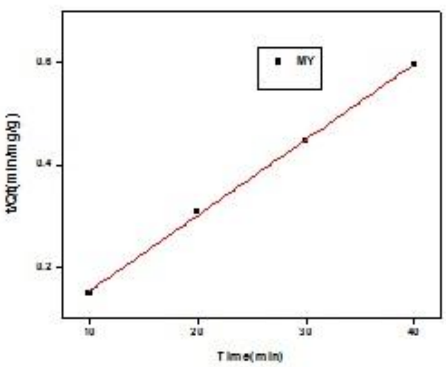
$$t/Q_t = 1/k_2 Q_e^2 + t/Q_t$$

k_2 = Pseudo second order rate constant.(gm^{-1} min^{-1})
Q_e = amount of dye adsorbed at equilibrium (mg g^{-1})
Q_t = amount of dye adsorbed at time 't' (mg g^{-1}).
t = time in minutes

The slope and intercept of (t/Qt) Vs t are used to calculate the pseudo second order constant k_2 and Qe. Linear plots of the t/Qt Vs t is given in the figure 8 & 9 for dyes adsorption on onion sheath. The linear regression coefficients close to 1 (Table 2) indicated that the adsorption of dyes on onion sheath is fitted with the pseudo second order kinetics.

Table 2: Pseudo second order kinetic parameters

Adsorbent	**Dye**	**K_2 (s^{-1})**	**R^2**
OS	RB	0.0167	0.9989
	MY	0.0148	0.9992



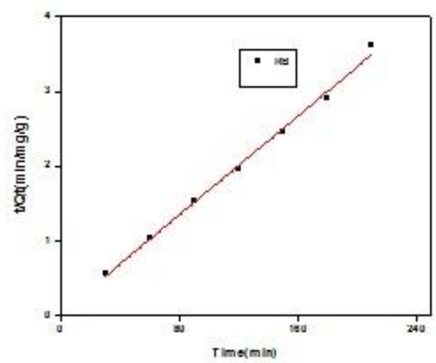


Figure 8: Pseudo second order plot of cationic dye on OS **Figure 9:** Pseudo second order plot of anionic dye on OS

Adsorption Isotherms

Langmuir adsorption isotherm: Adsorption isotherm data at different concentrations are measured for the adsorption of organic dyes and fitted with Langmuir adsorption isotherm equation given below. This adsorption isotherm has been carried out for understanding the monolayer adsorption and multilayer adsorption of RB and MY on onion sheath.

The Langmuir equation is represented as

$$C_e/Q_e = 1/\ Q_{ma}\ k_L\ +\ C_e/Q_{max}$$

Q_{max} = maximum adsorption (mg g^{-1}).
K_L = Langmuir constant (L mg^{-1}).
C_e = equilibrium dye concentration in solution (mg/L).
Q_e = adsorption capacities (mg/g).
K_L is an adsorption affinity and plot of C_e / Q_e Vs C_e is given in the Figure 10 &11. The R^2 values for the adsorption of dyes on onion sheath are given in Table 3.

The correlation coefficient (R^2) values for RB (R^2 = 0.8730) and MY (R^2 = 0.8230) are given in the table 3. RB and MY adsorption on OS does not follow Langmuir adsorption isotherm.

Table 3: Langmuir adsorption isotherm parameters

Adsorbent	Dye	Q_{max}	R^2	K_L
OS	RB	12.2339	0.8730	2.3594
	MY	3.5241	0.8294	5.7991

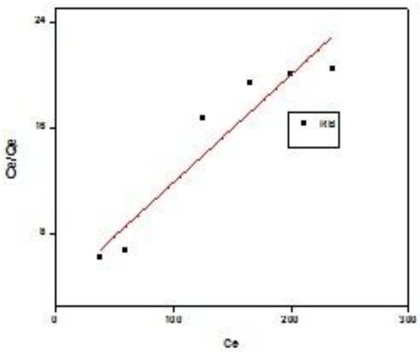


Figure 10: Langmuir adsorption isotherm of cationic dye RB on OS

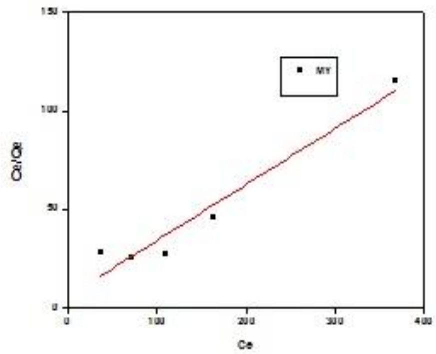


Figure 11: Langmuir adsorption isotherm of anionic dye MY on OS

Freundlich Adsorption Isotherm: The adsorption studies are carried out at various concentrations for the adsorption of organic dyes and the adsorption values are applied to the Freundlich equation to verify the adsorption isotherm (Table 4).
The Freundlich adsorption equation is,

$$\ln Q_e = \ln k_F + (1/n) \ln c_e$$

Where,
k_F = Freundlich constant.
n = number of layers.

The value of n discloses the adsorption pattern. The favorable adsorption is understood from the values of $1<n<10$ while irreversible adsorption is noticed from $n>10$ and unfavorable from $n<1$. Thus, one can see that the Freundlich equation is an empirical expression that encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies.

The plot of lnQe Vs lnCe gave a straight line (Figure 12 & 13) with the intercept $\ln K_F$ and the slope 1/n. The correlation coefficient for the adsorption of RB is (R^2 = 0.5055) and MY is (R^2 = 0.3431). This result revealed that the adsorption processes are not followed the multilayer adsorption.

Table 4: Freundlich adsorption isotherm parameters

Adsorbent	Dye	n	R^2	K_F
Onion Sheath	RB	4.2808	0.5055	2.8470
	MY	2.7166	0.3431	0.4903

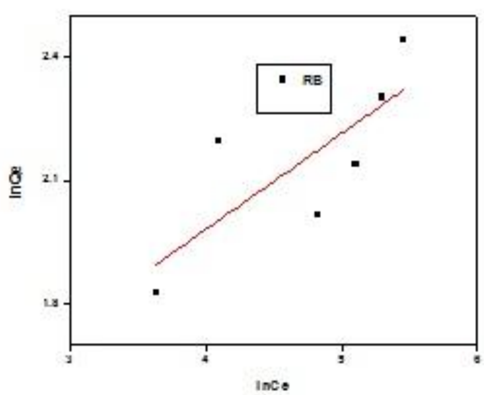


Figure 12: Freundlich adsorption isotherm of cationic dye on OS

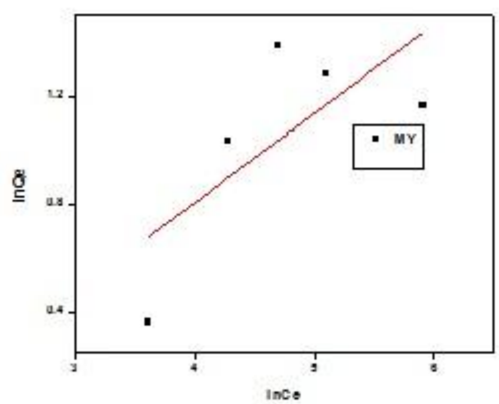


Figure 13: Freundlich adsorption isotherm of anionic dye on OS

Adsorption Thermodynamics: The thermodynamic parameters, namely free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) have main role to determine spontaneity and heat exchange for adsorption process. The thermodynamic parameters are calculated by using the following relations.

$$K_D = q_{e\,/}\, c_e$$

$$\Delta G = -RT \ln k_D$$

$$\ln K_D = (\Delta S/R) - (\Delta H/RT)$$

From the above equation

$$\Delta G = \Delta H - T\Delta S$$

Where,

K_D is the distribution coefficient, respectively q_e and c_e are the equilibrium dye concentration on onion sheath and in solution. R is the universal gas constant (8.314J mol^{-1} K^{-1}) and T is the temperature (K). ΔH and TΔS parameters can be calculated from the slope and intercept of the plot (Figure 14 and 15). ΔG is calculated by the above equation at various temperatures. Results are summarized in table 5. ΔG value in the temperature range 30 °C to 70 °C (303 K - 333 K) is positive. This indicated that it is not a feasible process. Enthalpy (ΔH) values are greater than 40 kJ mol^{-1} for MY (ΔH =67.427kJ mol^{-1}) dye indicated that the adsorption of dye on onion sheath is chemisorptions and less than 40kJ mol^{-1} for RB (ΔH =8.376 kJ mol^{-1}) indicated that the adsorption of dye on onion sheath is physisorption.

The positive value of enthalpy for RB indicated that the adsorption process is endothermic. Moreover, the positive value of ΔS indicated that the degrees of freedom increased at the solid-liquid interface during adsorption. The negative value of ΔS for MY indicated that the degrees of freedom decreases at the solid-liquid interface during adsorption process.

Table 5: Thermodynamic parameter for adsorption of dyes on OS

Adsorbent	**Dye**	**Temperature (K)**	**ΔG^0(KJ mol^{-1})**	**ΔH (KJ mol^{-1})**	**ΔS (KJ mol^{-1})**
Onion sheath	RB	313 323 333	0.6701 0.6594 0.6486	8.376	8.9591
	MY	303 313 323	15.3093 15.5469 15.7845	67.427	-197.54

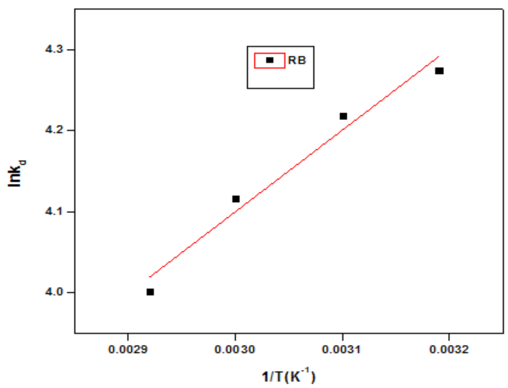


Figure 14: Adsorption thermodynamic plots of cationic dye on OS

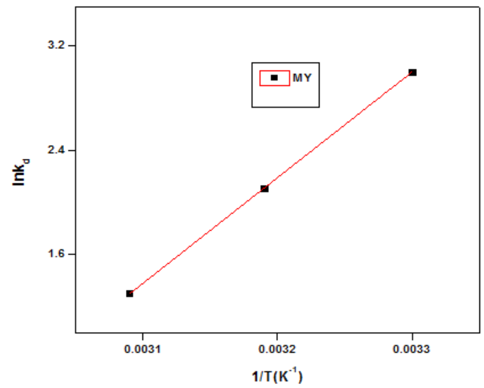


Figure 15: Adsorption thermodynamic plots of anionic dye on OS

CONCLUSIONS

Onion sheath is an agricultural waste. The MY and RB are waste textile dye. The adsorption of textile waste on agricultural waste is low cost economic process. Equilibrium adsorption attained at 180 min for Rhodamine B and 20 min for Metanil Yellow on OS. Adsorption of organic dyes (RB and MY) on onion sheath does not follow the pseudo first order kinetics and follow pseudo second order kinetics. The adsorption isotherm results showed that the adsorption of organic dye (RB & MY) on onion sheath does not follow Langmuir and Freundlich isotherm. It indicated that the adsorption layers are not uniform. The thermodynamic studies shown that the free energy will not change with respect to temperature. This proved that the RB and MY adsorption on OS are independent of temperature.

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