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RESEARCH ARTICLE

PARAMETRIC OPTIMIZATION FOR ADSORPTION OF REACTIVE ORANGE 16 ON WATER HYACINTH ROOT POWDER

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Abstract

This experimental study was performed to explore out the potential of WHRP for the adsorptive removal of RO16 from aqueous solution. The effect of pH, adsorbent dose, concentration and contact time have been investigated. Experimental results for pH indicated 3 as optimum pH. The adsorption isotherms fitted to both Langmuir and Freundlich models. The dye adsorption equilibrium was attained after contact time of 100 minutes. For all the range of concentration taken into accounts at optimum conditions of pH, adsorbent dose, concentration maximum 93% removal of RO16 was achieved in 100 minutes. Based on the results it is concluded that WHRP has great potential for the removal of RO16 from aqueous solution.
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Keywords: Adsorption, Dye, Reactive Orange 16, Water hyacinth root powder, Isotherms.

Introduction

Color is the first contaminant to be recognized in wastewater. The presence of very small amounts of dyes in water is highly visible and undesirable (Robinson et al., 2001). For some dyes, the dye concentration of less than 1 ppm in receiving water bodies is highly visible thus stated as "Visible pollutant". The decolorization of waste water is a major environmental concern. Synthetic dyes have been extensively excreted in the wastewater from different industries particularly from dye manufacturing, textile, paper, rubber, lather, cosmetic, food and drug industries which used dyes to color their products. It is reported that over 100000 commercially available dyes exist and the global annual production of synthetic dyes is more then 7x 10^5 metric tons (Pearce et al., 2003). As dyes are designed to be chemically and photolytically stable, they are highly persistent in natural environments. The extensive use of dyes and their structural complexity often poses pollution problems in the form of colored wastewater discharged into environmental water bodies. This not only affects aesthetic merit but also interfere the sunlight penetration, reduces photosynthetic activity and inhibits the growth of aquatic biota. In addition, many dyes or their metabolites pose toxic, carcinogenic, mutagenic and teratogenic effects on aquatic as well as human life.

Reactive dyes are an important group of dyes and widely used in textile industry. Reactive dyes have some advantages such as wide variety of color shades, ease of application, good color fastness and brilliant color. During dyeing with reactive dyes, approximately 50 % of the dye cannot be reacted with the fibers and stay put hydrolyzed in water phase (Netpradit et al., 2004). If it is released into the environment, it can cause environmental problems. High solubility in water and structure complexity of reactive dyes makes their removal difficult by conventional process. Adsorption process provides an attractive alternative for the treatment of colored water (Robinson et al 2001). Adsorption technique has been proved to be an excellent way to treat dye effluent. Adsorption on activated carbon is one of the most effective adsorbent but the high cost and regeneration problem has motivated many researchers to search for alternative low cost adsorbent materials. Various cheap adsorbents have been tested and reported to give encouraging results in several areas of application (Rajamohan,2009).In this study acid modified water hyacinth root powder (WHRP) has been tested for their potential to adsorb Reactive Orange 16 (RO16) dye from synthetic wastewater by adsorption.

Materials and Methods

Adsorbent preparation

Water hyacinth is listed as one of the most productive plants on earth and is considered one of the world's worst aquatic plants. Water hyacinth plant was collected from local river Kshipra, Ujjain. The roots of collected water hyacinth plant were separated from plant and extensively washed under running tap water to eliminate mud and slimy materials. Finally roots were washed thoroughly with distilled water and sliced in pieces manually. It is then dried over night at 50°C in oven. The dried roots then ground in domestic mixer and sieved. Finally root powder is stored in air tied container for further use.

Reagents and equipments

All the chemicals used in this study were of analytical grade. Reactive Orange 16(RO 16) was supplied by Merck India private limited. The structure of RO 16 is shown in Fig.1 and general characteristics of RO 16 ($C_{20}H_{17}N_3Na_2O_{11}S_3$) are molar mass = 617.54, C.I. No. = 17757, λ_{max} = 494 nm. Stock solution of dye was prepared by dissolving accurately weighted 1gm RO16 dye in 1000 ml distilled water. Afterward it was diluted by using distill water according to concentration required. pH was adjusted by adding 0.1 M NaOH and 0.1 M HCl solution. Dye solution concentrations were analyzed by UV-visible spectrophotometer (Systronics 2101). Surface morphology of adsorbent was analyzed by Scanning Electron Microscopy (JEOL JSM-6390A) with different magnifications.

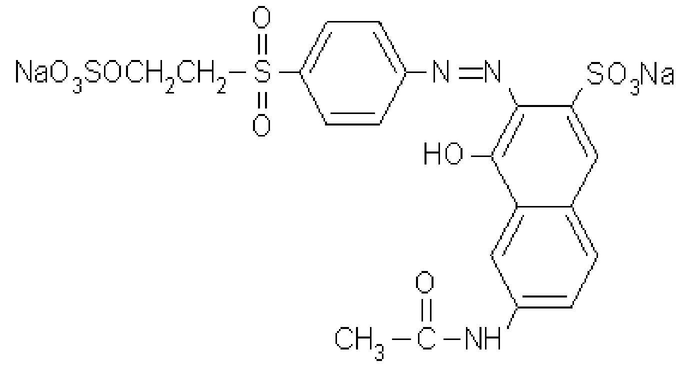

Fig.1 Structure of Reactive orange 16

Batch adsorption experimentation

Batch experimentation were carried out at room temperature to study the effects of important parameters such as effect of pH, contact time, initial concentration and amount of adsorbent. Dye concentration before and after adsorption was estimated spectrophotometrically at the wavelength corresponding to maximum absorbance, 494 nm, using a UV-visible spectrophotometer.

A fixed amount of water hyacinth root powder (WHRP) adsorbent was placed in 250 ml flasks containing 100 ml of dye solution (concentration 20 to 100 mg/l) at pH ranging from 2 to 10. Then flasks were shaken in orbit shaker with a speed of 60 rpm at room temperature for 20 to 120 minutes. After filtration final concentration of dye solution were analyzed by UV-visible spectrophotometer. The amount of equilibrium uptake of dye is calculated by using equation.

$$q_e = \frac{(C_0 - C_e)V}{W}$$

Where, q_e is the dye up taken by adsorbent mg/g, C_0 is the initial RO 16 concentration, C_e is the RO 16 concentration (mg/l) after the adsorption process, W is the Mass of adsorbent taken (g), V is the Volume of dye solution taken (l).

The percentage removal of dye is defined as the ratio of difference in dye concentration before and after adsorption ($C_0 - C_e$) to the initial concentration of the dye of the aqueous solution of the dye (C_0) and was calculated by using equation.

$$Percentage\ Removal = \frac{(C_0 - C_e)100}{C_0}$$

Results and Discussion

Scanning Electron Microscopy (SEM) analysis

The Surface Structural morphology of WHRP was analyzed by Scanning electron microscope (SEM) image as shown from Figs. 2 and 3. It is clear from SEM images that the adsorbent have considerable number of heterogeneous micro and mesopores, a cave like uneven and rough surface morphology. Thus there is a good possibility for dye molecules to be trapped and adsorbed.

Effect of pH

The interaction between dye molecule and adsorbent is basically a combined result of charge on dye molecules and the surface of the adsorbent (Maurya et al., 2006). RO 16 exhibit good adsorption behavior at lower pH. The removal of RO 16 decreased from 93% to 41% with the increase of pH from 3 to 10 (Fig. 4). Reactive dyes are known to ionize to a high degree in aqueous solutions to form colored anions due to the presence of sulfonate groups in their structures. Two sulfonate ($–SO_3^-$) groups of RO 16 dye are easily dissociates and produces negatively charged anion in aqueous medium. At lower pH adsorptive surface is protonated and facilitate the sorption of negatively charged dye anion. The number of positively charged sites increases resulting in an increase of binding sites for anionic dye molecules RO16 (Chiou and Li 2003). As the pH of the solution increases, the number of negatively charged site increased. Strong electrostatic repulsion exists between the dye anion and negatively charged surface. This has contributed to the decreased uptake of RO 16 in alkaline condition. Al-Degs et al.(2008) also reported same trend for reactive dyes.

Effect of Adsorbent Dose

Adsorbent dose is representing of important parameter due to its strong effect on the capacity of an adsorbent at given initial concentration of adsorbate. Effect of adsorbent dose on removal of RO 16 was monitored by varying adsorbent dose from 1g/l to 8g/l. Fig. 5 shows that the removal percentage of dye increased with the adsorbent dose and reached on equilibrium value of 93% at 6.0 g of adsorbent. As one was expected, the percentage of dye removal increased with increasing amount of WHRP, however the ratio of dye adsorbed to WHRP (mg/g) decreased with increasing amount of adsorbent WHRP. The reason for such behavior may be attributed to greater surface area and large number of vacant sites thus favoring more dye adsorption (Gong et al., 2005). When the WHRP further increases after 6.0 there was no significant change in adsorption thus 6.0 g WHRP adsorbent dose was chosen for study of other parameters. Results indicate that the adsorption capacity of adsorbent decreased with increasing of adsorbent dose, from 9.38 mg/g at 1 g of adsorbent to 2.32 mg /g at 8 g adsorbent. This may be due to the increase in vacant sorption site to dye molecules ratio with increasing adsorbent dose with fixed dye concentration at 20 mg/l. Similar findings were reported by Ozer et al., (2007).

Effect of Initial Concentration and Contact Time

The variation in percentage removal of dye with contact time at different initial concentration range from 20 mg/l to 100 mg/l with fixed amount of adsorbent (6g/l) was tested. It was observed from the Fig.6 that the maximum amount of dye adsorption taking place within the contact time of 20 min and becomes gradual thereafter. Data has been taken up to 100 minutes of operation to attain the equilibrium. After that there is no significant change in the extent of adsorption. The rapid removal of dye at initial stage is attributed to the abundant availability of vacant active sites on the adsorbent and with the gradual occupancy of these sites; the adsorption becomes less efficient in the later stage. Concentration gradient between adsorbate in solution and adsorbate in the adsorbent also is a driving force for rapid adsorption at initial stage (Ju et al., 2008). The equilibrium adsorption capacity of WHRP is increased from 3.10 mg/g to 13.16 mg/g as increasing concentration from 20 to 100 mg/l. It was significantly different with percentage removal that decreased from 93% to 79% as initial concentration increased similarly. At lower dye concentration, the available adsorption sites are relatively high and consequently the dye species can find easily the accessible adsorption sites . Wong et al. (2009) also observed similar results with Reactive Orange 16 and Basic Blue 3 adsorption onto quartenized sugar cane bagasse. Equilibrium parameters for tested concentration ranges are summarized in Table 1.

Isotherm modeling

The equilibrium adsorption isotherm is fundamentally important in designing the adsorption

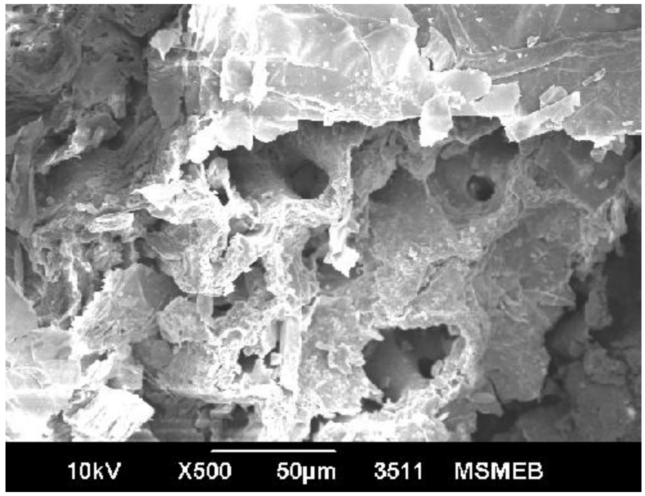

Fig.2 : SEM Image of Water Hyacinth Root Powder at Magnification X500

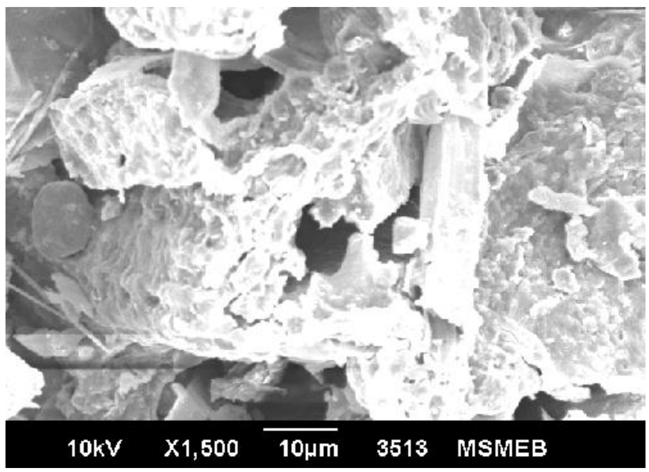

Fig.3 : SEM Image of Water Hyacinth Root Powder at Magnification X1500

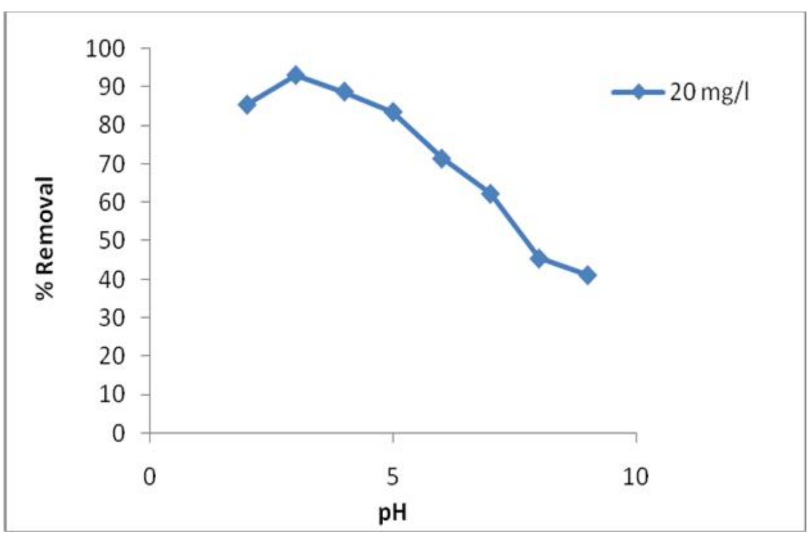

Fig.4 Effect of pH on adsorption of RO16.

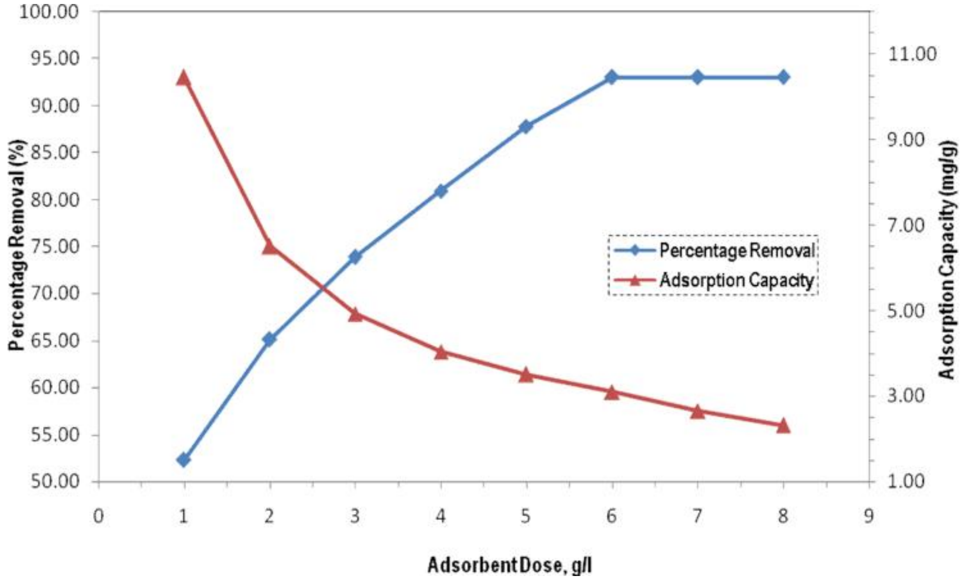

Fig.5 Effect of Adsorbent dose on adsorption of RO16.

Table 1: Equilibrium Parameters for adsorption of RO 16

Concentration		Equilibrium Capacity (q_e)	Percentage Removal
Initial (C_o)	Final (C_e)		
20 mg/l	01.40 mg/l	03.10 mg/g	93.0 %
40 mg/l	04.00 mg/l	06.00 mg/g	90.0 %
60 mg/l	09.00 mg/l	08.50 mg/g	85.0 %
80 mg/l	14.40 mg/l	10.93 mg/g	82.0 %
100 mg/l	21.00 mg/l	13.16 mg/g	79.0 %

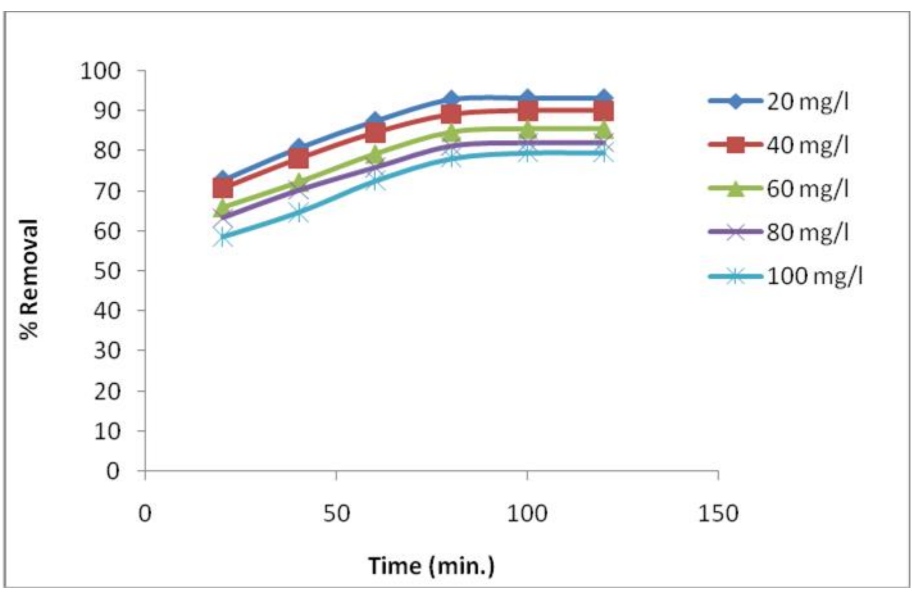

Fig.6 Effect of initial concentration and contact time on adsorption of RO16.

Table 2: Data Processing Isotherm Equations

S.No.	Isotherm model	Isotherm equation	Separation factor
1	Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{1}{q_{max}}C_e$	$R_L = \frac{1}{1+bC_o}$
2	Freundlich	$log q_e = log K_f + \frac{1}{n} log C_e$	-
3	Temkin	$q_e = B \ln A + B \ln C_e$ $B = [RT/b_T]$	-

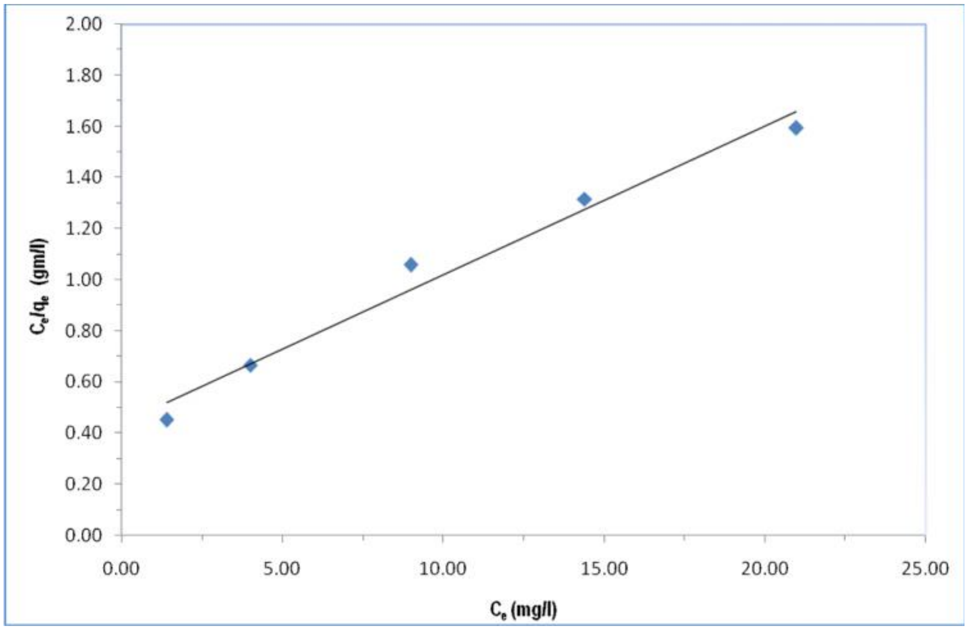

Fig.7.The Langmuir plot for adsorption of RO 16 on WHRP.

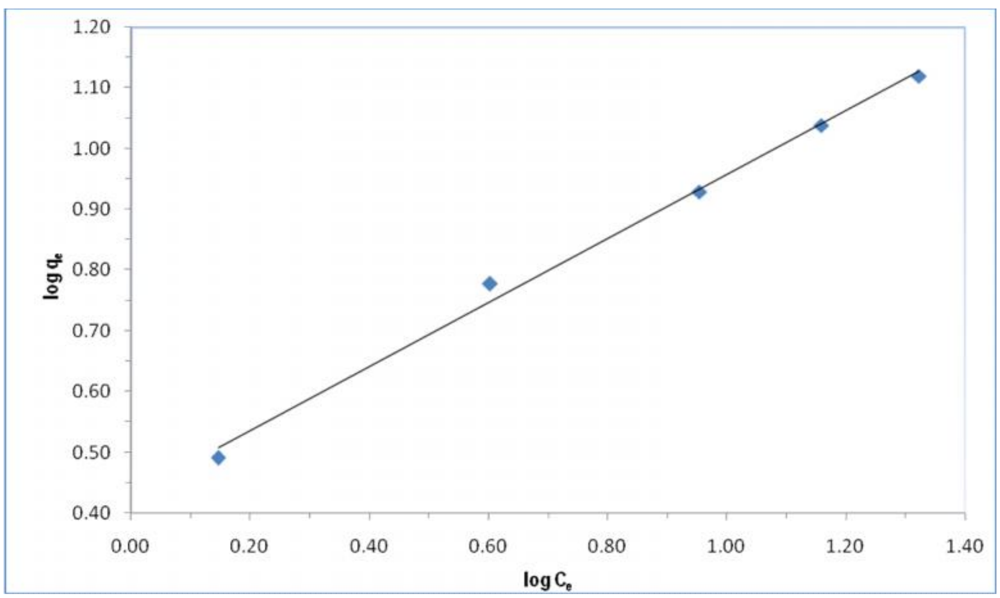

Fig.8. The Freundlich plot for adsorption of RO 16 on WHRP

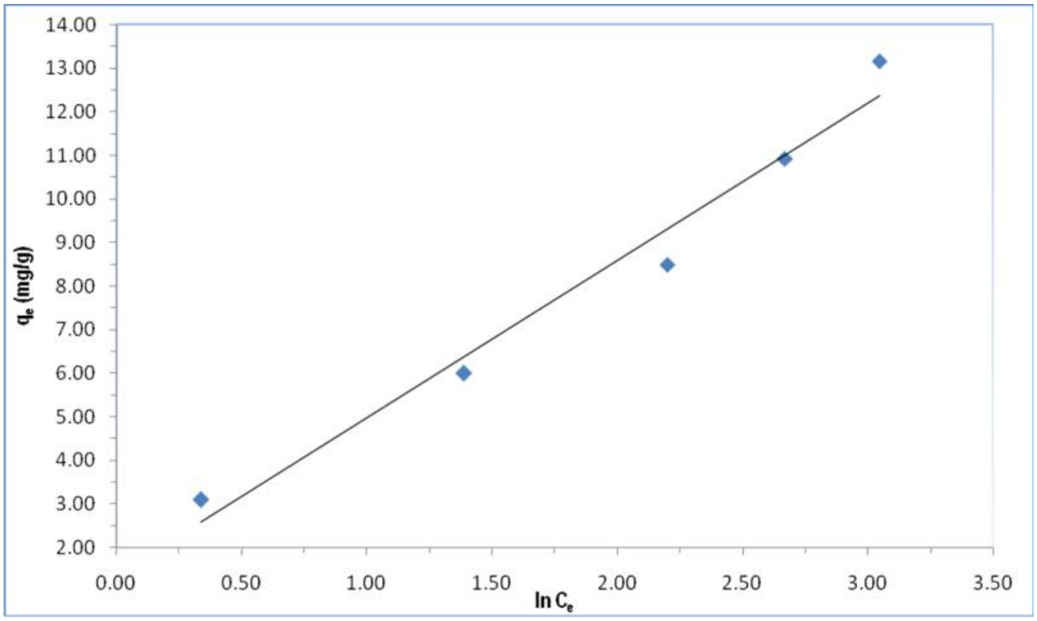

Fig.9. The Temkin plot for adsorption of RO 16 on WHRP

Table 3: The isotherm parameters for RO 16 adsorption onto WHRP.

Langmuir parameters	**q_{max} (mg/g)** 17.24	**b (l/mg)** 0.1321	**R_L** 0.2745	**R^2** 0.977
Freundlich parameters	**1/n** 0.525	**n** 1.904	**K_f (mg/g)** 2.697	**R^2** 0.994
Temkin Parameters	**B (J/mol)** 3.613	**A (l/g)** 1.464	**b_T** 685.73	**R^2** 0.973

systems. The isotherm expresses the relation between the mass of dye adsorbed at constant temperature per unit mass of the adsorbent and liquid phase concentration. In this study, the Langmuir, Freundlich and Temkin isotherm model were applied to experimental data.

Langmuir isotherm refers to homogeneous monolayer adsorption and favorable adsorption of the Langmuir isotherm is expressed in terms of a dimensionless constant separation factor R_L(Langmuir,1916; Hall et al., 1966) The Freundlich isotherm is the earliest known relationship describing the adsorption equation (Freundlich,1906). The Freundlich isotherm is derived to model the multilayer adsorption and for the adsorption on heterogeneous surfaces. Temkin considered the effects of some indirect adsorbate/adsorbent interactions on adsorption isotherms and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage rather than logarithmic, as implied in the Freundlich equation and the free energy of adsorption is simply a function of surface coverage (Bulut et al., 2008; Choy et al., 1999). The linearized form of the above mentioned isotherm equations are represented in Table 2:

The Langmuir, Freundlich, Temkin plots for adsorption of RO 16 are presented in Fig. 7, Fig. 8, Fig. 9 respectively.

Table 3 gives the values of parameters and correlation coefficient of the Langmuir, Freundlich and Temkin isotherm models. The experimental results indicated that the adsorption isotherms of RO 16 adsorption on WHRP followed both Langmuir and Freundlich models. The separation factor is found to be less than one, indicates favorability of process. Wong et al. (2009) also reported the same observation for RO 16.

Conclusion

In the present study, the adsorption of RO 16 onto WHRP was investigated. The results demonstrated that WHRP exhibited comparable adsorption efficiency and could be potentially used for the removal of RO16 from aqueous solution. Up to 93% removal of dye was achieved with contact time of 100 minutes and initial concentration of 20 mg/l. pH also play a significant role in adsorption process and optimum pH was found to be 3. The adsorption of dye increased with the adsorbent dosage and reached on equilibrium value on 6.0 g of adsorbent dose. The adsorption isotherms were well fitted to both Langmuir and Freundlich isotherm models. From the results of this study it is concluded that WHRP could be economically and effectively used for RO 16 removal from wastewater.

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Nomenclature

C_o is Initial adsorbate concentration (mg/l)
C_e is the equilibrium concentration of dye (mg/l)
q_e is the amount of dye adsorbed at equilibrium (mg/g)
q_{max} represents the maximum adsorption capacity for monolayer adsorption assumption
K_L is the Langmuir isotherm constants.
R_L is separation factor
b is Langmuir constant (l/mg)
K_f is Freundlich isotherm constants related to adsorption capacity
1/n is adsorption intensity respectively.
B corresponds to the heat of adsorption (J/mol),
R is the ideal gas constant,
T is the absolute temperature in K,
b_T is the Temkin isotherm constant and
A (l/g) is the equilibrium binding constant corresponding to the maximum binding energy.

