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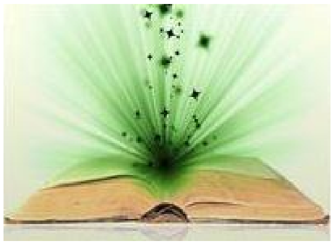

A Comparative study of Sonosorption of Reactive Red 141 Dye on TiO_2, Banana Peel, Orange Peel and Hardwood Saw Dust

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ABSTRACT

This work deals with the removal of Reactive Red 141 from its aqueous solution through adsorption by few discarded natural materials as adsorbent such as Orange Peel, Hardwood Sawdust and Banana Peel. Adsorption capacity of shade dried samples were determined experimentally under sonicated and unsonicated condition and compared with the adsorption capacity of TiO_2. Dye concentration was varied from 12 ppm through 16 ppm, 20 ppm and to 24 ppm. The adsorbent dose of 0.1gm and 0.2gm was taken at each concentration of dye. The adsorption capacity of different adsorbents was calculated for different time intervals 15, 30, 45, 60 and 75 min respectively, in the presence and absence of ultrasound. The isotherm data could be well described by the following adsorption isotherms; Langmuir, Freundlich and Temkin. The adsorption capacity was found to be in the order $TiO_2 \approx$ Orange Peel > Sawdust > Banana Peel. The adsorption of dye onto different adsorbent's surface followed pseudo second order kinetics. A mechanism for the adsorption and degradation of RR141 has also been explained. The present work revealed that the TiO_2, orange peel and hardwood sawdust were promising materials for the removal of dye from aqueous solutions under ultrasonic conditions, whereas, results with the banana peel were not encouraging.

Keywords: Adsorption, Banana Peel, Orange Peel, Saw Dust, TiO_2.

INTRODUCTION

Water is one of the vital necessities for the survival of human beings. Wastewater reclamation, recycling and reuse are vital to meet the water requirements for irrigations, industry and domestic uses due to increasing population and development in many parts of the world. Industrial wastewaters largely possess organic and inorganic materials such as dyes, phenolic compounds, aromatic compounds and heavy metals [1]. Textile industries discharge a large quantity of highly coloured effluent which is unscrupulously released into nearby land or rivers without any treatment because the conventional treatment methods are very expensive. Dye effluent if discharged untreated affects the photosynthesis of aquatic plants by preventing the light to penetrate through water. The oxygen levels are affected and in extreme cases may lead to suffocation of aquatic flora and fauna [2] as azo dye can be degraded to more dangerous substances under anaerobic conditions [3]. The contamination of wastewater by dyes poses two types of problems. The first is due to its visibility and colour [4] whereas the second problem is due to chemical effects of the dissolved toxic organics and dye molecules [5].

Various conventional methods of removing these dyes include coagulation and flocculation [6], oxidation or ozonation [7] and membrane filtration [8]. However, these methods are not widely used due to their high cost, non feasibility and economic disadvantage. In comparison to various physical, chemical and biological methods available for the treatment of textile industry effluent, adsorption is an effective and economical method for dye removal due to simple, flexible design and easy operation. Today, researchers have come out with study that has been focused on the low-cost adsorbents that are mainly obtained from agriculture waste and industrial by product since they required little processing and are abundant in nature.

The most common low cost adsorbent materials reported in the literature are: orange peel [9], banana pith [10], cotton waste, rice husk [11], betonite clay [12], neem leaf powder [13], powdered activated sludge [14], perlite [15], bamboo dust, coconut shell, groundnut shell, rice husk and straw [16], duck weed [17] and sewage sludge [18] for the removal of various dyes from wastewaters. Materials with higher adsorption capacity, easier availability and low cost are desirable for such removal. Some studies involving natural waste products such as orange and banana peel, TiO_2 and hardwood sawdust have been found to be effective and economical adsorbents [19-20] but no such work is reported in literature in the presence of ultrasound. Therefore, a systematic study of the adsorption of RR 141 dye, involving some of these adsorbents, in the presence and absence of ultrasound, has been undertaken, to find out most economical and effective method for removing textile dyes from the effluents.

MATERIALS AND METHODS

Highly pure sample of RR 141 dye (99.9%) was obtained as gift from M/s Spectrum Dyes and Chemicals, Surat, India. Tetra-n-butyl orthotitanate $(n\text{BuO})_4\text{Ti}$ [Sigma Aldrich] was used without further purification. Banana and orange peel were obtained from a local fruit Market and Hardwood sawdust was obtained from local carpenter shop.

Activation of different adsorbent: Banana and orange peels, obtained from a local fruit Market, were washed, shade dried, crushed and washed again thoroughly with deionised water to remove the adhering dirt. They were air dried in an oven at 100-120°C for 24 h. After drying, the adsorbents were sieved and stored in airtight bottles for use in experiments.

Hardwood sawdust was boiled with dilute hydrochloric acid for 30 min, and thoroughly washed with distilled water to remove the surface adhered particles and water soluble materials, and then dried at a temperature of 60-80°C in an electric oven. Acid hydrolyzed sawdust was finally sieved.

Adsorption Experiments: Stock solution (1000 ppm) of dye RR 141 was prepared in deionised water. 10 mL of dye solution at different initial concentration (12-24 ppm), prepared with further dilution with water, was mixed with 0.1 or 0.2 g of adsorbents [Orange peel/banana peel/TiO_2/hardwood saw dust, but only one at a time]. The adsorption of RR 141 was then carried out on respective adsorbents both in the presence or absence of ultrasound for different time intervals either by a magnetic stirrer or sonicated using an ultrasonic bath, Vibronics, operating at a fixed frequency of 20 kHz and 250W. Test solutions were quickly filtered through Whatman filter paper no. 3, after the stirring or sonolytic treatments. The concentration of the residual amount of dye was determined using Shimadzu UV-VIS spectrophotometer, 1601 PC, at λ_{max} = 544 nm.

RESULTS AND DISCUSSION

Effect of adsorbent dose and time interval: The decolourisation percentage improved with sonication, increase in amount of adsorbent and the treatment time as shown in Table.1. The increased decolourisation was due to increased surface area of sorbent and the availability of new sorption sites as a result of sonication.

Table 1: Percentage removal of RR 141 after 75 min with different amount of adsorbent, C_0 =12 ppm.

Adsorbent	Adsorbent Dose (gm)	Condition	% Decolorization of Dye with Time (min)				
			15	30	45	60	75
Banana Peel	0.1	Unsonicated	5.25	10.50	18.83	21.00	24.08
		Sonicated	24.02	24.58	25.17	25.66	27.75

	0.2	Unsonicated	28.83	29.33	29.83	33.00	36.66
		Sonicated	68.08	73.33	75.42	79.08	79.58
Sawdust	0.1	Unsonicated	28.56	35.58	37.67	39.75	41.92
		Sonicated	51.83	57.67	59.17	60.75	65.42
	0.2	Unsonicated	59.20	60.82	65.40	73.33	75.42
		Sonicated	75.39	78.86	79.42	89.00	92.17
Orange Peel	0.1	Unsonicated	67.02	74.87	76.44	79.58	85.34
		Sonicated	70.68	78.01	79.58	86.38	92.15
	0.2	Unsonicated	76.44	79.58	85.34	89.53	90.57
		Sonicated	90.58	92.15	94.76	95.91	97.38
TiO_2	0.1	Unsonicated	69.66	75.42	82.17	86.42	89.00
		Sonicated	75.42	79.58	89.05	93.16	94.75
	0.2	Unsonicated	82.19	86.72	91.08	91.17	93.17
		Sonicated	95.29	97.38	98.43	98.95	99.48

Adsorption Isotherms: Adsorption isotherms describe interaction with adsorbent materials and are very important for optimization of adsorption system. Equilibrium relationships between sorbent and sorbate are described by sorption isotherms, usually the ratio between the quantity sorbed and that remaining in the solution at equilibrium. There are several isotherm models available for analyzing experimental data and for describing the equilibrium of adsorption. Langmuir, Freundlich and Temkin isotherm equations were tested in our work. The Langmuir equation can be written as;

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \qquad (1)$$

where C_e (mg/L) is the equilibrium concentration of dye, q_e is the amount of dye adsorbed at equilibrium (mg/g), q_m and b are the Langmuir constants related to the capacity and energy of adsorption respectively and were calculated from the slope and intercept between $1/q_e$ and $1/C_e$ (Table.2). The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using separation factor or dimensionless constant R_L [21].

$$R_L = \frac{1}{1 + bC_o} \qquad (2)$$

where C_o (mg/L) is the initial concentration of dye, b is the Langmuir constant. The value of R_L indicates the type of Langmuir isotherm to be irreversible (R_L=0), favourable ($0 < R_L < 1$), linear or unfavourable (1 or > 1), respectively. In the present study, the R_L values were found to be between 0 and 1(Table.2) indicating a favourable adsorption.

Isotherm data were also studied with the Freundlich isotherm, which can be expressed by the following equation ;

$$\log q_e = \log K + n \log C_e \qquad (3)$$

where C_e is the equilibrium concentration of dye (mg/L), K and n are the Freundlich constants related to the capacity and intensity of adsorption respectively and were calculated from the slope and intercept of log q_e and log C_e (Table.2).

Temkin isotherm describes the behaviour of adsorption on heterogeneous surfaces and is given by equation (4)

$$q_e = a + b \log C_e \qquad (4)$$

where the two constants, a and b, calculated from the intercept and slope of the plot of q_e versus log C_e respectively (Table.2), are related to adsorption capacity and intensity of adsorption.

Table 2: Different Isotherm parameter for the adsorption of RR 141 at different experimental conditions

Different Adsorbents	Experimental condition	Langmuir Isotherm				Freundlich Isotherm			Temkin Isotherm		
		q_m	b	R_L	R^2	K	n	R^2	a	b	R^2
Banana Peel	Unsonicated	0.76	0.05	0.63	0.98	0.41	0.90	0.96	0.40	1.25	0.98
	Sonicated	0.95	0.10	0.45	0.97	0.57	0.56	0.97	0.55	1.05	0.97
Saw Dust	Unsonicated	2.12	0.09	0.48	0.98	1.18	0.70	0.99	1.15	2.55	0.99
	Sonicated	2.39	0.30	0.21	0.96	1.90	0.40	0.98	1.85	1.65	0.97
Orange Peel	Unsonicated	5.12	0.17	0.32	0.99	2.37	1.35	0.98	2.30	2.00	0.98
	Sonicated	5.40	1.27	0.06	0.99	2.71	0.30	0.98	2.65	2.45	0.99
TiO_2	Unsonicated	5.14	0.72	0.10	0.98	2.81	0.41	0.97	2.75	2.18	0.97
	Sonicated	5.46	1.75	0.04	0.99	2.90	0.23	0.96	2.85	2.20	0.96

Adsorption Kinetics : The kinetics of adsorption of dye on the adsorbent surface follows pseudo second order kinetic [22] which is expressed as

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \qquad (5)$$

where $h = kq_e^2$; k is the second order adsorption rate constant; q_e is the adsorption capacity calculated by pseudo second order kinetic model. q_e and k values shown in (Table.3) were determined from the slope and intercept of the plot of t/q_t vs t. The q_e values calculated from the pseudo-second order are in good agreement with the experimental value of q_e and the high R^2 (>0.993) for all sorption system indicated that the sorption kinetics could be best described by this model.

Table 3: Kinetic model and statistical parameters for adsorption of dye

Different Adsorbents	Experimental Conditions	**Pseudo second order**							
		q_e (cal) mg/L		**h (mg $g^{-1}sec^{-1}$)**		**k**		**R^2**	
		0.1gm	**0.2gm**	**0.1gm**	**0.2gm**	**0.1gm**	**0.2gm**	**0.1gm**	**0.2gm**
Banana Peel	**Unsonicated**	0.70	0.45	0.01	0.05	0.02	0.15	0.99	0.99
	Sonicated	0.80	0.60	0.05	0.10	0.10	0.25	0.99	0.99
Saw Dust	**Unsonicated**	1.30	0.85	0.07	0.05	0.04	0.09	0.99	0.99
	Sonicated	1.90	0.95	0.15	0.10	0.05	0.10	0.99	0.99
Orange Peel	**Unsonicated**	2.40	1.25	0.17	0.10	0.05	0.05	0.99	0.99
	Sonicated	2.50	1.30	0.20	0.15	0.03	0.10	0.99	0.99
TiO_2	**Unsonicated**	2.95	1.25	0.17	0.30	0.02	0.30	0.99	0.99
	Sonicated	3.10	1.35	0.18	0.65	0.01	0.35	0.99	0.99

Adsorption Mechanism: There are four main stages in the process of adsorption: (i) solute transfer from the bulk solution to the boundary film that surrounds the adsorbent's surface, (ii) solute transport from the boundary film to the adsorbent's surface, (iii) solute transfer from the adsorbent's surface to active intraparticular sites, and (iv) interactions between the solute molecules and the available adsorption sites on the internal surfaces of the adsorbent. One or more of these four steps controls the rate at which solute is adsorbed. The mechanism and rate controlling steps affecting the kinetics of adsorption were analysed by the Weber and Morris intra-particle diffusion and Boyd kinetic models.

The Intraparticle diffusion model [23] is expressed as:

$$q_t = k_p t^{1/2} + c \tag{6}$$

The Boyd kinetic model [24] is given as under;

$$Bt = -0.4997 - \ln(1-F) \tag{7}$$

where c and k_p, the intercept and intraparticle diffusion rate constant were evaluated from the linear plot of q_t vs $t^{1/2}$ (Table.4). F is the fraction of dye adsorbed at time t and can be expressed as $F=q_t/q_e$. q_t and q_e represent the amount of dye adsorbed at time t and at equilibrium respectively. According to these models, if the Intraparticle diffusion is the rate limiting step, then the plot of q_t vs $t^{1/2}$ and Bt vs t should be linear and pass through the origin.

In our studies, the plots of q_t vs $t^{1/2}$ and Bt vs t were linear but did not pass through the origin as predicted from intercept 'c' (Table.4) indicating that the adsorption process was controlled only by the film diffusion.

Table.4: Intraparticle diffusion and liquid film diffusion rate constants coefficients

Different Adsorbents	Experimental Conditions	Weber and Morris Intraparticles diffusion model						Boyd Kinetic Liquid film diffusion model			
		k_P		c		R^2		c		R^2	
		0.1gm	0.2gm	0.1gm	0.2gm	0.1gm	0.2gm	0.1gm	0.2gm	0.1gm	0.2gm
Banana Peel	**Unsonicated**	0.01	0.01	0.10	0.45	0.98	0.99	0.07	1.00	0.99	0.98
	Sonicated	0.02	0.02	0.70	1.00	0.98	0.97	1.45	1.01	0.99	0.98
Saw Dust	**Unsonicated**	0.03	0.04	0.85	0.90	0.97	0.98	0.50	0.85	0.99	0.97
	Sonicated	0.05	0.03	1.55	1.10	0.96	0.96	1.05	1.20	0.97	0.97
Orange Peel	**Unsonicated**	0.04	0.07	0.05	1.10	0.97	0.98	0.10	1.55	0.98	0.98
	Sonicated	0.03	0.03	0.03	1.35	0.97	0.98	1.08	1.90	0.95	0.95
TiO_2	**Unsonicated**	0.15	0.05	2.00	1.25	0.99	0.98	0.65	1.25	0.97	0.96
	Sonicated	0.25	0.01	2.15	1.45	0.97	0.98	2.45	2.35	0.96	0.99

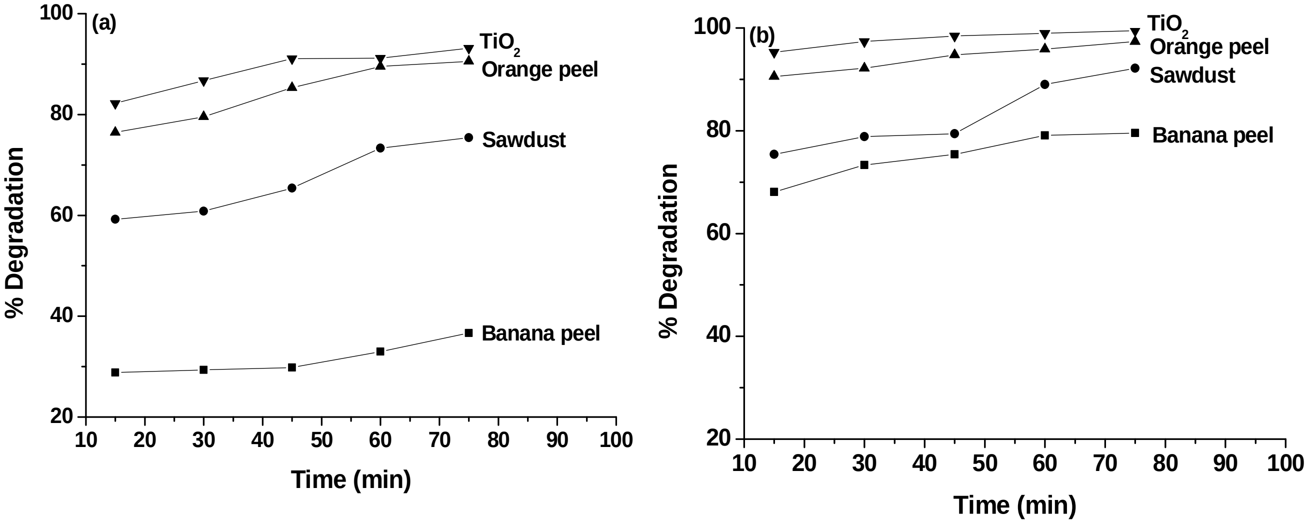
Structural Correlation For Adsorption : The chemical structure of the dye and adsorbents both influence adsorption rate on various adsorbents. In general, the adsorbents used in this study carry an overall (-) ve charge on their surface due to the presence of respective functional groups. The surface of TiO_2 nanoparticles dispersed in water is generally covered with hydroxyl group [25], whereas the main functional groups present in the saw dust are phenol and alcohol [26]. The surface of orange and banana peels are characterised by carboxyl and hydroxyl groups [27-28]. Thus these different functional groups, present on the surface of adsorbents, enable an interaction with the chromophores present in the dye. A negatively charged surface site on the adsorbent does not favour total adsorption of dye, with anionic functional group, due to the electrostatic repulsion. Therefore, lower adsorption of Reactive red 141 dye, on different natural adsorbents (Hardwood Saw dust, Banana peel and Orange peel), should be expected as a result of electrostatic repulsion between negative surface of adsorbent and negatively charged sulphonic groups in the dye. However, during this transitional adsorbed state, when dye molecules are adsorbed but still unstable, the cavitational field of ultrasound initiates the degradation process of dye molecules, resulting into the formation of cationic species such as $\Phi\text{-}NH_3^+$. The aqueous system is thus stabilised but only after the degradation of dye molecules has occurred. This causes a decrease in colour intensity.

Above mechanism is also supported with our experimental results of the maximum adsorption capacity. The maximum adsorption capacity measured for RR 141 on TiO_2, Orange peel, Hardwood Saw dust and Banana peel was 5.46 mg/L, 5.40 mg/L, 2.39 mg/L and 0.95 mg/L respectively. The relative adsorption capacity, therefore, varied in the order; $TiO_2 \approx$ Orange Peel > Hardwood Sawdust > Banana Peel and related to the type of functional groups present on the surface of adsorbent. Orange peel is found to be more effective compared than banana peel due to the presence of high amount of total dietary fibre [28] which have good water and oil holding capacity of 74.87% and 50.25% respectively. The results of this study indicate that natural materials can be successfully used as an efficient and cost-effective biosorbents for the removal of dye from aqueous solutions. Nevertheless, a better insight of the mechanism of degradation of RR141 would be possible only when the intermediate species are characterised through further studies later

CONCLUSIONS

After 75 min of ultrasonic treatment, the percentage removal of RR141, in the adsorbent load of 0.1gm/25 ml and 0.2 gm/25 ml respectively for different adsorbent has been found to be TiO_2, (94.75 and 99.48%), Orange Peel (92.75 and 97.38%) Hardwood Sawdust (65.42 and 92.17%) and Banana Peel (24.08 and 36.66%). The relative adsorbent capacity, therefore, varied in the order of $TiO_2 \approx$ Orange Peel > Hardwood Sawdust > Banana Peel.
However, the removal of dye was significantly enhanced in the presence of ultrasound with all adsorbents as shown in (Figure.1) and the decolourisation improved with increase in amount of respective adsorbents, under experimental conditions due to increased sorbent surface area and availability of more sorption sites resulting from the increased dose of the different adsorbents from 0.1 gm to 0.2 gm. The adsorption obeyed Langmuir, Freundlich and Temkin isotherms. The adsorption of dye on different adsorbents surface followed pseudo second order kinetics and Boyd kinetic plot confirmed that the external mass transfer was the slowest step in the adsorption process. The present work revealed that the TiO_2, orange peel and hardwood sawdust have the potential of being a promising material for the removal of dyes from aqueous solutions under ultrasonic conditions, where as banana peel was a rather poor adsorbent.

Figure.1: Percentage removal of RR 141 on 0.2 gm of adsorbent and C_0 = 12 ppm under Unsonicated (a) and Sonicated (b) conditions



APPLICATIONS

In this method TiO_2 and orange peel have been found to be most economical and effective adsorbents for removing RR 141 textile dye from effluents.

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