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Comparative Study of Adsorptive Removal of Red, Green and Violet Fabric Dyes from Water bodies Using Pomegranate peel

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ABSTRACT

The use of cheap and eco-friendly adsorbents studied as an alternative substitution of activated carbon for removal of a fabric dyes (red, green and violet) from waste water. Adsorbent prepared from pomegranate peel which is domestic waste, successfully used to remove the dye from waste water in a batch wise column. This study investigates the potential use of pomegranate peel pre-treated with nominal treatment method, for removal of dyes from simulated wastewater. Treated pomegranate peel used to adsorb dyes at varying adsorbent pH, contact time and dosages. The adsorption capacity of activated carbon prepared from pomegranate peel decreased in the order of red > green > violet. The sorption data were then correlated with Langmuir and Frenudlich isotherm models.

Keywords: Adsorption, Dyes, pH, Activated carbon, Isotherm.

INTRODUCTION

The usage of water is increasing day by day due to the increasing number of the industries. The textile industries are the major water consuming industries and a main source of environment pollution [1]. Dyes are widely used in industries such as textile, rubber, paper, plastic, cosmetic etc. Among these various industries, textile ranks first in usage of dyes for coloration of fiber [2]. Textile industries discharge a large quantity of highly colored effluent which is unscrupulously released into nearly land or rivers without any treatment which is increasing water pollution [3]. Dyes are sometimes being viewed as something other than ordinary chemical. But, actually it is an individual chemical itself like all other chemical such as sodium chloride, acetic acid and benzidine. They are similar in their reactions to some other chemicals, and distinctly different from other. Therefore, there is a possibility that they are toxic. This is because many dyes are made from known carcinogens, such as benzidine and other aromatic compounds which may show toxic or carcinogenic effects on living things [4].The three methods of treatment generally employed for dye removal are: Many techniques have been used to remove harmful dyes from colored waste water, such as filtration, flocculation, ion exchange, membrane separation, oxidation, advance oxidation and adsorption. Adsorption is the separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. In adsorption activated carbon is the most popular adsorbent, which is capable of adsorbing many dyes with high adsorption capacity. But it is expensive and the cost of regeneration are high because desorption of the dye molecules id not easily achieved [5]. availability of agricultural by- products makes them good sources of raw materials for the preparation of an activated carbon. Lots of studies have been carried out for the removal of different kinds of dyes using activated carbon derived from agricultural wastes [6].

The analysis and design of adsorption process requires the relevant adsorption equilibrium, which is the most important piece of information in understanding an adsorption process. Adsorption equilibrium provides fundamental physiochemical data for evaluating the applicability of adsorption process as unit operation. The two equilibrium relations which are often used to study the adsorption in research are Freundlich and Langmuir isotherm equations [7].The influences of various operating parameters on adsorption, such as the effect of pH, contact time, and adsorbent doses were studied. Pomegranate peel has been showed good capacity of adsorption of Red, Green and Violet fabric dyes in very short period of agitation.

MATERIALS AND METHODS

All the chemicals involved in the present investigation were obtained from PG lab, Chemistry department, SHIATS, Allahabad. The plant material was obtained from local market, Allahabad.

Preparation of stock solution: The fabric dyes were obtained from local market. Stock solution of 3 fabric dyes (Red, Green, and Violet) was prepared by dissolving 2.5 g of dye in 500 mL distilled water. Concentration of stock solution for each dye was 5 gm L^{-1}

Preparation of adsorbents: Pomegranate peel was washed in running tap water and then in distilled water, dried in an oven for 2 h, at 105^0 C and then grinded in a grinder and sieved to particle size range 0.3 - 0.6 mm. The dried powder was then treated with nitric acid (10% wt) for 24 h. It was carbonized at 500^0 C for one hour in muffel furnace. The carbonized powder was kept in an air tight container for adsorption study.

Batch adsorption experiment: The batch adsorption experiment was conducted with 30 ml of dye solution, the pH values of the dyes solution were adjusted with dilute 0.1 N HCl or 0.1N NaOH. Adsorbent Pomegranate peel, 0.6 g was kept in conical flask with 30 ml of pH maintained dye solution to study optimum removal of colour. The flask was kept on electrical shaker at 30^0 C at 150 r.p.m. for 60 min. The adsorbent was filtered using filter paper obtained filtrated was investigated using UV - Vis single beam spectrophotometer (Globe instrument microprocessor) at 715, 583, 441nm for Red, Green and Violet colour respectively.

Effect of pH: To study the effect of pH on effective removal of dye was studied at pH range between 4 to 10 by maintaining pH of dye solution with dilute 0.1 N HCl or 0.1 N NaOH by pH meter (Digital pH meter MK VI). In this parameter every 30 ml of dye solution with pH change solution at constant adsorbent dose 0.6 g, and constant shaking time of 60 min at 150 r.p.m. at room temperature was observed. The process was repeated for all colours.

Effect of time: To study the effect of time on effective removal of dye from the water samples, the following study was carried out. The effect of contact time was investigated for 15, 30, 45, 60, 75, 90, 105 min at constant pH 7 and constant adsorbent doses 0.6 g. The process was repeated for all three fabric dyes.

Effect of adsorbents doses: The effect of adsorbent doses on adsorption of dyes solution by pomegranate peel was investigated with adsorbent dose of 0.2, 0.4, 0.6, 0.8 g in 4 sets of 30 ml dye solution of Red, Green, and Violet colour with constant shaking time of 60 minute, pH 7, and room temperature at 150 r.p.m. The dye sample was filtered and analyzed in terms of absorbance with the help of UV-spectrophotometer at different wavelength for different dyes- red, green and violet.

Determination of % removal: Percent removal R (%) was calculated [8] as:

$$R\ (\%) = \{(c_i - c_f)/c_i\} \times 100 \quad \ldots\ldots (1)$$

The adsorption capacity q_e (mg g^{-1}) after equilibrium was calculated by mass balance relationship equation as follows:

$$q_e = (c_i - c_f)v/m \quad \ldots\ldots (2)$$

Where C_i and C_f are the initial and final dye concentrations in mg L^{-1} respectively, initially and at a given time t, respectively, v is the volume of solution in ml, m is weight of the adsorbent taken.

Adsorption isotherms: Adsorption isotherm, are the presentation of the amount of solute adsorbed per unit of adsorbent. Two commonly used adsorptive isothermal models, Langmuir and Freundlich equations, were used to evaluate the experimental data and are described as:

Langmuir Isotherm: This isotherm represents one of the first theoretical treatments of nonlinear sorption and suggested that uptake occurs on a homogenous surface by monolayer sorption with interaction between adsorption molecules.

$$q_e = q_{max} b c_f / 1 + b c_e \quad \ldots\ldots (3)$$

Where q_{max} (mg/g) and b is Langmuir constants related to adsorption capacity and the energy of adsorption respectively.Eq (3) is usually linearized to obtain the following from [12]

$$1/q_e = 1/c_f(1/q_{max} b) + (1/q_{max})$$

q_{max} and b were determined from the lineal plot of $1/q_e$ versus $1/c_f$.

Freundlich isotherm: This isotherm also considers monolayer sorption with a heterogeneous distribution of active sites of the sorbent [9].

$$q_e = k_f c_f^{1/n} \quad \ldots\ldots (4)$$

Where K_f stands for adsorption capacity and n for adsorption intensity. Logarithmic form of Eq (4)

$$\log q_e = \log (k_f c_f^{1/n}) \quad \ldots\ldots (5)$$

Where k_f and 1/n were determined from the linear plot of log (q_e) vs log (C_e).

RESULTS AND DISCUSSION

Effect of pH on adsorption: To study the effect of pH on dye colour removal capacity of pomegranate peel, colour removal was studied for pH ranging between 4 to 10 by maintaining pH of dye sample with dilute HCl and NaOH solution. The adsorption of dyes increased with increasing pH of the dye solution. Dye adsorption efficiency is affected by pH variation. The optimum pH for the adsorption of dyes was found to be in the range 7-8 for red, green, and violet dyes which is shown in fig 1 and table 1. This can be explained by considering the electrostatic attraction that exists between the negatively charged surface of the adsorbent and dye, a cationic dye. Lower adsorption at acidic pH was probably due to the presence of excess of H^+ ions competing with dye cation for adsorption sites. At alkaline pH, the number of positively charged sites decrease and the number of negatively charged sites increase which favours the removal of the cationic dye [10]. Table 1 show the result obtained effect of pH on red, green, and violet fabric dyes on all variable pH.

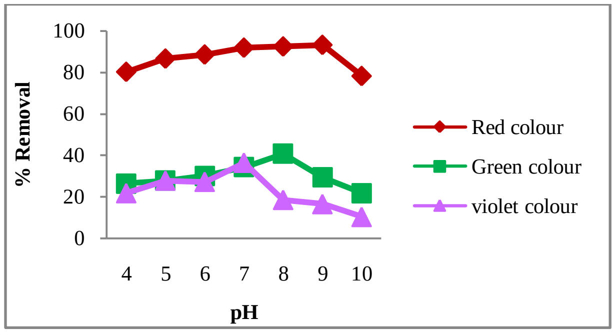

Fig 1: % Removal of dyes at different pH using Pomegranate peel

Table 1: Maximum removal of dyes at different pH

Adsorbents	Colour of dyes	Adsorbent dose (g)	Dye Solution(ml)	Time(min)	pH	Maximum (%) removal
Pomegranate peel	Red	0.6	30	60	7	93.134
	Green	0.6	30	60	8	40.62
	Violet	0.6	30	60	7	36.447

Effect of shaking time: The effect of contact time in the range 15 min to 105 min was studied at constant adsorbent dose 0.6 g in 30 mL of dye solution with pomegranate peel, at pH 7.0 and a temperature of 30^0 C. Pomegranate peel gave percent removal with shaking time for red, green, violet colour shown in fig 2 and table 2.

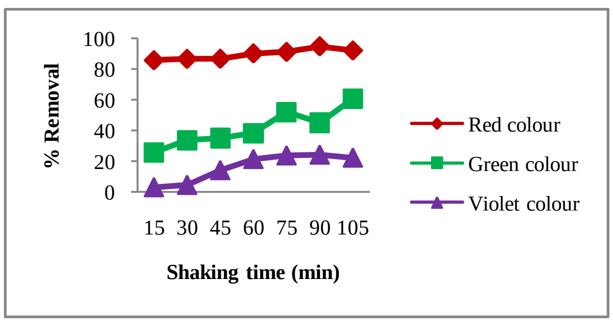

Fig 2: Removal of dyes at different shaking time using pomegranate peel.

Table 2: Maximum removal of dyes at different shaking time.

Adsorbents	Colour of dyes	Shaking time(min)	Solution(ml)	Adsorbent dose(g)	pH	Maximum (%) removal of dye
Pomegranate peel	Red	90	30	0.6	7	94.925
	Green	105	30	0.6	7	60.759
	Violet	90	30	0.6	7	24.41

In batch type adsorption systems, a monolayer of adsorbate is normally formed on the surface of adsorbent, and the rate of removal of adsorbate species from aqueous solution is controlled primarily by the rate of transport of the adsorbate species from the exterior/ outer sites to the interior site of the adsorbent particles [11]. Gradual change in adsorption at 15 min increase was observed in adsorption with increasing contact time up to 90 min for pomegranate peel, after which a maximum value of adsorption is attained. After this time, the amount of dye adsorbed was not significant, very small decreases in the amount of the dye adsorbed were observed, indicating to desorption process [9].

Effect of adsorbent dose: The result showed in table 3 and fig 3 that the percent adsorption and amount adsorbed was increased as the adsorbent doses were 0.2, 0.4,0.6 and 0.8 g with 30 mL of dye solution in orbital shaker at 30^0 C and 150 r.p.m. Removal of dyes by Pomegranate peel 86% on 0.2 g, 90% on 0.4 g, 91% on 0.6 g, 88% on 0.8 g for red colour ,17% at 0.2 g, 29% at 0.4 g, 30% at 0.6 g 33% at 0.8 g, for green colour, 7% at 0.2g, 12% at 0.4 g, 21% at 0.6 g, 20% at 0.8 g for violet colour adsorbent doses when shaking time is 60 min.

It is readily understood that the number of available adsorption sites and the surface area increase by increasing the adsorbent dose, it therefore, results in the increase of amount of adsorbed dye. After formation of equilibrium, there was observed a decrease in adsorption. This may be attributed to overlapping or aggrsegation of adsorption sites resulting in a decrease in total adsorbent surface area available to dye and as an increase in diffusion path length [12].

Table 3: Maximum removal of dyes at different doses.

Adsorbents	Colour of dyes	Adsorbent doses(g)	Solution(ml)	pH	Shaking time(min)	Maximum (%) removal
Pomegranate peel	Red	0.6	30	7	60	91.294
	Green	0.8	30	7	60	33.996
	Violet	0.6	30	7	60	21.57

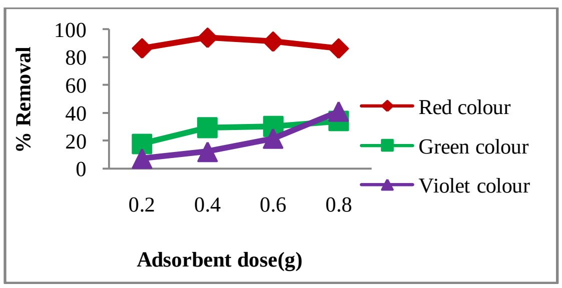

Fig 3: Removal of dyes with different doses using Pomegranate peel.

Adsorption Isotherm: In order to optimize the design of an adsorption system to remove the dye, it is important to establish the most appropriate correlation of the equilibrium data of each system. Equilibrium isotherm equations are used to describe the experimental adsorption data. The parameters obtained from the different models provide important information on the adsorption mechanisms and the surface properties and affinities of the adsorbent.The most widely accepted surface adsorption models for single-solute systems are the Langmuir and Freundlich models. The correlation with amount of adsorption and the liquid-phase concentration was tested with them. Linear regression is frequently used to determine the best-fitting isotherm, and the applicability of isotherm equations is compared by judging the correlation coefficients.

Langmuir isotherm: The theoretical Langmuir isotherm is valid for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Langmuir isotherm model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of surface [12]. Therefore, the Langmuir isotherm model was chosen for the estimation of the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. The Langmuir equation is commonly expressed as follows:

$$1/q_e=1/c_f(1/q_{max}b)+(1/q_{max})$$

q_{max} and b can be determined from the lineal plot of $1/q_e$ versus $1/c_f$.

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L which is defined by

$$R_L = 1/(1+b\ Ce).$$

The influence of isotherm shape on "favourable" or "unfavourable" adsorption has been considered. The R_L values indicate the type of the isotherm to be either unfavourable ($R_L >1$), Linear ($R_L = 1$), favourable ($0< R_L <1$) or irreversible ($R_L = 0$). In the present experiment the results were found for R_L for pomegranate peel in between 0.74714 to 0.96234 which clearly indicate the adsorption was favourable. C_e (equilibrium concentration) for all dyes is 0.34328, 2.96866 and 3.17766 for red, green and violet colour respectively with respect to pH.

Table4: Value of $1/q_e$, $1/C_e$, log q_e and log C_e with pH

Colour of dyes	$1/q_e$	$1/C_e$	log q_e	log C_e
Red	0.00429	2.19307	2.21696	0.23146449
Green	0.00985	0.33685	1.860239	0.5502687
Violet	0.01077	0.3147	1.37936	0.6552287

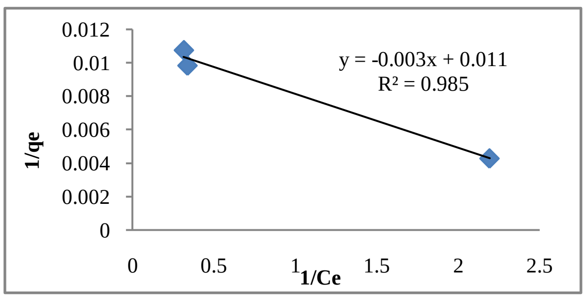

Fig 4 Langmuir isotherm for pomegranate peel

For dye removal on pH: Fig 4: shows the plot of 1/qe versus 1/ce for the adsorption of dyes onto pH at constant dose, temperature and shaking time according to the linear forms of Langmuir isotherm.

Freundlich Isotherm: The Freundlich equation was employed for the adsorption of dye on the adsorbent. The Freundlich isotherm was represented by:

$$\log q_e = \log (K_f Ce^{1/n}) \quad \textbf{or} \quad \log q_e = \log K_f + 1/n \log Ce.$$

Where q_e is the amount of dye adsorbed (mg g^{-1}), Ce is the equilibrium concentration of dye in solution (mg L^{-1}), and K_F and n are constants incorporating the factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plot log qe versus log Ce. Fig 5and table 5 shows that the adsorption of dye obeys the Freundlich adsorption isotherm. The values of n >1 indicate favourable adsorption conditions [9]. In this experimental value of n > 1which is indicating that favourable freundlich adsorption isotherm. The value of linear R^2 coefficient was high (> 0.9927) for pomegranate peel.

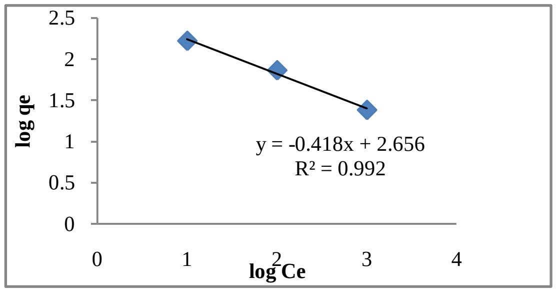

Fig 5: Freundlich isotherm for pomegranate peel adsorption of dye with pH.

Table 5: Langmuir and Freundlich equation for adsorption of dyes with pH

Adsorbents	Colour of dyes	Langmuir				Freundlich		
		Qmax	R_L	K_L	R^2	K_F	Value of 'n'	R^2
Pomegranate peel	Red	232.836	0.96234	0.0114	0.9854	0.977	2.3877	0.9927
	Green	101.567	0.74714					
	Violet	91.117	0.73408					

Adsorption Isotherm with respect to dose: C_e (equilibrium concentration) for all dyes is 0.43532, 3.49307and 3.9215for red, green and violet colour respectively with respect to dose (Tables 6,7 and Figs. 6,7) .

Table 6: The value of $1/q_e$, $1/C_e$, log q_e, and log C_e for all three dyes with dose

Colour of dyes	$1/q_e$	$1/C_e$	log q_e	Log C_e
Red	0.00438	2.29716	2.35838	0.361191379
Green	0.01177	0.30301	1.92937	0.518536
Violet	0.01853	0.61387	1.73082	0.5937179

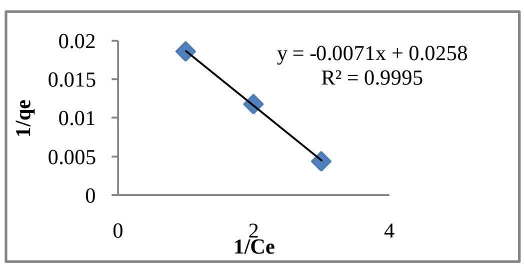

Fig 6: Langmuir isotherm for dye removal on dose

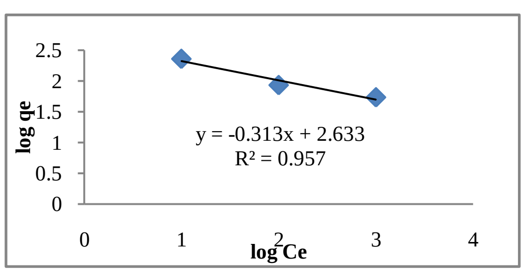

Fig 7: Freundlich isotherm for dye removal on dose

Table 7: Langmuir and Freundlich equation for adsorption of dyes with dose.

Adsorbent	Colour of yes	Langmuir				Freundlich		
		Qmax	R_L	K_L	R^2	K_F	Value of 'n'	R^2
Pomegranate peel	Red	228.384	0.9889	0.0258	0.9995	0.9684	3.1867	0.9572
	Green	84.991	0.92154					
	Violet	53.805	0.90807					

Adsorption Isotherm with respect to shaking time: C_e (equilibrium concentration) for all dyes is 0.25373, 1.29898 and 3.77949 for red, green and violet colour respectively with respect to shaking time **(**Tables 8,9 and Figs 8,9).

Table 8: The value of $1/q_e$, $1/C_e$, log q_e, and log C_e for all three dyes with shaking time

Colour of dyes	$1/q_e$	$1/C_e$	log q_e	Log C_e
Red	0.00421	3.9412	2.375322	0.5959281
Green	0.00658	0.26459	2.1815535	0.11360246
Violet	0.01639	0.50968	1.785511	0.577433

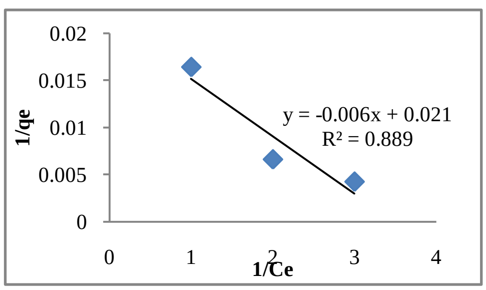

Fig8: Langmuir isotherm for dye adsorption with shaking time

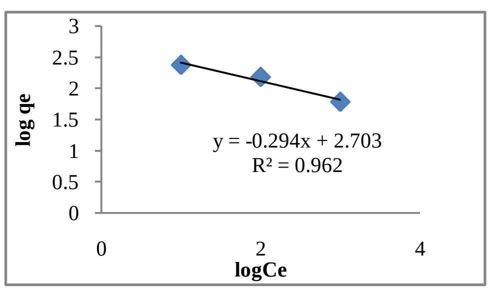

Fig9: Freundlich isotherm for dye adsorption with shaking time

Table 9: Langmuir and Freundlich equation for adsorption of dyes with respect to shaking time.

Adsorbents	Colour of dyes	Langmuir				Freundlich		
		Qmax	R_L	K_L	R^2	K_F	Value of 'n'	R^2
Pomegranate peel	Red	237.3135	0.92289	0.0061	0.8894	0.9946	3.3909	0.9623
	Green	151.8985	0.9442					
	violet	61.0255	0.98931					

APPLICATIONS

This study on the potential use of pomegranate peel pre-treated with nominal treatment method, for removal of dyes from simulated wastewater is useful as adsorbents for removing red, green, violet fabric dyes.

CONCLUSIONS

The removal of colour from aquatic system caused by presence of synthetic dyes is extremely important from the environmental viewpoint because most of these dyed are toxic, mutagenic and carcinogenic. Possible method for dye removal from textile effluent includes chemical oxidation, adsorption, coagulation, electro dialysis etc. Among these mesthods, adsorptions are the most versatile and widely used method because of its low cost and ease of operation. In the present study, the use of low cost, abundantly available, highly efficient and eco friendly adsorbents, activated carbon prepared from chemically treated pomegranate peel have been reported as an alternative to the current expensive methods of removing of dyes from wastewater. The effects of different variables, pH, shaking time and adsorbent doses were investigated and optimum experimental conditions were ascertained. The Langmuir and Frendlich model have been given a conformity result. From the result of the present study, it is concluded that, the adsorption process is a very effective process for the removal of dyes from water bodies.

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