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Adsorption of congo red dye from aqueous solution onto a low-cost natural orange peel and groundnut shell powder

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ABSTRACT

Color components present in waste water are hazardous to environment. More research work is needed to remove the dye components present in wastewater. The adsorbents used for the waste water treatment should be eco-friendly. So, Orange peel and Groundnut shell powder are used as natural adsorbents for the removal of Congo red from aqueous solutions which is a carcinogenic compound from textile industry. The effects of Contact time, Initial dye concentration and Adsorbent dosage are studied in batch mode. At different adsorbent dosages(0.5g/100ml,0.75 g/100ml,1.0 g/100ml,1.25g/100ml and 1.5 g/100ml) the concentrations of the dye solutions are measured at different contact times (2hrs,4hrs,6hrs,24hrs and 30hrs) for different concentrations of dye(100ppm,150 ppm,200 ppm,250 ppm and 300ppm). Kinetic Modeling is performed using different Kinetic models like Pseudo 1st order model, Pseudo 2nd order model and Elovich model.

Keywords: Congo red, Orange peel, Groundnut shell, Adsorption.

INTRODUCTION

In India there are many textile industries and the production of cloth takes place from both cotton and synthetic fibres. These textile industries require large amount of water for the processes and so waste water discharged from industry will be polluted. The visible pollution includes colour and this persists in water streams. Dyes generally are difficult to be decolourised when it mixes with water and are hazardous [1]. Environmental problems are being faced due to the release of these dyes in water streams. Many of the dyes are toxic to humans also. Presence of dye in water affects aquatic life due to their intense colour, so that reduction of sunlight transmission into water takes place [2]. Majority of the dyes can be detected visually even at the concentration of less than 1 mg/l. Due to the complex aromatic structure, dyes become more stable and less biodegradable. The contaminants that come out from dyeing industry include mainly suspended solids, high in both BOD and COD, as well as high pH and strong colouration [3].

Congo red dye is a sodium salt of 3, 3`-([1,1`-biphenyl]-4,4`-diyl)bis(4-aminonapthalene-1-sulfonic acid) (formula: $C_{32}H_{22}N_6Na_2O_6S_2$) and its molecular weight is 696.66 g/mol [4]. Congo red dye is water soluble and reactive dye used in textiles and medicine [5].

For removing dyes from effluents of industry, some biological and physical or chemical methods have been used such as coagulation, flocculation, ozonation, electrochemical oxidation, membrane separation, microbial oxidation and combination treatment. Adsorption is one of the best methods employed since it is simple to design and inexpensive compared to other methods [6].

The groundnut belt in south India generates sizeable quantities of crop residue that can be recycled. Such recycle helps in improving soil fertility and productivity of crops. Groundnut shell contain sizeable amounts of organic compouds and other nutrients [5].

The groundnut haulms and husks contain on average 1-1.8% N, 0.3-0.5% P, 1.1-1.7% K. High amounts of NPK could be recycled in to groundnut eco system through residues. Groundnut shell is recycled to improve soil fertility, soil structure and its quality. Most importantly groundnut shells induced microbial population and nutrient transformations in soil. Groundnut shell can be used for low strength application in the building industry most likely as a particle board, roofing sheet and panel board. This material is light in weight and resistant to corrosion. The addition of fillers to the shell, e.g. Wood dust or calcium carbonate would improve the composite adhesion; likewise reduction of high grams of Urea in the solution to appropriate ratio may improve adhesion greatly, hence increasing the strength of the composite [7].

During the arid months the cattle graze on the dry grass. Their diet includes various agricultural wastes including maize and groundnut stover. Millet straw is another type that is used for the purpose. Agricultural wastes are given to the livestock [8]. Orange peel is an edible part of orange specially where there is demand for the nutrient and waste minimization. But higher concentration of pesticides limits the consumption. Orange peel essentially consists of low molecular weight hydrocarbons. The functional groups attached to these hydrocarbons make them a viable adsorbent for colour removal in aqueous solutions. In the current study, Congo red dye is adsorbed on orange peel and groundnut shell powder (a low cost adsorbent) was studied and kinetic and mechanisms were evaluated.

MATERIALS AND METHODS

Congo red is purchased from Himedia Laboratories Pvt.Ltd (Chennai, Tamilnadu, India). Groundnut was collected from a local oil mill near Thanjavur, Tamilnadu, India. Orange peel was collected from a fruit mart at Thanjavur, Tamilnadu, India.

1. METHODOLOGY

100ml of Congo red dye solution of known concentration is prepared in 5 different conical flasks. Dried orange peels and groundnut shells were cut into small pieces and different weights ranging from 0.5g to 1.5g are placed in 5 different conical flasks. Conical flasks are placed on a shaker. For every 2 hours samples from 5 different flasks are collected and are centrifuged at 8000 rpm for 5 minutes. Readings were taken at regular intervals of time. OD values are measured using UV absorbance of 500 nm. The same procedure is repeated for different concentrations of dye. Various concentrations of the dye are found from the standard chart. The different concentrations done are 100, 150, 200, 250, 300 ppm [10, 11].

3.1 Adsorption isotherm and kinetic studies

Often the amount of adsorption is measured as a function of concentration and the result expressed as an adsorption isotherm. There are many empirical adsorption isotherms, but the most commonly used are the Langmuir and Freundlich adsorption isotherms [12].The monolayer adsorption of adsorbate on adsorbent is explained by Langmuir isotherm. The process of adsorption is not a function of adsorbed species on the nearby site.

Langmuir isotherm:

$$\theta = \frac{q_e}{q_m} = \frac{bC_e}{1+bC_e} \qquad \text{......... (1)}$$

C_e, equilibrium concentration of adsorbent
q_e, amount adsorption at equilibrium.
q_m, maximum adsorption capacity,
b, equilibrium constant.

Freundlich:
$q_e = K_f C^n$ .... (2)

K_f and n are Freundlich constants

Following models are used to fit the data obtained from the adsorption of Congo dye on the orange peel and groundnut shell powder. Lagergren proposed a model for adsorption of oxalic acid on charcoal (liquid solid phases) by first order rate kinetics given in the equation 3 [13]. Pseudo-second order rate equation was given by the Eqn. 4 which is based on the solute concentration and adsorption capacity. Eqn.5 describes the Elovich's model for the solid -solute adsorption [14].

Pseudo first order rate equation:

$$\log(q_e - q_t) = \log q_e - (k_1 / 2.303)t \qquad \text{............ (3)}$$

Where q_t and q_e (g/g) are the amount adsorbed at time t and at equilibrium, and k_1 (min^{-1}) is the rate constant of the pseudo first order adsorption process

Pseudo second-order kinetics:

$$t/q_t = 1/h + \left(1/q_e\right)t \qquad \text{................. (4)}$$

$h=k_2q^2_{e,}$

k_2 is rate constant

Elovich's equation:

$$\frac{dq}{dt} = ae^{-\alpha q} \qquad \text{................ (5)}$$

Where, q represents the amount of solute adsorbed at time t, a the desorption constant, and α the initial rate of adsorption.

Linear form:

$$q = \left(\frac{2.3}{\alpha}\right)\log(t + t_0) - \left(\frac{2.3}{\alpha}\right)\log t_0$$

With $t_0 = \frac{1}{\alpha a}$

RESULTS AND DISCUSSION

Adsorption isotherms for the Congo red onto orange peel and groundnut shell were investigated.

As shown in Fig.1, Langmuir type isotherm is the best fit for the adsorption behaviour of Congo red. q_{max} values of 97 mg/g.l (b = 0.118) was obtained for the adsorption of dye. For the dye adsorption on groundnut shell shown in Fig. 2, the adsorption data is fitted (n = 2.85 and K_F = 0.006) and this shows that adsorption of Congo red is heterogeneous (Freundlich isotherm) rather than monolayer interaction [15].

The adsorbents used in our study are orange peel and groundnut shell powder. The dye that is targeted to remove was the diazo anionic dye, the Congo Red. The adsorption process must be effective. This can be done by varying the parameters. The initial value must be brought down to permissible limits before discharging into the environment [16]. The models that are used were pseudo first order model, pseudo second order model and Elovich model. From the Table.1 and Table. 2 Elovich model can be used to describe the sorption process satisfactorily. R^2 values for all the models for different concentrations of the dye and different adsorbent dosages are calculated. It can be concluded that this model suits well for the given data. For adsorption using orange peel, Elovich model suits best and adsorption using groundnut shell, again Elovich model suits best. We have obtained maximum R^2 values for the Elovich model for different concentrations for both the adsorbents, orange peel and groundnut shell powder. Therefore we can say that adsorption mechanism suits best for the Elovich model.

Table.1. Comparison of R^2 values from different models for orange peel

Concentration(ppm)	Dosage(g)	Pseudo 2nd order model	Elovinch model	Pseudo 1^{st} order model
100	0.5	0.594	0.97	0.822
	0.75	0.908	0.879	0.8894
	1	0.524	0.988	0.9242
	1.25	0.552	0.99	0.7922
	1.5	0.573	0.963	0.9251
150	0.5	0.975	0.838	0.6447
	0.75	0.611	0.978	0.6504
	1	0.956	0.868	0.6738
	1.25	0.599	0.858	0.6644
	1.5	0.947	0.865	0.671
200	0.5	0.659	0.821	0.6338
	0.75	0.656	0.798	0.6275
	1	0.652	0.817	0.6621
	1.25	0.656	0.818	0.6622
	1.5	0.588	0.804	0.6448
250	0.5	0.817	0.808	0.6221
	0.75	0.808	0.8032	0.6203
	1	0.839	0.815	0.6221
	1.25	0.722	0.792	0.6437
	1.5	0.514	0.801	0.6162
300	0.5	0.931	0.77	0.6061
	0.75	0.521	0.769	0.6074
	1	0.489	0.768	0.619
	1.25	0.435	0.772	0.6135
	1.5	0.635	0.803	0.6256

Table.2. Comparison of r^2 values from different models for groundnut shell

Concentration(ppm)	Dosage(g)	Pseudo 2nd order model	Elovich model	Pseudo 1st order model
100	0.5	0.58	0.878	0.6912
	0.75	0.557	0.9337	0.7715
	1	0.615	0.9943	0.9806
	1.25	0.653	0.9738	0.9195
	1.5	0.782	0.937	0.7245
150	0.5	0.875	0.959	0.8102
	0.75	0.843	0.9416	0.978
	1	0.796	0.8944	0.9708
	1.25	0.869	0.906	0.8955
	1.5	0.868	0.845	0.8356
200	0.5	0.874	0.928	0.7223
	0.75	0.861	0.956	0.8648
	1	0.811	0.929	0.9191
	1.25	0.883	0.944	0.9525
	1.5	0.879	0.921	0.8354
250	0.5	0.632	0.892	0.9752
	0.75	0.668	0.988	0.9548
	1	0.815	0.977	0.8686
	1.25	0.879	0.9766	0.8754
	1.5	0.874	0.987	0.9336
300	0.5	0.626	0.761	0.8499
	0.75	0.805	0.898	0.886
	1	0.811	0.984	0.9427
	1.25	0.888	0.972	0.8658
	1.5	0.879	0.972	0.9726

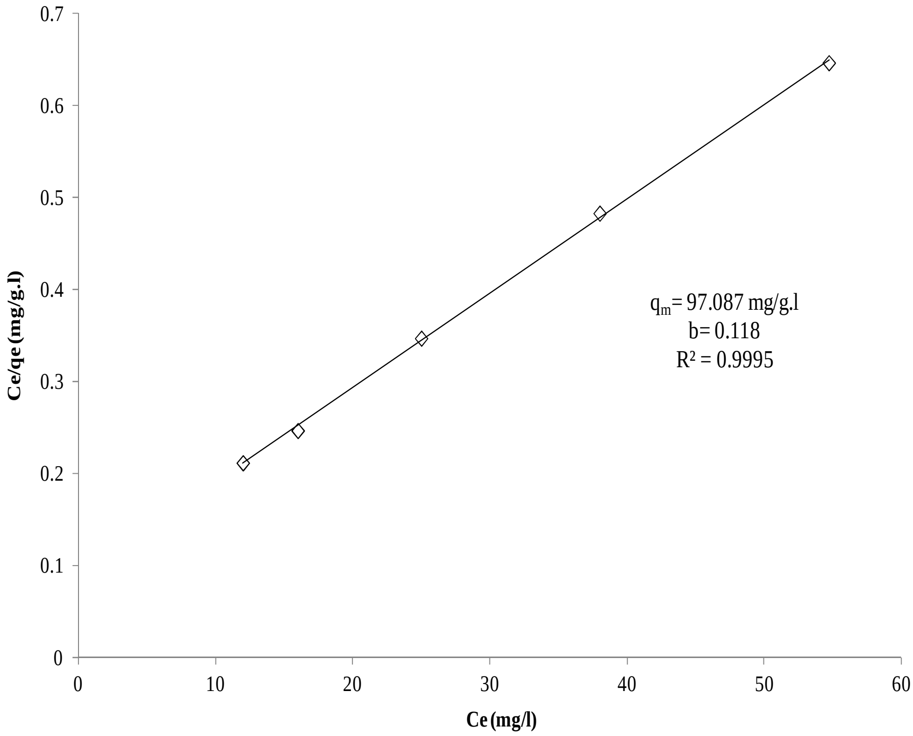

Figure.1. Langmuir plots for the adsorption of congo red onto orange peel

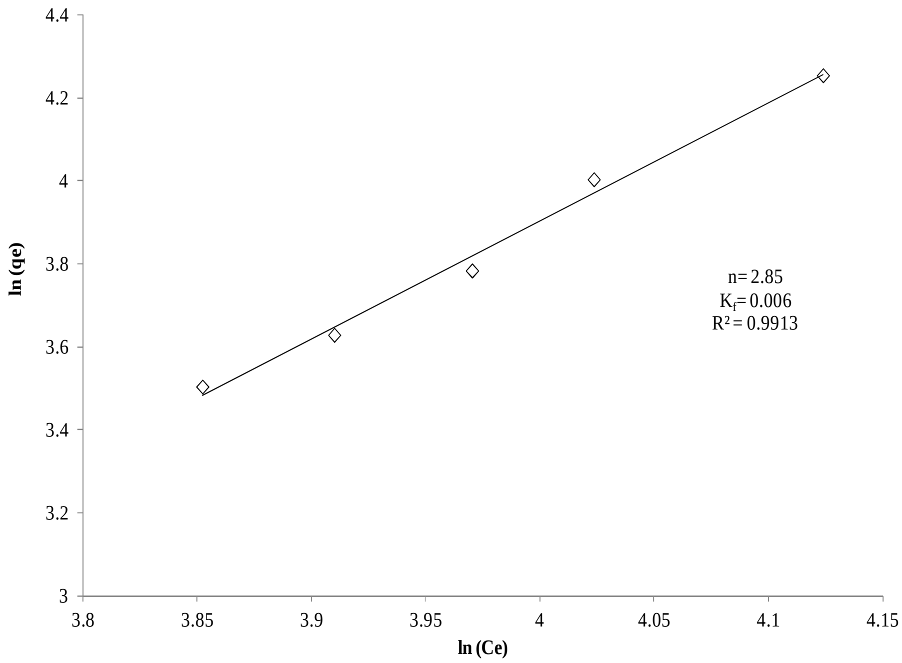

Figure.2. Freundlich plots for the adsorption of Congo red onto groundnut shell

CONCLUSION

The interactions involved in this experiment obeys surface phenomenon. The interaction is between three components. The reaction is involved between the adsorbent, adsorbate and the solvent. The major contribution is due to the interaction affinity between the adsorbent and adsorbate of the system. The results of this study indicate that orange peel and groundnut shell powder is a naturally abundant adsorbent which can be successfully used as a source for the removal of Congo red aqueous solutions. The behaviour of orange peel and groundnut shell powder in the adsorption of the Congo red show that the experimental results were well fitted with the Langmuir isotherm and Freundlich isotherm.

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