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Adsorption of Fast Green on to Coffee Husk

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Abstract:
In the present study, agricultural waste coffee husk were used for the adsorption of the dye fast green. The operating variables studied were initial concentration, initial solution pH, adsorbent dosage and contact time. Experimental equilibrium data were fitted to Freundlich and Langmuir isotherms. The kinetics of fast green onto coffee husk was found to follow a pseudo first order kinetics. The maximum adsorption of fast green was mg/g of the adsorbent respectively. The Fourier transformed infrared spectroscopy reveals that –OH, C=O and C-O groups are involved in the adsorption process. The optimum pH for the adsorption of fast green was 2. Characterization of the coffee husk shells showed that the relative percentage of protein is very less making it an excellent adsorbent for the removal of dyes from wastewater effluents.

Keywords: *Coffee husk, fast green, adsorption, isotherm.*

Introduction:

Dyes have long been used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries. Colour stuff discharged from these industries poses certain hazards and environmental problems. These coloured compounds are not only aesthetically displeasing but also inhibit sunlight penetration into the stream and affecting aquatic ecosystem. Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade (Bhattacharya and Sharma, 2005). Furthermore, many dyes are toxic to some microorganisms and may cause direct destruction or inhibition of their catalytic capabilities.

Textile industry use dyes and pigments to colour their product. There are more than 100,000 commercially available dyes with over 7×10^5 tonnes of dyestuff are produced annually. Many types of dye are used in textile industries such as direct, reactive, acid and basic dyes. There are various conventional methods of removing dyes including coagulation and flocculation, oxidation or ozonation and membrane separation (Aksu, 2005). These methods are not widely used due to their high cost and economic disadvantage. The main focus of this study was to evaluate the biosorption capacity of a novel, low cost, and renewable biomass, coffee husk for the removal of fast green. In a tropical country like India, coffee husk is found in plenty and is discarded as waste, as they have very less calorific value.

Objectives:

The objectives of the study are:

- Evaluate the biosorption capacity of coffee husk for the removal of fast green
- To study the effects of pH, contact time, initial dye concentration and biomass dosage on the biosorption capacity.
- Use of equilibrium models to fit the experimental data.

Review of Related Literature:

Several research works has been performed to search for efficient and low-cost materials to remove methylene blue and other basic dyes from aqueous solution, including rice husk (Vadivelan and Kumar, 2005) beech sawdust (Batzias and Sidiras, 2004), agro-industry wastes (Garg *et al*., 2004) and activated carbon from date pits (Abdulkarim *et al*, 2002). However, as the adsorption capacities of the above adsorbents are not large, new absorbents are still under development.

Research Methodology:

Biomass and dye solution preparation: The coffee husk (CH) were collected from dehulling unit and were washed extensively in running tap water to remove dirt and other particulate matter. This was later subjected to colour removal through washing and boiling in distilled water repeatedly. Subsequently the husks were oven dried at 105°C for 24 hours, stored in a desiccator and used for biosorption studies in the original piece size. Fast green has been used as dye in the present study. Stock solutions were prepared by dissolving accurately weighed samples of dye in distilled water to give a concentration of 1000 mg/L and diluting when necessary. Initial pH was adjusted by adding dilute solutions of HCl or NaOH.

Batch adsorption experiments: Batch adsorption studies were conducted in a routine manner. 250 ml flasks containing 100 ml of the dye solution was contacted with the predetermined amount of the coffee husk at equilibrium time. The flasks were agitated at a 120 rpm constant shaking rate to ensure that equilibrium is achieved. The dye solution was separated from the biosorbent using Whatmann No.1 filter paper. Adsorption uptake values were determined as the difference between the initial dye concentration and the one in the supernatant. All the experiments were carried out in duplicates and the average values were used for further calculations.

Analysis of the dyes: The concentration of the unadsorbed fast green in the sorption medium was measured colorimetrically using a spectrophotometer. The absorbance of the colour was read at 620 nm.

Findings and Discussion:

Characterisation of coffee husk: The carbon, hydrogen and nitrogen content of the husk showed very low percentage of nitrogen (0.63) in comparison to the carbon quantities (45.33%). This indicates that few nitrogen containing compounds are involved in the adsorption of dyes. A relatively larger percentage of hydrogen (6.21%) in comparison to nitrogen compounds indicates that carbon-hydrogen groups might be available for adsorption of metals and dyes. The relatively low percentage of nitrogen shows that very less percentage of protein might be present in the husks. This is advantageous over protein rich adsorbents since proteinious materials are likely to putrefy under moist conditions

FT-IR spectra of the coffee husk in the range of 400-4000 cm^{-1} were taken in order to obtain information on the nature of functional groups on the husk and dye interaction. It exhibits absorption bands at 3412, 2921 - 2851, 1733 and 1652-1512 cm^{-1}, which indicate the presence of –OH, -CH, C=H and C=O groups respectively.

Determination of optimum biosorption conditions:

Effect of initial pH: Initial pH is one of the most important environmental factors influencing not only site dissociation, but also the solution chemistry of the dyes: hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, precipitation are strongly influenced by pH and, on the other side, strongly influence the speciation and the adsorption availability of the dyes. The effect of initial pH on the biosorption of fast green is presented in Figure. 1. Fast green**,** an anionic dye showed maximum adsorption in the pH of 2. The percent removal of fast green decreased with increase in initial pH. In highly acidic media the adsorbent surfaces are highly protonated (positively charged) and favour the uptake of negatively charged dye – fast green. With increase in the initial pH of the dye, the degree of protonation of the adsorbent surface decreases gradually. Namasivayam and Yamuna, 1992 have reported the percent adsorption of congo red (anionic, direct dye) decreased with increase in pH. The anionic dyes namely amaranth, fast green and sinsset yellow was maximally adsorbed by peanut hull at pH 2.0 (Gong et al, 2005).

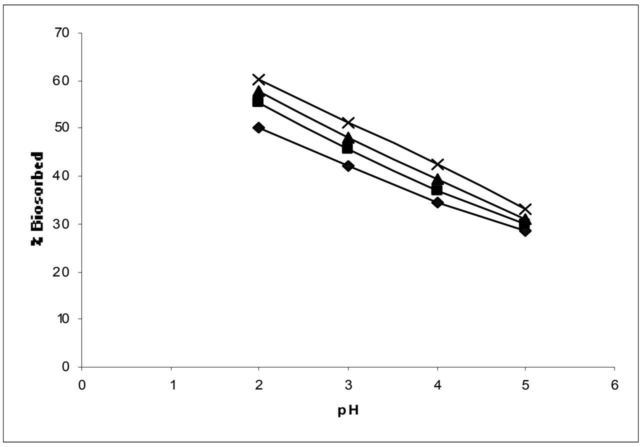

Figure. 1: Effect of pH on the fast green adsorption respectively by coffee husk(♦ 10 mg/L ■ 20 mg/L ▲50 mg/L x 100mg/l)

Effect of adsorbent dosage: The biosorption of fast green by coffee husk was studied at various biosorbent concentrations ranging from 0.5 to 5 mg/L. The percentage removal of the dye increased with increase in the sorbent dosage (Figure. 2). The results revealed that the colour removal increased with increase in adsorbent dosage upto 1 g l^{-1} and then it remained almost constant. Increase in the percentage of dye removal with adsorbent dosage could be attributed to an increased in the adsorbent surface area, which increased the availability of more adsorption sites. In the further experiments the adsorbent dosage was fixed at 1 g l^{-1} for adsorption of fast green.

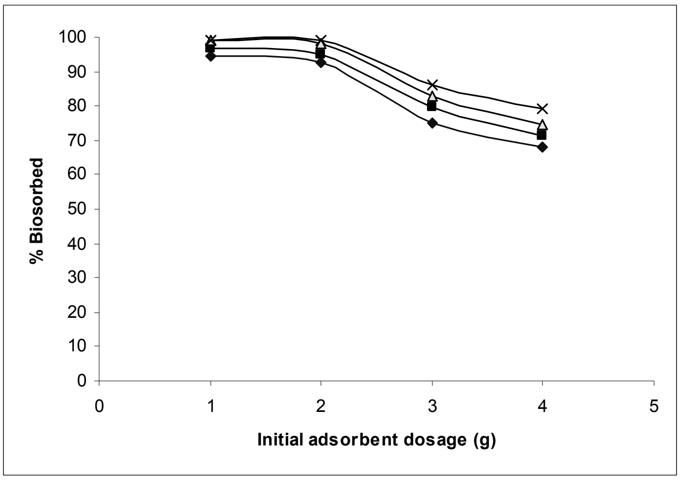

Figure. 2: Effect of adsorbent dosage on adsorption of fast green respectively by tamarind pod shells (♦ 10 mg/L ■20 mg/L ▲50 mg/L x 100mg/l)

Effect of contact time: The uptake of fast green by coffee husk increased with the increase in contact time and it remained constant after an equilibrium time as shown in Figure. 3. The percent dye removal at equilibrium time decreased with increase in dye concentration, although the amount of dye removed increased with increase in initial dye concentration. It is clear that the percentage removal of dyes depends on the initial concentration of the dye. The time taken to attain equilibrium was less than 100 minutes.

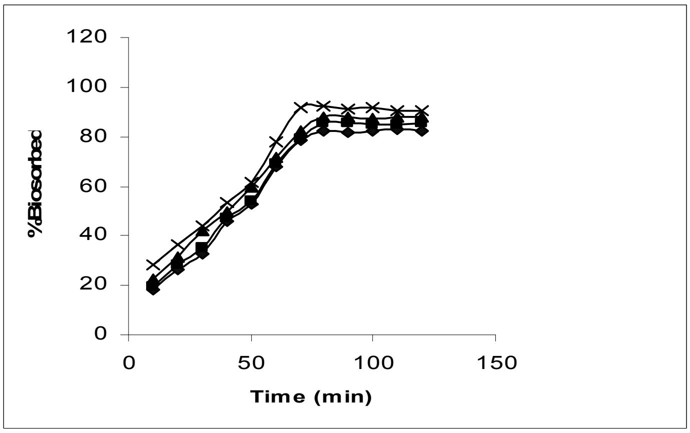

Figure. 3: Effect of contact time on the adsorption of fast green by coffee husk (♦ 10 mg/L■ 20 mg/L▲50 mg/L x 100mg/L)

***Isotherm modelling*:** In order to optimize the design of a sorption system to remove dyes from aqueous solutions, it is important to establish the most appropriate correlation for the equilibrium curves. The isotherms data were analyzed using two of the most commonly used equilibrium models, Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1906) isotherm models (Fig 4 & 5). The mathematical expressions are given by Equations 1 and 2, respectively, as follows:

$q = q_{max}\, b\, C_{eq} / 1 + b\, C_{eq}$ ....(1)

$q = Kf\, C_{eq}^{1/n}$ .... (2)

The calculated isotherm constants given in Table 1 were evaluated from the linear plots represented by Equations 3 and 4, respectively for Langmuir and Freundlich isotherms.

$C_{eq}/q = 1/q_{max}.b + C_{eq}/ q_{max}$ ………………… (3)
$\ln q = \ln K_f + 1/n \ln C_{eq}$……………………..….... (4)

The best-fit equilibrium model was determined based on the linear squared regression correlation coefficient R^2. From Table 1, it was observed that the equilibrium sorption data were very well represented by Langmuir isotherms followed by the Freundlich model with high correlation coefficients. Hence, the best fit of equilibrium data in Langmuir isotherm expressions confirm the monolayer coverage process of fast green by coffee husk. Furthermore, the value of Freundlich exponent n in the range of 1–10, indicates a favourable adsorption (Ho and McKay, 1998). Also, high adsorption capacity (Table 2) indicates the strong electrostatic force of attraction between dye molecules and biosorbent binding-sites (Kaewsarn and Yu, 2001).

Table 1: Sorption isotherm constants and coefficients of determination for adsorption of dyes by Tamarind pod shells

	Langmuir equation			**Freundlich equation**		
	q_{max} (mg/g)	b (l/mg)	R^2	K_F (mg/g)	n	R^2
Fast green	96.6	0.01	0.97	1.446	1.82	0.99

Table 2: Comparison of adsorbent capacities of low cost adsorbents

Adsorbent	**Adsorbate**	q_{max} **(mg/g)**	**References**
Coir pith carbon	Congo Red	6.72	Namasivayam and Kavitha, 2002
Spent brewery	Acid Orange 7	30.5	Silva *et al.*, 2004
Rice husk	Methylene Blue	40.6	Vadivelan and Kumar, 2005
Powdered peanut hull	Amaranth	14.90	Gong *et al.*, 2005
	Sunset Yellow	13.99	
	Fast Green FCF	15.60	
Bagasse fly ash	Orange G	18.8	Mall *et al.*, 2006
	Methyl Violet	26.2	
Coffee husk	Fast green	96.6	This study

Mechanism of adsorption of dyes: Based on the results obtained, the mechanism of adsorption of methylene blue and amaranth is discussed below.

Adsorption of Fast green: When dye anions (fast green) are introduced in the system containing adsorbents, they may be adsorbed onto the positively charged surface in two ways (Sharma and Forster, 1994):
The first way: $C_xOH_2^{2+} + 2\ Dye^- \rightarrow C_x\ OH_2\ dye^+$……………….. (8)

This reaction does not account for the change in pH of the solution after dye adsorption compared to the blank i.e. in the absence of dye anion.

The second way: $C_xOH^+ + Dye^- \rightarrow Cx\ O\ (Dye)^+ + OH^-$ ………. (9)

This accounts for the increase in pH of the solution after dye adsorption.

Conclusion:

The results of the present investigation show that coffee husk is an effective adsorbent for the removal of fast green from aqueous solutions, and its adsorption capacity is quite comparable to the other adsorbents reported in literature. Coffee husk was selected for studying adsorption due to its availability in India, as well as to assess the possibility of utilising an agricultural waste for dye removal. The results show that initial dye concentrations, pH and adsorbent dose highly affect the dye uptake capacity of adsorbents. The equilibrium has been analyzed using Freundlich and Langmuir adsorption isotherms.. The calculated isotherm constants were used to compare the adsorptive capacities of adsorbents for dye removal. Thus the use of coffee husk as an adsorbent can be viewed as an effective waste management strategy.

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