ISSN: 0976-3031

Available Online at http://www.recentscientific.com

International Journal of Recent Scientific Research
Vol. 7, Issue, 4, pp. 10401-10405, April, 2016

International Journal of Recent Scientific Research

Research Article

REMOVAL OF SAFRANIN –O FROM AQUEOUS SOLUTION BY ADSORPTION ONTO CARBONIZED SPENT COFFEE GROUND

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ARTICLE INFO

Article History:

Received 11th January, 2016
Received in revised form
14th February, 2016
Accepted 18th March, 2016
Published online 28th April, 2016

Keywords:

Adsorption, Langmuir, pollutants, safranin – O.

ABSTRACT

Dyes or colored compounds are the most effortlessly identifiable pollutants in the environment. Maximum of the industries use dyes and pigments to color their products. In the present study, carbonized spent coffee ground had been converted into a low cost adsorbent and characterized for SEM and FTIR. Batch adsorption studies are carried out by observing effect of amount of adsorbent dose, contact time, pH, and initial concentration of safranin-O on the adsorption capacity of the adsorbent were studied. The adsorption of safranin - O over carbonized coffee spent ground obeyed second order kinetics. It was found that the adsorption followed the Langmuir isotherm.

INTRODUCTION

Dyes have wide application and found in all segment of environment. Safranin-O is considered as a highly toxic substance but found use in food, textile, paper, rubber industry, etc.Safranin-O dye is one of the most commonly used azine dye, which are amongst the oldest known synthetic dyes. It is also used for dyeing tannin, cotton, bast fibers, wool, silk, leather and paper. (Dwivedi, *et al*, 2015). Presence of high concentration of Safranin-O in aquatic system has a tremendous effect on the health of human, animals and plants. Contamination of Safranin-O in water can cause allergic dermatitis, skin irritation, cancer and mutation in human being. Existence of dyes in water bodies restricts sunlight penetration and photosynthetic process and inhibits the development of biota and tendency to chelate metal ion (Gupta *et al*, 2006). Usually, the dye-bearing wastewater is released directly into the adjacent water sources such as rivers, lakes and seas. Textile dyeing method is a chief source of contamination of water responsible for the continuous pollution of the environment. Contamination of drinking water above 0.1 mg/L can make it unsuitable for human consumption (Garg *et al*, 2004). The conventional methods for treating dye – containing waste water are coagulation, flocculation, reverse osmosis and adsorption onto various adsorbing materials (Rajeshwar *et al*, 1994).

A considerable amount of interest has recently been focused on the adsorption technique for the removal of dyes from waste water onto various adsorbent such as treated ginger waste (Rais Ahmad and Rajeev Kumar, 2010), sepiolite (Rytwo *et al*, 2002; Ozcan and Ozcan, 2005; Armagan *et al*, 2003), kaolinite (Harris *et al*, 2001), montmorillonite (Wang *et al*, 2004; Ogawa *et al*,1996), bentonite (Ozcan and Ozcan, 2004), activated carbon (Wang and Li, 2007; Tan *et al*, 2007), rice straw (Gong *et al*, 2008), sphagnum Peat (Allen *et al*, 1989), untreated coffee husks (Leandro *et al*, 2008), chitosan (Li Wang *etal*,2011), bagasses pith (McKay *et al*,1991), agriculture wastes (Namasivayam and Kadirvelu,1994), industrial waste products (Namasivayam and Sumithra, 2005)respectively. The main objective of the present work isto find the use on the locally available material of spent coffee grounds and to know the optimum condition for maximum efficiency of Safranin-O removal by varying pH, time and adsorbent dose.

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MATERIALS AND METHOD

Coffee spent grounds were collected from the Ashoka hotel, Kadapa was used as adsorbent. It was washed with distilled water three times to remove any adhering dirt and color. It was then dried in a hot air oven at 100° C for 5 hrs. The powder was ground and sieved for uniform particle size of 60 µm. The powder was carbonized by placing in muffle furnace at 500 ° C for 15 min.

Preparation of dye solution

Safranin is a cationic red dye having chemical formula $C_{20}H_{19}CIN_4$, MW, 350. 84 $gmol^{-1}$ IUPAC name as 3, 7 – diamino – 2, 8 – dimethyl -5 – phenyl phenazinium chloride was supplied by qualigens, India and used as adsorbate. The stock solution was prepared by dissolving 1 g dye is 1000 ml distilled water. The chemical structure of safranin-O is shown in fig. 1 The solutions were stored in brown glass bottles to avoid degradation to light. The pH of dye Solution was adjusted with NaOH or HCl using a pH meter.

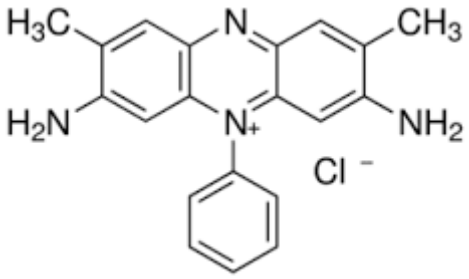


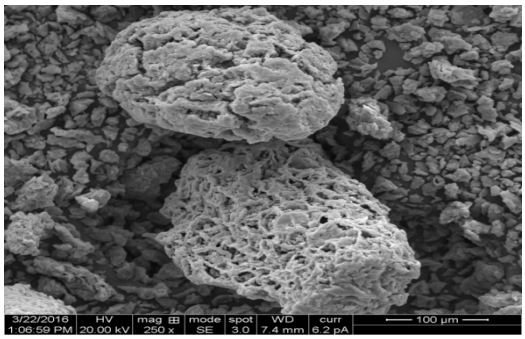
Figure 1 Structure of safranin - O

Batch adsorption experiment

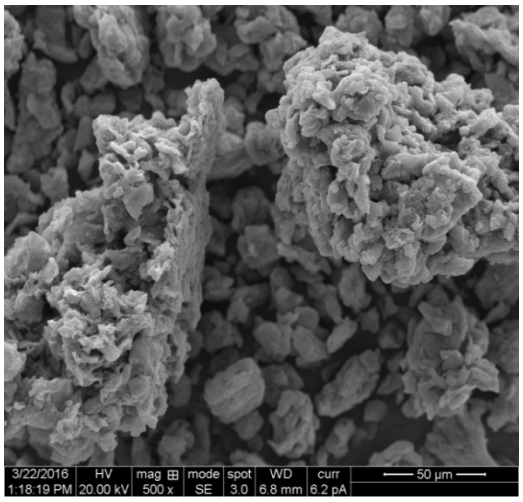
Batch mode experiment were carried out in orbital shaker at a constant speed of 160 rpm at 32°c in a 250ml conical flask containing 300mg of adsorbent with 50ml of dye solution after separated from the solution by centrifuge (REMI make) at 10,000rpm for 20 min. The dye concentration was determined spectrophotometrically using Shimadzu UV visible spectrophotometer at λmax= 519 nm.

RESULT AND DISCUSSION

The p^H_{zpc} of the adsorbent was found to be 7.0. SEM photographs show morphological changes in the adsorbent before and after adsorption of Safranin-O (Fig. 2). The presence of pores in the adsorbent, favored the diffusion of the Safranin-O to its surface.



(a)

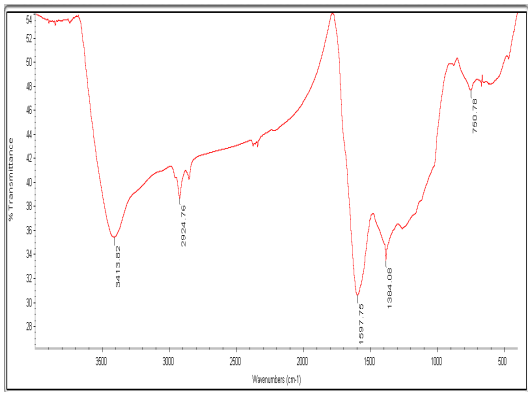


(b)

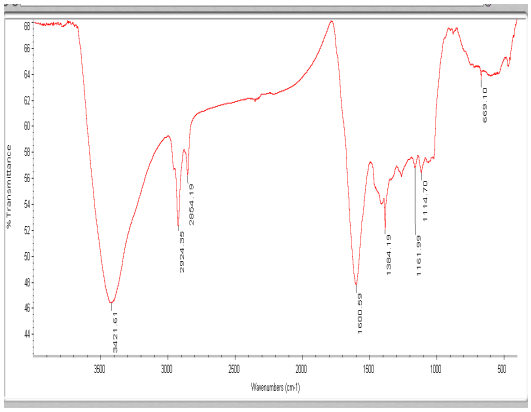
Fig. 2 SEM images ofcoffee spend ground (a) before adsorption(b) after adsorption.

FTIR Spectral analysis of the Adsorbent

Fourier transformed infrared spectra in the range 4000 - 500 cm 1 are shown in Figure 3 associated with the functional groups that are on the surface of spent coffee ground. FTIR spectrum of before and after adsorption showed a strong peak shift of hydroxyl (O- H) group at wave number 3413 and 3421 cm^{-1}. The vibration of band 2924 cm^{-1} was attributed to aromatic C – H bending.



(a)



(b)

Fig. 3 FTIR spectrum of (a) unloaded adsorbent and (b) dye loaded adsorbent

Batch adsorption studies

Effect of initial dye concentration and contact time

The uptake of dye was increased from 1.37 to 3.33 mg/g with the increase in dye concentration from 10 to 40 mg/Lthis may be attributed to an increase in the driving force of the concentration gradient with the increase in the initial dye concentration (Hameed *et al*., 2008; Ashtouskhy, 2009).The uptake of safranin - O as a function of contact time is shown in the Fig. 4. The maximum removal of safranin– Ofrom aqueous solution was obtained after 40 and 80 min contact time. Similar study was reported by the adsorption of safranin – T onto activated carbon and activated rice husks (Gupta *et al*, 2006).

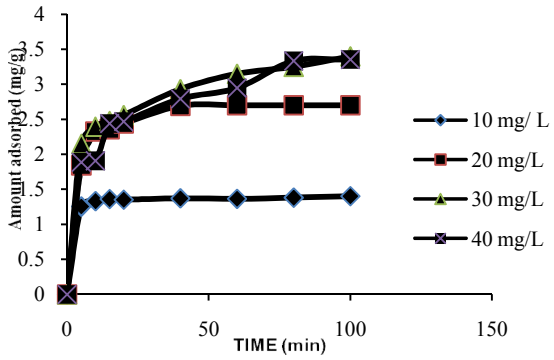


Fig. 4 Effect of contact time on safranin – O adsorption

Effect of pH

The effect of pH was observed over the entire pH range (3.0 – 10.0). The results obtained are presented in Fig. 5 which describes maximum adsorption of around 92 % for 10 mg/L at pH 3.0.

Similar trend was observed for the feasibility studies on the coffee spent grounds as Biochar as an adsorbent for colour removal (Chinmai *et al,* 2014).The pH effect can be interpreted as the protonation and deprotonation of safranin-O occurring in the acidic and basic medium. Furthermore, the adsorption behavior of such adsorbent at various pH may be due to surface charges and availability of active sites.

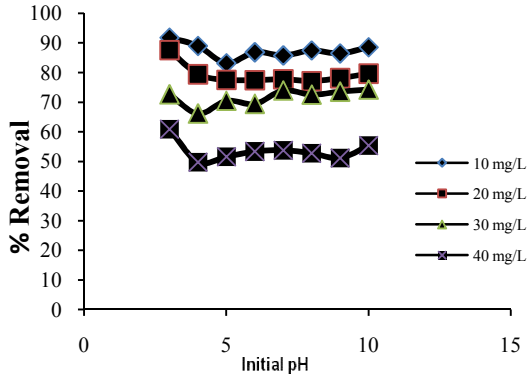


Fig. 5 Effect of pH on safranin – O adsorption

Adsorption Isotherm

The equilibrium data were analyzed by Langmuir and Freundlich isotherms. These isotherms are useful for estimating the total amount of adsorbent needed to adsorb a required amount of adsorbate from solution.

Langmuir Isotherm (Langmuir, 1918)

Langmuir isotherm is based on the adsorption on a homogenous surface, i.e. the surface consists of identical sites, equally available for adsorption and with equal energies of adsorption, and that the adsorbent is saturated after one layer of adsorbate molecules forms on its surface.

The Langmuir isotherm can be expressed as

$$C_e/q_e = 1/Q_o b + C_e/Q_o \quad (1)$$

Where $C_{e\ is}$ the equilibrium concentration (mg Adsorbate per liter of solution) and q_e is the amount adsorbed (mg Adsorbate per g of adsorbent) at equilibrium. Langmuir isotherms were obtained by agitating the adsorbent of fixed dose and the Safranin-O of different concentrations for a contact time greater than the equilibrium time. The constant Q_o signifies the monolayer adsorption capacity (mg/g) and b is related to the energy of adsorption (mg/L). Plot of $q_e$vsC_e show the agreement of experimental data with Langmuir plots for Safranin-O studied (Fig. 6) by adsorbent. At room temperature 32 ^{0}C, the adsorption capacity, $Q_{o,}$ by adsorbent for Safranin-O was found to be 3.76 mg/g.

Freundlich isotherm (Freundlich, 1906)

The Freundlich isotherm is an empirical equation employed to describe heterogeneous surface systems. It is common model used in wastewater studies, which relates the residual impurity in solution at equilibrium to the amount adsorbed as follows:

$$\log q_e = \log k_f + 1/n \log C_e \quad (2)$$

Where k_f denotes approximate adsorption capacity and n is related to intensity of adsorption. (Figure 6) show little agreement of experimental data with Freundlich isotherm (plot $q_e$vsC_e) of Safranin-O studied.

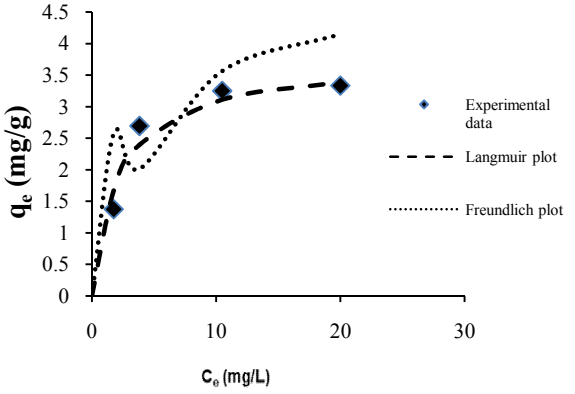


Fig. 6 Adsorption isotherms of Safranin-O

Adsorption Kinetics

In order to investigate the kinetics of the process, pseudo – first order and second order equations are described by Lagergren (1898) and Ho (1998), respectively.

Lagergren first order model can be represented as:

$$\log (q_e\text{-}q) = \log q_e - k_1 t/2.303 \quad (3)$$

Where q_e and q are the amounts of Safranin-O adsorbed (mg/g) at equilibrium and at time t, respectively, and k_1 is the rate

constant of first order adsorption (1/min). Values of q_e and k_1 were calculated from the slope and intercept of the plot of log (q_e-q) vs t for different concentrations of Safranin-O (Fig. 7).

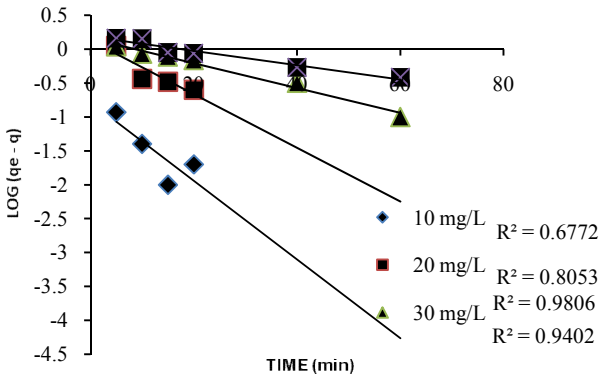


Fig. 7 Lagergren plots for Safranin-Oadsorption

The second order kinetic model is represented as:

$$t/q = 1/k_2q_e^2 + t/q_e \quad (4)$$

Table 1 Comparison of first order and second order model for adsorption of Safranin-O

Initial conc. (mg/L)	Equilibrium time(min)	q_e (exp) (mg/g)	First order kinetics			Second order kinetics		
			k_1 (1/min)	q_e (cal) (mg/g)	R^2	k_2 (g/mg/min)	q_e (cal) (mg/g)	R^2
10	40	1.372	0.134	0.166	0.677	1.515	1.392	0.999
20	40	2.693	0.089	1.346	0.805	0.179	2.703	0.997
30	80	3.25	0.041	1.442	0.98	0.069	3.322	0.996
40	80	3.333	0.023	1.524	0.94	0.062	3.175	0.997

Values of k_2 and q_e were calculated from the slope and intercept of the plots t/q vs t. Comparison of the $q_e$values obtained experimentally with those calculated from first and second order kinetic models (Table 1) shows that there was a good agreement between the experimental q_e values and the calculated q_e values from second order equation for the Safranin-O by adsorbent. This indicates that the adsorption process of the Safranin-O follow second order kinetic model. The regression coefficients for the linear plots from the second order equations are also good. Similar phenomenon has been observed in the adsorption of safranin-O onto Kaolinite Clay (Kayode *et al*, 2014).

Desorption studies

For economical adsorption process, it is necessary to regenerate spent adsorbent therefore desorption test on spent coffee ground were carried out with 0.1 M solution of sodium hydroxide, potassium chloride and water. The reversibility of adsorption depends on binding bond such as ionic or covalent bonding or weak binding forces such as Vander Waals forces or a dipole-dipole interaction formed between the adsorbent surface and the dye molecules.

Table 2 Maximum adsorption capacities of safranin-O reported for different adsorbents

Adsorbents	Capacities Qo (mg/g)	References
Kaolinite clay	16. 23	Kayode *et al*, 2014
Fly ash	1.76	Dwivedi *et al*, 2015
Natural Palygorskite clay	200	Taha *et al*, 2013
Mango seed Integuments (untreated)	34. 48	Mohammad *et al*, 2012
Mango seed Integuments (treated)	43. 47	Mohammad *et al*, 2012
Pineapple peels	26. 08	Yusuf *et al*, 2015
Coffee spent grounds	3.76	This work

CONCLUSIONS

The experimental result from this study suggests that spent coffee grounds are potential adsorbents for removal of safranin-O from aqueous solutions. The kinetic data were well fitted with pseudo second - order model with high correlation coefficient almost with a unit value (0.999). The experimental data were correlated reasonably well by Langmuir adsorption isotherm. The maximum adsorption capacity (Qo) was found to be 3.76 mg/g. Adsorption percentage increase with increasing the adsorbent loading.

Acknowledgement

The authors would like to gratefully acknowledge Central Instrumentation facility of Yogi Vemana University for the successful completion of this work.

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How to cite this article:

Lakshmi Prasanna M., Sumithra S and Madakka M.2016, Removal of Safranin –O from Aqueous Solution by Adsorption Onto Carbonized Spent Coffee Ground. *Int J Recent Sci Res.* 7(4), pp. 10401-10405.