Advances in Environmental Research, *Vol. 6, No. 1 (2017) 1-14*
DOI: https://doi.org/10.12989/aer.2017.6.1.001

Evaluation of refused tea waste activated carbon for color removal: Equilibrium and kinetic studies

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(Received March 26, 2016, Revised February 21, 2017, Accepted February 24, 2017)

Abstract. New technologies or improvement of the existing technologies are required to enhance the efficiency of removal of pollutants from wastewater. In this study we attempted to produce and test the activated carbon produced from the refused tea waste for the removal of dyes from wastewater. The objectives of this investigation were to produce activated carbon from refused tea waste by chemical activation, evaluate its performance for the removal of color produced from Acid Yellow 36, and the modeling of its dye removal with the kinetic study. The activation was performed in two steps namely carbonization at 375±25°C and chemical activation with HCl at 800°C under the absence of Oxygen. Adsorption isotherms and kinetic studies were performed with a textile dye, Acid Yellow 36, at different concentrations (20-80 mg/L). The maximum dye removal (~90%) observed at 80 mg/L dye concentration and it reduced at low dye concentrations. Maximum adsorption (71.97 mg/g) was recorded at 96 h at 29±1°C. Low pH increased the dye adsorption (pH=2; 78.27 mg/g) while adsorption reduced at high pH levels indicating that the competition occurs in between OH- ions and AY36 molecules for the adsorption sites in RTAC. The Langmuir isotherm model clearly explained the dye adsorption, favorably, by RTAC. Moreover, kinetic studied performed showed that the pseudo second order kinetic model clearly describes the dye adsorption. Based on the results obtained in this study, it can be concluded that RTAC can be used for the removal of textile dyes.

Keywords: refused tea activated carbon; adsorption; textile dye; isotherm

1. Introduction

Environmental degradation due to human activities severely impacts on all living beings in the world. Waste (solids, liquids and gaseous) is one of the major environmental depredators for environmental pollution. Considerable efforts have already been taken to minimize the pollution arising from waste by using different treatment technologies. Even though some technologies have a little use due to various limitations, others have already been well established (Pepper *et al.* 2006). Dyes are refractory organic chemical compounds frequently used in various industries such as textile, printing, food, construction, etc. (Foo and Hameed 2010). Annual worldwide dyes and pigments production is more than 7×10^5 tons and they belongs to approximately 10,000 different

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http://www.techno-press.org/?journal=aer&subpage=7 ISSN: 2234-1722 (Print), 2234-1730 (Online)

Refused tea waste was obtained from a leading commercial tea factory in the Southern province of Sri Lanka. Off color and large matters in RTW were removed. Then, RTW was packed in polythene bags, transported and kept in the laboratory until they were used. Activated carbon production was performed in two steps. In the first step, RTW after washing and drying was carbonized at 375±25°C temperature in a sealed metal container. Carbonized RTW was mixed with 0.1M HCl until it forms a paste and kept an overnight. The paste was heated to 800°C in a muffle furnace for two hours in the absence of Oxygen for activation. The refused tea waste activated carbon (RTAC) sample was cooled to room temperature, and washed with distilled water and added 0.1M HCl to adjust pH (6±0.5), and dried in an oven at 105°C. The product was sieved (mesh no 44) to obtain more homogenize samples. Dye (AY36) used in the study was in analytical grade (Sigma, Aldrich, China). The chemical formula, molecular weight and Chemical Index no of AY36 are $C_{18}H_{16}N_3NaO_3S$, 377.39 and 13065, respectively.

Four concentration levels (20 mg/L, 40 mg/L, 60 mg/L and 80 mg/L) of AY36 were used for the studies. Quantification of dye removal was assessed using the maximum adsorption wave length (λ_{max}, 439 nm) of AY36 using a UV-Visible spectrophotometer (Maiti *et al.* 2007). Adsorption studies with RTAC were performed in triplicates and the mean values were used for the calculation of dye removal. pH and temperature were measured following the standard methods (APHA 1995). Moisture content, ash content and bulk density of RTAC were determined according to the procedure outlined in test methods of for activated carbon(TMAC 1986).

Adsorption equilibrium experiments were performed in a set of conical flasks (250 ml) containing 0.1 g of RTAC and 100 mL of dye solution with different initial dye concentrations (20, 40, 60 and 80 mg/L). Flasks with RTAC and dye solutions were shaken in reciprocal box shaker (29±1℃). Final concentration of dye in solution was determined after 96 h. Amount of adsorption of dye at equilibrium, q_e (mg/g), was calculated using the equation.

$$q_e = \frac{(C_o - C_e)V}{M} \tag{1}$$

Where, C_o and C_e (mg/L) are the initial and equilibrium liquid-phase dye concentrations, respectively. *V* is the volume of solution (L) and M is the mass (g) of dry adsorbent used (Kunwar 2003). The procedures of kinetic experiments were basically identical to those of the equilibrium tests. Aqueous samples were taken at predefined time intervals, and the concentrations of dye were similarly measured. The amount of adsorption of dye at time *t*, q_t (mg/g), was calculated using the following equation.

$$q_t = \frac{(C_o - C_t)V}{M} \tag{2}$$

Where, C_o and C_t is the initial AY36 concentration and AY36 concentration at time *t* (mg/L), *V* is the volume of dye solution (L) and *M* is the mass (g) of dry RTAC (adsorbent) used. Further batch studies were conducted in order to determine the effect of pH on AY36 adsorption by RTAC. Dye adsorption studies at different initial pH levels (2, 4, 6, 8 and 10) by RTAC were performed at 80 mg/L concentration. Finally, sorption capacities of RTAC for AY36 were evaluated using famous Langmuir and Freundlich isotherms models. Kinetics of adsorption of AY36 was also checked by pseudo first order and pseudo second order models.

3. Results and discussion

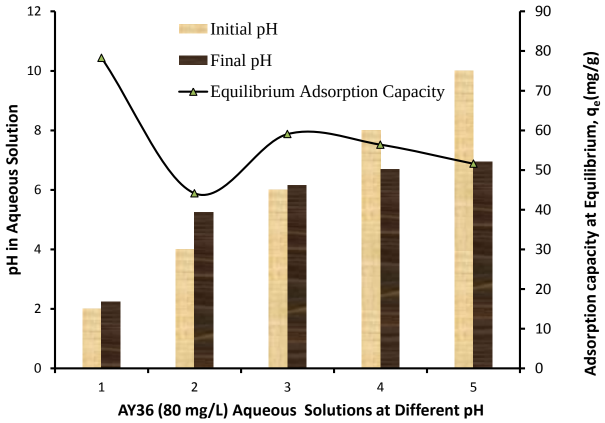

Fig. 3 Effect of pH on adsorption capacity of RTAC (V=100 ml, C_o=80 mg/l, Adsorbent Dose=0.1 g, pH (2-10), Temperature=29±1℃)

Effects of initial AY36 concentration on contact time for adsorption by RTAC are shown in Fig. 1. Dye removal was high at the beginning and then the adsorption appears to be occurred slowly towards the end. High dye removal percentages were observed at high dye concentrations (Fig. 1). Higher rate of sorption at the beginning is due to the high concentration gradients between adsorbate in solution and adsorbate in the sites of adsorbent surface. As time proceeds, concentration gradient is reduced due to the accumulation of dye molecules in the vacant sites of adsorbent decreasing the rate of sorption at the latter stages. The maximum adsorption (AY36-80 mg/L) was reached (71.97 mg/g) at the end of 96 h and the dye removal was ~89.97% (Figs. 1 and 2). At the low dye concentrations, the adsorption was reduced since the lack of adsorbate in aqueous solution at the end of contact time. Similar trend has been observed in the adsorption of reactive red 120 from aqueous solution by activated carbon from waste tea(Auta 2012). Khosla *et al.* (2013) have reported that in a study conducted for the removal of Acid Orange 7 by adsorption using tea waste, maximum dye removal was found to be 5.73 mg/g. The adsorption values obtained in our study was much higher (71.97 mg/g) than that of their values. Even though, both studies have been used Acid Dyes (anionic in nature), their chemical structures are different. Further, it is important to report that the instead of tea waste (discarded tea after preparing the tea) of their study, we used refused tea waste (produced in the black tea production process) having comparatively higher lignocellulose material.

One of the most important parameter controlling the adsorption process is pH (Malkoc and Nuhoglu 2007). The effect of pH on AY36 adsorption was evaluated (Fig. 3). The pH of aqueous solution was adjusted at the beginning of the experiment by adding of 0.1M Hydrochloric Acid or 0.1M Sodium Hydroxide where necessary.

The adsorption capacity of RTAC at high pH levels (pH>4) was low (removal: ~55%). The maximum adsorption capacity (78.27 mg/g) was recorded at pH 2 (removal: ~98). The properties of RTAC and electrostatic attraction properties of dye molecules may play an important role in dye adsorption. The reduction of AY36, anionic dye, adsorption by RTAC at higher pH may be due to the competition of dye molecules with OH^- ions in aqueous solution for adsorption sites. The size of the dye molecule may have a little benefit over small OH^- ions in competition for the positively charged adsorption sites in aqueous solution. Almost similar results have been recorded by Demiral *et al.* (2008) where they have used activated carbon prepared from agricultural wastes for

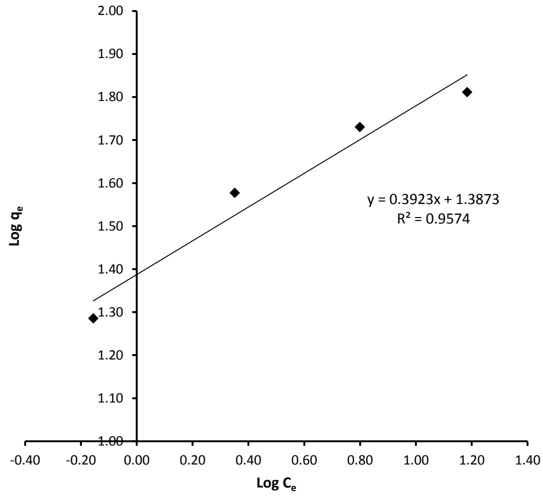

Fig. 5 Freundlich isotherm for AY36 on RTAC

indicating that the adsorption of AY36 on RTAC follows the Langmuir isotherm (Fig. 4). The calculated Langmuir constants 'b' and 'Q_o' are 0.4755 L/mg and 73.5294 mg/g.

One of the very important characteristics of Langmuir isotherm could be expressed in terms of a dimensionless factor called separation factor, R_L, which explains the nature of isotherm (Gerçel and Gerçel 2009). The separation factor can be calculated using following equation.

$$R_L = \frac{1}{1 + b\,C_0} \tag{4}$$

Where, b is Langmuir constant and C_0 is the highest initial dye concentration. The separation factor, R_L, explains the shape of the isotherm. If R_L value is in between 1 to 0, the adsorption is favorable while it is greater than 1, the adsorption is unfavorable. The linear and unfavorable adsorption is represented by value 1. Zero value indicates the irreversible adsorption. Separation factor determined (0.0256) in this study clearly indicates that the adsorption AY36 by RTAC was favorable.

Further, the results of the study agree (R^2=0.999) with the Langmuir isotherm equation confirming the homogeneous nature of the surfaces of the activated carbon and also demonstrates the formation of monolayer coverage of the dye molecules at the outer surface of the activated carbon.

Freundlich model describes the sorption occurs on heterogeneous surfaces and the ability of adsorbate in aqueous solution to influence the adsorption capacity of adsorbent. The linear form of Freundlich equation can be written as $\log q_e = \log K_F + \frac{1}{n} \log C_e$. Where, q_e (mg/g) is the amount of adsorbate (AY36) adsorbed to unit mass of adsorbent (RTAC) at equilibrium, C_e is the equilibrium concentration of AY36 in aqueous solution (mg/L), K_F is the adsorption capacity of the adsorbent (mg/g) and 1/n represents the Freundlich constant which indicates the how favorable the adsorption process is.

Freundlich adsorption equation is of greater significance for chemisorption, although some physical adsorption data have also been found to fit with this equation and it has been extensively used to adsorption isotherms from solutions (Bansal and Goyal 2005).

Table 2 Continued

Mahogany Saw Dust	Steam	Acid Yellow 36	30°C	0.987	118.25	0.02149	0.0445	0.987	25.440	0.239	(Santra *et al.* 2008)
Coconut Shell				0.999	90.28	0.00683	0.1277	0.988	5.330	0.420	
Rice Husk				0.998	54.87	0.00317	0.2398	0.991	1.600	0.490	
Fly Ash				0.999	11.90	0.00338	0.2283	0.995	0.540	0.418	
Coconut Flower	H_3PO_4	Reactive Red	28°C	0.990	181.94	N/A	0-1	N/A			(Senthilkumaar *et al.* 2006)
Harmal Seeds Residue	HNO_3	Methylene Blue	25°C	0.990	1111.11	0.02	0.0200	0.840	107.990	0.340	(Tofighy and Mohammadi 2013)
Sugarcane Bagasse	$ZnCl_2$	Acid Blue 9	30°C	0.925	39.9601	16.1441		0.938	3.730	0.356	(Tsai *et al.* 2001)
Sugarcane Bagasse		Acid Orange 51		0.905	52.5955	12.7090		0.982	4.750	0.402	
Refused Tea Waste	HCl	Acid Yellow 36	29±1°C	0.999	73.529	0.476	0.0260	0.957	24.395	0.392	This study

The plot of log q_e versus log C_e produce a straight line (Fig. 5) having the slope of 1/n and intercept of log K_F. R^2 (0.9574) indicates that the adsorption of AY36 by RTAC follows the Freundlich isotherm, giving reasonable evidences that dyes adsorbed to RTAC by chemisorption. K_F and 1/n constants are 24.3950 mg/g and 0.3923, respectively.

The intensity of adsorption is also represented by the constant "n". The value of "n" varies with the heterogeneity of the adsorbent surface. If the surface of adsorbent is more heterogeneous, the value of "1/n" reaches more close to zero while if it is zero (1/n = 0), the adsorption is irreversible. The adsorption process is favorable when 1/n value lies between 0 and 1 while unfavorable conditions could be expected when 1/n value greater than 1(Behnamfard and Salarirad 2013, Hameed *et al.* 2007). The value of 1/n shows (0.3923) the favorable adsorption of AY36. The correlation coefficients (R^2) of Langmuir (0.9995) and Freundlich isotherm (0.9574) indicate that the adsorption of AY36 by RTAC is best represented by the Langmuir isotherm model. Correlation coefficients and other important parameters related to two models in the adsorption of different dyes by activated carbon produced from different types of agricultural wastes are shown in Table 2.

Chemical activation using oxidative agents, HCl, H_3PO_4 and HNO_3 substantially enhance the volatile content, significantly, surface acidic groups mainly carboxyl groups in activated carbon (Figueiredo *et al.* 1999). The presence of Oxygen containing groups such as carboxyl groups may have electron withdrawn properties, which in turn induce a repulsion forces toward anionic groups while providing good binding sites for cationic groups. Acid yellow 36, anionic dye, was used in this study and the reason for the lower adsorption capacity of RTAC may basically be the oxidative agent (HCl) used for the activation. Low values of adsorption capacity for textile anionic dyes were reported when acids (H_2SO_4, H_3PO_4, HNO_3) were used for activation in the preparing of activated carbon from agricultural wastes as precursors (Phana *et al.* 2006, Singh *et al.* 2003) while high adsorption capacities were noted in cationic dyes under similar conditions (Aljeboree *et al.* 2014, Chen *et al.* 2013, Tofighy and Mohammadi 2013). Further, particle size of activated carbon (produced from a plant material) and the adsorption temperature in aqueous solution

Table 3 Pseudo-first-order kinetic and Pseudo second order kinetic parameters of AY36 adsorption on RTAC

Initial AY36 Con. (mg/L)	$q_{e\text{-exp}}$	Pseudo First Order Parameters				Pseudo Second Order Parameters			
		k_1 (min^{-1})	$q_{e\text{-cal}}$ (mg/g)	R^2	SSE%	k_2 (g/mg.min)	$q_{e\text{-cal}}$ (mg/g)	R^2	SES%
20	19.69	4.145x10^{-3}	22.26	0.9401	0.6425	5.4471x10-4	20.1207	0.9988	0.1077
40	39.38	2.303x10^{-3}	44.84	0.8828	1.3650	1.4746x10-4	40.4858	0.9987	0.2765
60	58.92	2.303x10^{-3}	137.40	0.6726	19.6200	6.31849x10-5	60.2410	0.9963	0.3302
80	71.97	6.909x10^{-4}	39.56	0.9785	8.1025	4.10575x10-5	73.5294	0.9906	0.3899

The linear form of pseudo second-order kinetic equation is as follows. Where, k_2 (g/mg.h) is the rates constant of second-order adsorption. The intercept and the slope of the linear plot are used for the determination of k_2 and q_e. Linear plot of second order kinetic model are shown in Fig. 7.

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e^2} + \frac{1}{q_e}\, t \tag{6}$$

The calculated parameters in pseudo-first order and pseudo-second order kinetic models are given in Table 3. The validity of kinetic models can be confirmed by its R^2 values. Further, it was observed that the validity of models have been verified by the sum of error squares (Hameed *et al.* 2007). The sum of error squares (SES) were calculated for both kinetic models using the following equation where N stands for numbers of data points. The high R^2 and low SES % represents the best goodness of fit of the model (Table 2).

$$\text{SES \%} = \sqrt{\frac{\sum(\text{qe.exp} - \text{qe.cal})^2}{\text{N}}}$$

The pseudo second-order kinetic model clearly describes the adsorption of AY36 by RTAC. Similar results have been observed in the adsorption of methylene blue onto bamboo based activated carbon (Hameed *et al.* 2007). In adsorption studies, pseudo-first order equation does not fit well with the whole range of contact time and it generally applicable on the initial stage of adsorption process (Ho and McKay 1999). It confirms in this study also where best fit with pseudo-first order equation was observed at the initials adsorption process in all dye concentrations. According to Foo and Hameed (2010) generally pseudo-first order kinetic model is followed when the adsorption proceeds in diffusion through a boundary. However, it seems that AY36 adsorption by RTAC occurs by forces through electron sharing or exchange in between adsorbate and adsorbents since adsorptions followed pseudo-second order kinetic model.

4. Conclusions

Activated carbon was prepared using the abundant waste material in tea manufacturing industry. Refused tea waste activated Carbon was tested for their suitability for the adsorption of AY36 textile dye. The maximum dye removal (~90%) was observed at 80 mg/L dye concentration and it was reduced in lower dye concentrations. Dye adsorption by activated carbon at the

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