

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

Somasiri Wijetunga* and Chathurika DFA Gunasekara

Department of Agricultural Engineering, Faculty of Agriculture, University of Ruhuna, Kamburupitiya, Sri Lanka

(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 $375\pm 25^\circ\text{C}$ 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 $29\pm 1^\circ\text{C}$. 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 deprecators 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

*Corresponding author, M.Phil, E-mail: swije2001@yahoo.com/swije@ageng.ruh.ac.lk

types (Senthilkumaar *et al.* 2006). It is estimated that more than 70,000 tons of dyes are discharged in effluents from textile and associated industries in the world every year (Zhang *et al.* 2012). Nowadays, the most of dyes used in textile industry are in synthetic in nature and resistant to natural degradation. Garg *et al.* (2003) reported that about 10-15% of the dye is lost in the effluent during the dyeing process. Therefore, textile wastewater generated in different stages of the textile processing should be properly treated to avoid environmental pollution, especially, water pollution (Senthilkumaar *et al.* 2006). Treatment technologies, biological, physical and chemical are being developed and used in the world for the treatment of textile wastewater (TWW), basically, to remove color arising from residual dyes present in wastewater (Khosla *et al.* 2013, Maiti *et al.* 2007). However, it has been noted that those treatment technologies are not always effective and economically feasible for different dyes and their concentrations in wastewater (Özbaş *et al.* 2013).

Adsorption is one of the very promising physical treatment technology frequently used for the removal of recalcitrant chemicals in water (Ioannidou and Zabaniotou 2007). Porous nature of the material (adsorbate) plays a key role for the binding of chemicals into its surfaces and removing them from the medium (Bansal and Goya 2005). Activated Carbon (AC) produced from lingo-cellulose materials are popularly used in the adsorption process to remove or separate chemical compounds in liquids as well as gaseous media (Ioannidou and Zabaniotou 2007). Physical and chemical methods are employed for the production of AC from various materials (Saib *et al.* 2013). Physical activation involves two steps namely carbonization and activation with carbon dioxide or steam. In the chemical activation, activation is performed by the decomposition of precursor with a chemical activator such as KOH, K₂CO₃, NaOH, ZnCl₂, and H₃PO₄ at elevated temperatures (Ozer *et al.* 2012). Production process employed and the materials used influence the performance of adsorption and the types of chemical to be adsorbed (Ioannidou and Zabaniotou 2007). Cheap and abundantly available raw materials will reduce the cost of AC production. It has been reported that various waste materials have been used for the production of AC using chemical or physical processes and produced AC have been applied for the removing of dyes in TWW in recent past (Foo and Hameed 2010, Kadirvelu *et al.* 2003).

The refused tea waste (RTW) is a major waste product generated in the black tea production process (Senaratna *et al.* 2007) and it will be ended up in the environment as waste material imposing threat to environmental resources. Sri Lanka is one of the major tea producers in the world (Uzun *et al.* 2010). Therefore, considerable amount of RTW is being produced imposing heavy burden for the tea producers to dispose them. Refused tea waste containing lingo-cellulose materials (Tee and Khan 1988) may be a good source of raw material for the production AC. Studies on the use of RTW for beneficial uses have not appropriately been reported. However, the use of AC produced from tea wastes (disposal component of black tea after using) has been described for the removal of color in TWW (Khosla *et al.* 2013, Özbaş *et al.* 2013) and heavy metals from aqueous solutions achieving the significant improvement of color and heavy metal removal (Attia 2012, Cheraghi *et al.* 2013, Zuurro and Lavecchia 2010).

Therefore, this investigation focused to produce AC from refused tea waste by chemical activation, to evaluate its adsorption performance, to model the adsorption isotherms and to study the kinetics of dye removal in dyeing water having Acid Yellow 36 (AY36).

2. Materials and methods

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 $375\pm 25^\circ\text{C}$ 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 $\text{C}_{18}\text{H}_{16}\text{N}_3\text{NaO}_3\text{S}$, 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 ($29\pm 1^\circ\text{C}$). 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.

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

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.

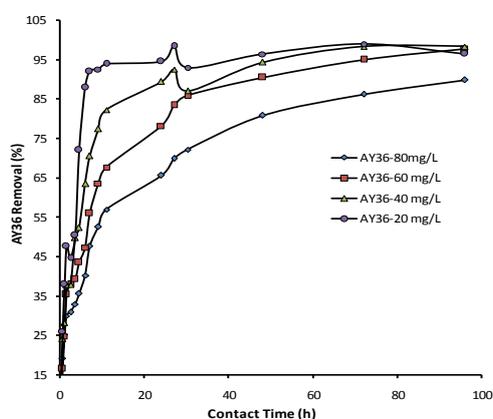
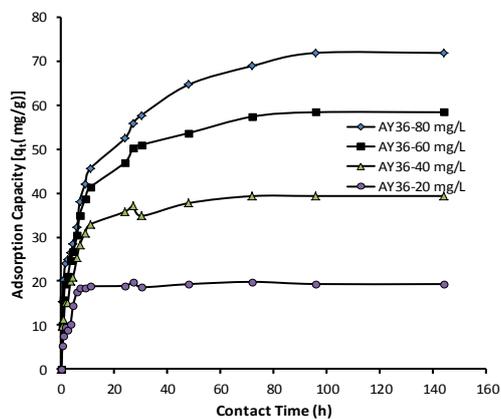
$$q_t = \frac{(C_o - C_t)V}{M} \quad (2)$$

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

Table 1 Some of physical characteristics of RTAC

Parameter	Value
Recovery percentage (%)	24.05
Moisture content (%)	12
Diameter (mm)	<0.355 mm
pH	7
Ash content (%)	3.33
Bulk density (g/cm ³)	0.32

Fig. 1 Initial AY36 concentration and removal by RTAC ($V=100$ ml, $C_o=20-80$ mg/l, Adsorbent Dose=0.1 g, $pH=6.5\pm 0.5$, Temperature= 29 ± 1 °C)Fig. 2 Effect of initial AY36 concentration on adsorption capacity of RTAC ($V=100$ ml, $C_o=20-80$ mg/l, Adsorbent dose=0.1 g, $pH=6.5\pm 0.5$, Temperature= 29 ± 1 °C)

The physical parameters of RTAC were determined and are shown in Table 1. It appears that the recovery rate is quite low. Basically, the quality of raw materials and the production process are the major reasons for the low recovery rate. Bulk density indicates the amount of pore volume in a material with respect to unit mass. Low bulk density of RTAC shows the increased the pore volume.

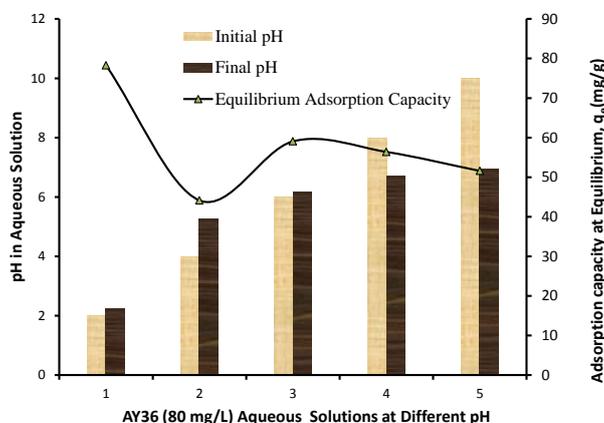


Fig. 3 Effect of pH on adsorption capacity of RTAC ($V=100$ ml, $C_o=80$ mg/l, Adsorbent Dose= 0.1 g, pH (2-10), Temperature= 29 ± 1 °C)

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

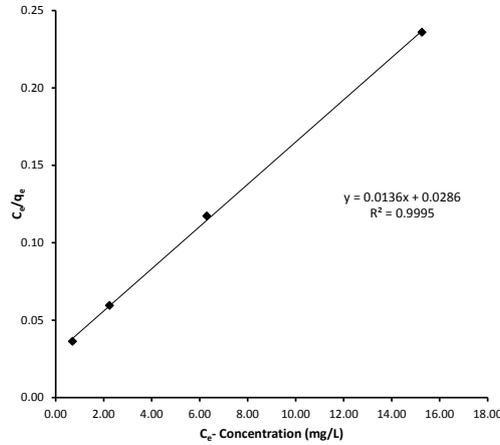


Fig. 4 Langmuir isotherm for AY36 on RTAC

the adsorption of textile dye, acid blue 350. It is quite important to note that the apparent changes of pH at initial and final aqueous solutions were not observed in first three pH levels (pH 2, 4 and 6). However, the considerable reduction of final pH (after adsorption) was observed in last two experiments where, initial pH was maintained at 8 and 10, respectively. It proves that the argument which is the competition of AY36 molecules with OH⁻ ions for the adsorption sites of RTAC.

At equilibrium, the rate of adsorption is equal to the rate of desorption. It is a dynamic equilibrium because the number of molecules sticking to the surface is equal to the number of molecules rebounding from the surface (Bansal and Goyal 2005). The adsorption equilibrium can be represented by the adsorption isotherms at constant temperature. The adsorption isotherm gives the useful information about the adsorbate, the adsorbent, the adsorption process and the relative ability of adsorption on a given adsorbent with respect to given conditions. It is very important for optimizing the adsorbent for the particular concentration of adsorbate.

Adsorption isotherms can be prepared by plotting the amount adsorbed per unit mass of adsorbent as a function of different concentrations in aqueous solution (Bansal and Goyal 2005). Several isotherm equations have been developed for the representing the adsorption data on solid liquid mediums (Ayanda *et al.* 2013). Freundlich and Langmuir adsorption isotherm equations are frequently used for adsorption in aqueous solutions (AL-Aoh *et al.* 2013, Hameed *et al.* 2007).

Widely used isotherm equation for modeling of adsorption data in aqueous solutions is the Langmuir equation and it is valid for monolayer sorption onto a surface with a finite number of identical sites (Bansal and Goyal 2005). Langmuir model can be used for the explaining the concepts of both physical and chemical adsorption. The linear form of Langmuir isotherm equation (Ayanda *et al.* 2013) is given as follows.

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (3)$$

Where, C_e is equilibrium concentration of adsorbate (AY36) in aqueous solution (mg/L), q_e is the amount of adsorbate (AY36) adsorbed per unit mass of adsorbent (mg/g), and Q_0 and b are constants which represent the adsorption capacity (mg/g) and Langmuir adsorption constant related to the energy of adsorption (L/mg), respectively.

Langmuir isotherm gives a straight line with the slope of $1/Q_0$ and the intercept of $1/Q_0 b$

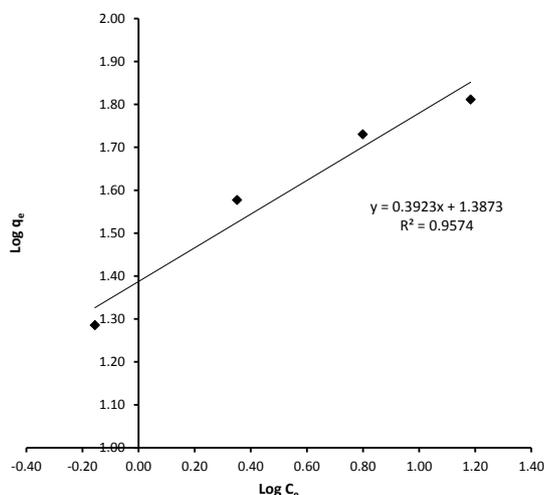


Fig. 5 Freundlich isotherm for AY36 on RTAC

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.

$$R_L = \frac{1}{1 + b C_0} \quad (4)$$

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 Correlation coefficient of Langmuir and Freundlich isotherm models in adsorption of dyes on activated carbon produced from agricultural wastes

Precursor	Activation agent	Name of the dye	Tempe.	Langmuir isotherm			Freundlich isotherm				Source
				R ²	Q _o (mg/g)	b (L/mg)	R _L	R ²	K _F	1/n	
Coconut Husk	ZnCl ₂	Methylene Blue	30 ^o ±1C	0.999	500	0.286	0.0039	0.8153	21.82	0.045	(AL-Aoh <i>et al.</i> 2013)
Coconut Husk	H ₂ SO ₄	Crystal Violet	25 ^o ±0.5C	0.943	396.977	0.035		0.983	50.062	0.341	(Aljeboree <i>et al.</i> 2014)
Cherry Stone	ZnCl ₂	Reactive Yellow 18	25 ^o C	0.991	50.76	0.121	0.027–0.142	0.879	9.986	0.383	(Angin 2014)
Tea Waste	KOH	Reactive Red 120	30 ^o C	0.966	200	0.024		0.916	43.850	0.471	(Auta 2012)
Thevetia Peruviana	H ₃ PO ₄	Reactive Orange 4	30 ^o C	0.985	113.64	0.0702	<1	N/A			(Baseri <i>et al.</i> 2012)
Rice Husk	H ₃ PO ₄	Methylene Blue	30 ^o C	0.990	578.1	0.6758	0.004–0.020*	0.9683	307.12	0.160	(Chen <i>et al.</i> 2013)
Hazelnut Bagasse	ZnCl ₂	Acid Blue 350	25 ^o C	0.997	357.14	0.054	0.057	0.909	40.620	0.448	(Demiral <i>et al.</i> 2008)
Euphorbia macroclada	K ₂ CO ₃	Acid Yellow 17	25 ^o C	0.995	125.00	0.137	0.013	0.918	79.000	0.077	(Gerçel and Gerçel 2009)
		Acid Orange 7		0.998	410.00	0.119	0.0127	0.9582	65.000	0.070	
Bamboo	KOH	Methylene Blue	30 ^o C	0.999	454.2	0.518	0.004	0.9641	171.400	0.268	(Hameed <i>et al.</i> 2007)
Olive Stone	H ₃ PO ₄	Basic Blue 9	20 ^o C	0.990	315.60	0.09	0.03	0.990	14.900	0.073	(Khalaf 2013)
Tea Waste	Raw	Basic Yellow 2	30 ^o C		2.81×10 ⁻⁴	0.0133		0.331	1.263		(Khosla <i>et al.</i> 2013)
		Acid orange 7	30 ^o C		1.55×10 ⁻⁵	0.0184		0.008	1.409		
Rice Husk	NaOH	Methylene Blue	30 ^o C	0.998	413.2	0.798	0.0031–0.0244	0.909	9.055	0.265	(Lin <i>et al.</i> 2013)
Jute Stalk		Methylene Blue	30 ^o ±2C	0.993	28.409	0.0639	N/A	0.985	2.080	0.625	(Maiti <i>et al.</i> 2007)
Bagasse				0.987	16.103	0.1064		0.961	1.990	0.588	
Wheat Straw				0.956	11.062	0.1277		0.974	1.620	0.526	
Sesame Stalk				0.964	10.559	0.0936		0.927	1.190	0.588	
Risk Husk				0.925	5.552	0.4133		0.976	2.250	0.256	
Mustard Stalk				0.833	2.651	0.5174		0.934	1.030	0.313	
Spent Tea Leaves	Raw	Basic Red 46	25 ^o C	0.890	4.5×10 ⁻³	0.00376		0.990	36.000	0.355	(Özbaş <i>et al.</i> 2013)
Spent Tea Bags				0.990	0.011	0.00487		0.880	21.00	0.278	
Date Palm Seed	H ₃ PO ₄	Methylene Blue	30 ^o C	0.910	455	0.0166	0.131	0.9901	50.000	0.153	(Reddy <i>et al.</i> 2013)

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 <i>et al.</i> 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 ₃ PO ₄	Reactive Red	28°C	0.990	181.94	N/A	0-1	N/A			(Senthilkumaar <i>et al.</i> 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 <i>et al.</i> 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, H₃PO₄ and HNO₃ 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 (H₂SO₄, H₃PO₄, HNO₃) 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

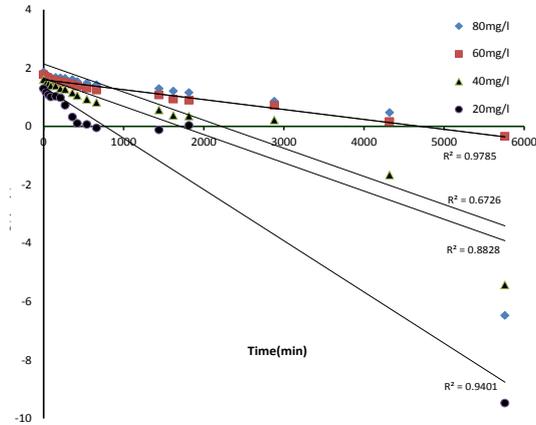


Fig. 6 Pseudo-first-order kinetics for adsorption of AY36 adsorption by TAC at $29\pm 1^\circ\text{C}$

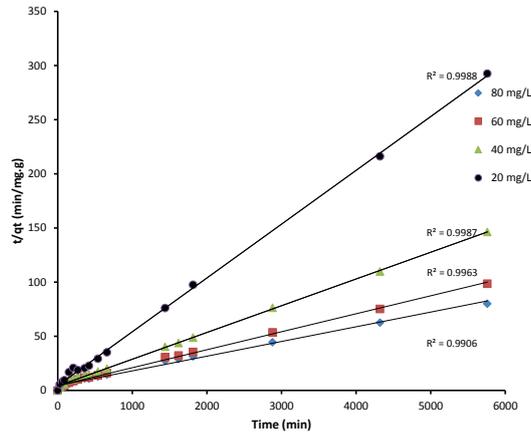


Fig. 7 Pseudo-second-order kinetics for adsorption of AY36 on TAC at $29\pm 1^\circ\text{C}$

directly affect to the correlation coefficients of the Langmuir and Freundlich isotherms (Singh *et al.* 2003).

Kinetics describes the rate of reaction in different physiochemical processes. In the case of adsorption, it shows the rate of adsorbate combined onto adsorbent and subsequently governs the residence time of adsorption process. The parameters of kinetics are very important for the prediction of adsorption rate as well as in large scale applications. Two kinetic models namely pseudo-first order and pseudo-second order models were checked in this study since they have been used extensively for adsorption studies (AL-Aoh *et al.* 2013, Aljeboree *et al.* 2014).

The linear form of equation and parameters involved in pseudo-first order model are given as follows.

$$\log(q_e - q_t) = \log q_e - k_1 \frac{t}{2.303} \quad (5)$$

Where k_1 is the rate constant of adsorption and q_e and q_t represent the amounts of AY36 adsorbed (mg/g) at equilibrium and at time t (min), respectively. Linear plots of $\log(q_e - q_t)$ versus time, t , with respect to AY36 adsorption onto RTAC are shown in Fig. 6.

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.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

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 R² 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 R² and low SES % represents the best goodness of fit of the model (Table 2).

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

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

beginning was low and it was increased at the end. Maximum adsorption (71.97 mg/g) was recorded at 96 h at $29 \pm 1^\circ\text{C}$. Low pH values significantly enhance the dye adsorption (pH=2; 78.27 mg/g) while it reduces at high pH levels indicating the competition in between OH^- ions and AY36 molecules for adsorption sites in RTAC. In the modeling of adsorption, it was found that Langmuir isotherm model clearly explains the dye adsorption, favorably, by RTAC. Moreover, the rate of adsorption followed the pseudo-second order kinetic model at studied dye concentrations. Based on the results obtained in this study, it can be concluded that RTAC can be used for the adsorption of textile dye. However, further studies on the adsorption of different environmentally sensitive chemical compounds such as heavy metals, agrochemicals and different dyes by RTAC under different conditions are necessary to find out the most effective conditions for the preparation of effective refused tea activated carbon.

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