Journal of Advanced Scientific Research

Available online through http://www.sciensage.info

ISSN
0976-9595
Research Article

MEASUREMENT OF ADSORPTION DYNAMICS OF REACTIVE RED DYE ONTO ACID AND BASE SURFACE MODIFIED ACTIVATED CARBON PREPARED FROM BARK OF *THESPESIA POPULNEA*

H. Sivasankari[1], K. Ramesh*[1], A. Rajappa[2]

[1]Department of chemistry, Poompuhar College (Affiliated to Bharathidasan University), Melaiyur, Nagapattinam, India
[2]Department of chemistry, Sri Manakula Vinayagar Engineering College, Madagadipet, Puducherry, India
**Corresponding author: rameshchem82@gmail.com*

ABSTRACT

The activated carbon from *Thespesia populnea* barks were prepared using orthogonal array experimental design method with the parameters such as microwave radiation power, radiation time and concentration of H_3PO_4 solution. Optimized conditions were found to be, radiation power 850W, radiation time 15 min, 50 % of H_3PO_4 and impregnation time 24 hours. Carbon prepared was designated as TPBC (*Thespesia Populnea* Bark Carbon). Ten (10) g TPBC was impregnated with 25% concentrations of hydrochloric acid and sodium hydroxide solution separately and heated in a microwave oven (radiation power 850 W, radiation time 10 min) to improve the structural characteristics of the adsorbents for enhanced reactive red dye removal. The other two carbons were designated as A20TPBC and B20TPBC. Influence of the parameters such as initial dye concentration and temperature on adsorption was studied. Batch mode adsorption experiments were carried out for the removal of Reactive Red dye (RR dye) from aqueous solution using TPBC, A20TPBC and B20TPBC. Influence of the parameters such as dose of the adsorbent, agitation time, initial dye concentration, pH of the solution on adsorption were studied. Kinetics of the system was studied with linearized forms of Legergren, Ho and Webber Morris models. The MSSE result revealed that present system followed pseudo second order kinetics equation with the intra particle diffusion as the rate determining step.

Keywords: Adsorption, H_3PO_4 activated microwave carbon, pH effect, Reactive Red dye, Kinetics.

1. INTRODUCTION

Water is one of the most indispensable expedients and is the elixir of life. It is a unique substance, because it can naturally renew and clean itself. It plays an important role in the world economy, as it functions as a universal solvent [1]. Water is probably the only natural resource to touch all aspects of human civilization from cultural and industrial development to the religious value embedded in the society [2]. Heavy metals and dyes which are of concern as major water pollutants all over the world, which arise from many industries like tanning, battery, electroplating, paper, sugar mills, petro-chemical, agrochemicals, distilleries, leather processing, pesticide manufacturing, textile, paper and pulp, dye industries, pharmaceutical industries, and Kraft bleaching industries, etc. [3-4]. Colour stuff discharged from industries poses certain hazards and environmental problems. The coloured compounds are easily discernible even if present in minute quantities (less than 1 ppm) which are not only aesthetically displeasing but also impeding light penetration into the water and thereby decreasing the efficiency of photo-synthesis in aquatic plants and hence having adverse impact on their growth [5-6].

The main objectives of the present investigations were to prepare activated carbons from barks of *Thespesia populnea* using microwave radiation with orthogonal array experimental design method. The study also aimed to optimize various experimental parameters to get an efficient carbon as an adsorbents and adsorbing behaviour of the prepared carbon with Reactive Red Dye.

2. MATERIAL AND METHODS

2.1. Preparation of Adsorbents

The small pieces of dried barks were powdered in a pulveriser. Twenty five (25) g of the powdered bark was mixed with 100 mL of phosphoric acid solution of desired concentration (25, 50 and 75 %). To ensure the access of the H_3PO_4 to the *Thespesia populnea* bark, the slurry was kept at room temperature for 24 hours. The slurry was placed to microwave heating (450, 600 and

850 watts and 10, 12 and 14 minutes) for simultaneous carbonization and activation. The carbonized samples were washed with cold distilled water followed with 0.5 M HCl, hot distilled water and cold distilled water until the pH of the washings reached to 7. The carbon was filtered and dried at 425 K. Adsorption of *Thespesia populnea* bark carbon with H_3PO_4 generates more interspaces between carbon layers to more surface area and micro porosity. The increase in porosity with H_3PO_4 activation suggests that the porosity created by this reactant is due to spaces left by H_3PO_4 after the corresponding washing. H_3PO_4 activation causes electrolytic action termed as swelling in the molecular structure of cellulose, which leads to the breaking of lateral bonds in the cellulose molecules resulting in increased inter and intra voids. Totally 27 numbers of activated carbons were prepared by varying preparation parameters. The carbon showing maximum percentage removal was chosen for further adsorption study and designated as TPBC (*Thespesia Populnea* Bark Carbon). Ten (10) g of the prepared carbons were mixed with 20% solutions of HCl and NaOH and placed in a microwave oven for 10 minutes. The carbons were again washed with hot distilled water and cold distilled water and designated as A20TPBC and B20TPBC (HCl 20% *Thespesia Populnea* Bark carbon and NaOH 20% *Thespesia Populnea* Bark carbon) [7-8].

2.2. Preparation of stock Solution

AR grade chemicals were used as such. The Reactive red dye (RR dye) solution was prepared in double distilled water to a concentration of 1000mg/L. The experimental solutions were prepared by proper dilution.

2.3. Adsorption experiments

Pre-determined dose of the adsorbent and pre-determined concentration of the 50 mL adsorbate solution was taken in 250 mL iodine flask with pH of the solution brought to 2 by adding concentrated HCl. The content of the flask was agitated using rotary shaker with 200 rpm for pre-determined duration. One ml of aliquot was taken from sample and diluted to 25 ml by double distilled water, adsorbents were then separated by centrifugation and percentage removal of the RR dye from the solution was calculated by the mass balance relationship. To study its effect, pH were brought to 2 to 10 by adding dil. HCl and 6 N NaOH. Kinetic experiments were performed with the working pH 7 and for contact times 5, 10, 20, 40, 60, 80, 100, 120 and 140 minutes [9-10].

3. RESULTS AND DISCUSSION

3.1. Effect of adsorbent dosage

The adsorption of RR dye onto TPBC, A20TPBC and B20TPBC were studied by varying the dose of the adsorbent from 10 mg/50 mL to 50 mg/50 mL by taking 20mg/L to 50 mg/L of the RR dye respectively. The percentage of removal of adsorbate from aqueous solution increased with an increase of carbon dose in all the cases (fig. 1). This is due to increased carbon surface area and availability of more adsorption sites. Based on the results, the remaining parts of the experiments were carried out with the adsorbent dose of 20 mg/50 mL of adsorbate solution for RR dye solution was used for the adsorption onto TPBC, A20TPBC and B20TPBC [11].

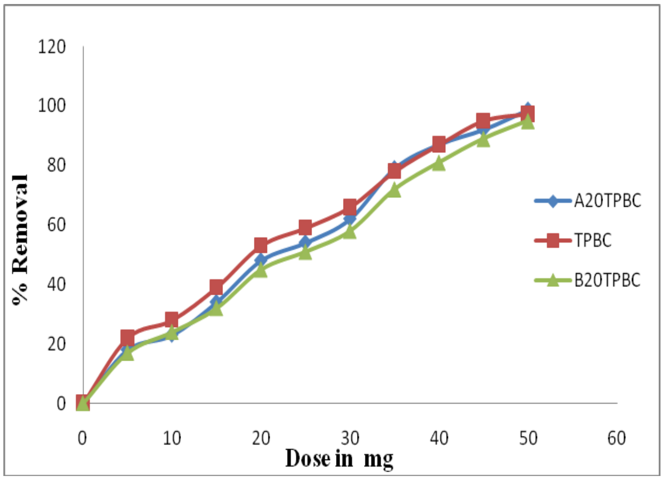

Fig. 1: Effect of Dose for RR dye onto TPBC, A20TPBC & B20TPBC

3.2. Effect of contact time

The effect of contact time on the percentage removal of RR dye from aqueous solution was studied by taking 20 mg/L, 30 mg/L, 40 mg/L and 50 mg/L solutions as initial concentrations for TPBC, A20TPBC and B20 TPBC (fig.2 to 4) [12].

3.3. Effect of pH

pH of the solution determines the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate, which affects the adsorption of RR dye on TPBC, A20TPBC and B20TPBC. Moreover, the hydrogen ion and hydroxyl ion are adsorbed strongly and subsequently decreases the adsorptions of other ions. The relationship between the initial solution pH and dye removal was illustrated in Fig. 5.

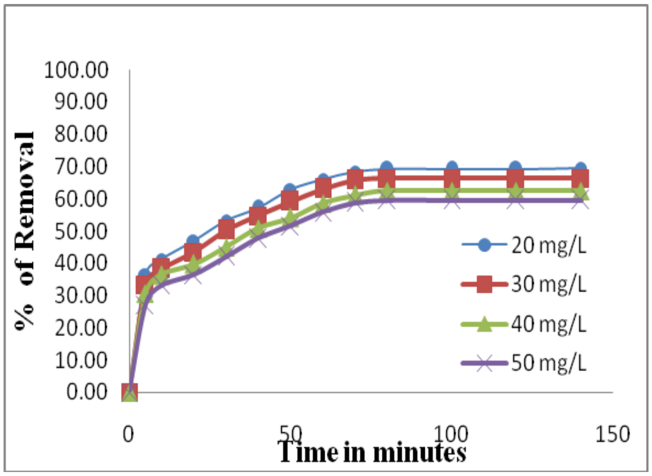

Fig. 2: Effect of contact time for RR Dye onto TPBC

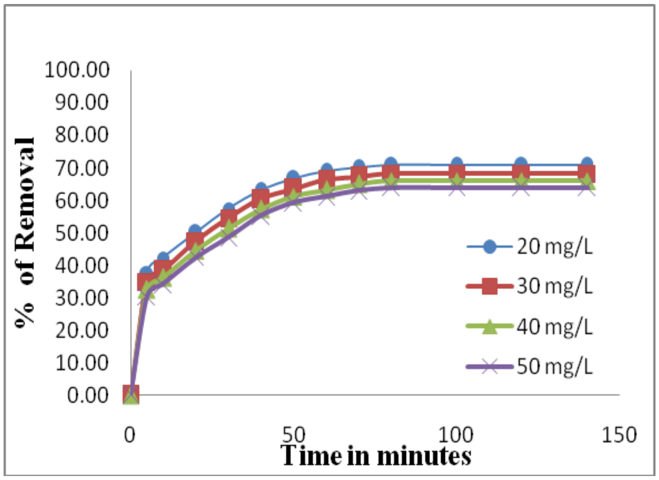

Fig. 3: Effect of contact time for RR Dye onto A20TPBC

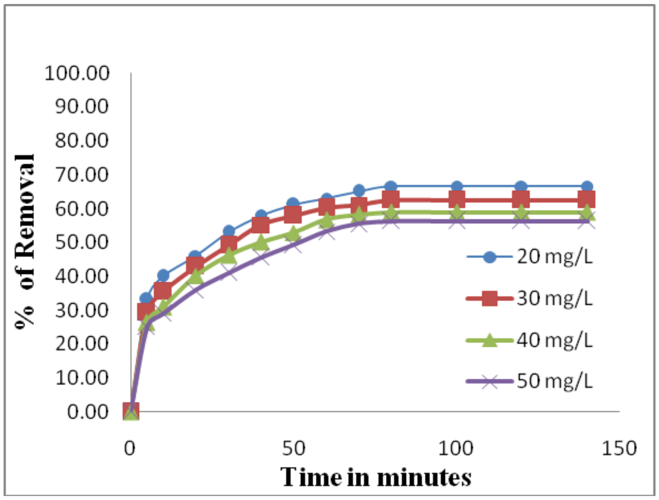

Fig. 4: Effect of contact time for RR Dye onto B20TPBC

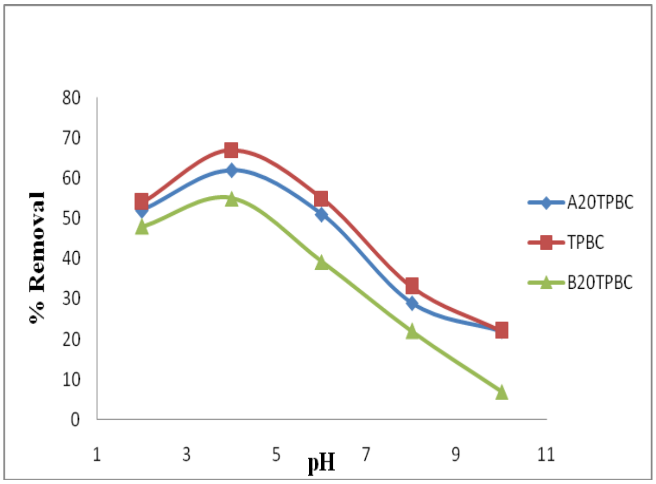

Fig. 5: Effect of pH

The removal percentages of three reactive dyes were maximum at acidic pH range of 2.0-4.0 and decreased with further increasing of pH. Similar optimal pH range that maximized the removal efficiency of reactive dyes was reported earlier. Further adsorption experiments were carried out at optimum pH of 4.0. Generally, electrostatic interaction between prepared carbons and dye molecules was the main force controlling the adsorption process. The protonated groups of activated carbon were mainly carboxylic group (-CO-), phenolic ($-OH^{2+}$) and chromenic groups. The de-protonated groups of reactive dyes were probably the sulphonate groups ($-SO^{3-}$). In the pH range of 2.0-4.0, the surface of prepared carbons were negatively charged (pH zpc=6.0) and reactive dyes were positively charged. The strong electrostatic attraction favoured the adsorption of reactive dyes onto prepared carbons, resulting in the high removal efficiency of dyes. When solution pH was less than 5, the sulphonate groups of the reactive dyes were almost protonated (SO_3H, *i.e.*, neutral). Furthermore, the protonation of nitrogen atoms, especially those not involved in aromatic systems, was also probable. The reactive dye molecules, therefore, are natural or positive charged in acidic solution. Subsequently, the attraction between reactive dyes and prepared carbons decreased, resulting in the slightly decreasing of dye removal. The low dye removal at highly basic solution could be due to the strong repulsion interaction between the negatively charged prepared carbons and the deprotonated reactive dye molecules. At the same time, hydroxide ion concentration increased with the incremental solution pH, and it could be adsorbed preferentially on the surface of the activated carbon. There was competition between OH^{-} (at high pH) and dye ions for positively charged adsorption sites. These results could be decreased evidently the removal efficiency of reactive dyes [13-14].

3.4. Kinetics Studies

Sorption kinetic models have been proposed to clarify the mechanism of sorption from aqueous solution to on an adsorbent. Several adsorption kinetic models have been established to understand the adsorption kinetics and rate-limiting step. These include pseudo-first and second-order rate model, Weber and Morris sorption kinetic models [15-17].

3.4.1. *Pseudo First order kinetics*

Legergren equation [15]

$\log (qe-qt)=\log qe - k1 /2.303 \times t$

Where qe and qt are the amounts of dye adsorbed (mg/g) at equilibrium and at time t (min), respectively and $k_1$is the rate constant of adsorption (l/min).

3.4.2. *Pseudo Second order kinetics*

Ho equation [16]

$t/qt = 1/ k_2.qe^2 +1/qe\ t$

The initial adsorption rate, h (mg/(g min)), as t⟶0 can be defined as $h = k_2qe^2$

The initial adsorption rate (h), the equilibrium adsorption capacity (qe), and the second-order constants k_2 (g/(mg.min)) can be determined experi-mentally from the slope and intercept of plot of t/qt versus t.

3.4.3. *Intra particle diffusion*

Weber-Morris equation [17]

$qt = kpt1/2 + C$

Where kp is the intra-particle diffusion rate constant, a plot of qt versus $t_{1/2}$ should be a straight line with a slope kp

Which is the rate constant for intra particle diffusion and intercept C is the thickness of the boundary film.

3.4.4. *Test for kinetics models*

The sum of error squares is given as follows;

$MSSE = \sqrt{\Sigma}[(qe)exp-(qe)cal]2/ N$

Where N is the number of data points, (qe)exp is the experimental qe, (qe)cal is the calculated qe [18].

In practice, kinetic studies were carried out in batch reactions using various initial sorbate concentrations. Sorption kinetic models have been proposed to clarify the mechanism of sorption from aqueous solution to on an adsorbent. Several adsorption kinetic models have been established to understand the adsorption kinetics and rate-limiting step. These include pseudo-first and second-order rate model, Weber and Morris [19] sorption kinetic models. The first order rate constant, k_1 (min^{-1}) ranged from 0.0267 to 0.0412. The pseudo first order theoretical adsorption capacity (qe_{cal}) values, obtained from the intercept of the linear plots, were compared with the experimental adsorption capacity (qe_{exp}) values. The initial sorption rate h increases directly with theincrease of initial RR dye concentration at each temperature for all the three carbons, while an inverse relationship exists between the overall sorption rate and initial RR dye concentration for all the three carbons.

The analysis of the results obtained in the present study with two kinetic models is presented in table 1 & 2 and shown in figs. 6 to 11.

Table 1: First order Kinetic parameters for the removal of RR dye onto adsorbents

Adsorbents	Concentration mg/L	K_1 min^{-1}	q_e(Cal) mg/g	q_e(Exp) mg/g	R^2	MSSE
TPBC	20	0.0295	11.6547	13.86	0.9922	4.97
	30	0.0283	7.5980	19.92	0.997	
	40	0.0269	14.5881	25.00	0.9691	
	50	0.0267	18.4162	29.82	0.9752	
A20TPBC	20	0.0412	1.0000	14.20	0.985	5.63
	30	0.0408	8.6517	20.45	0.9851	
	40	0.0382	17.1989	26.37	0.9865	
	50	0.0375	21.4585	31.96	0.9786	
B20TPBC	20	0.0295	12.6794	13.31	0.9857	4.07
	30	0.0378	8.1339	18.73	0.9904	
	40	0.0378	15.9993	23.60	0.9993	
	50	0.0302	18.4672	28.18	0.9972	

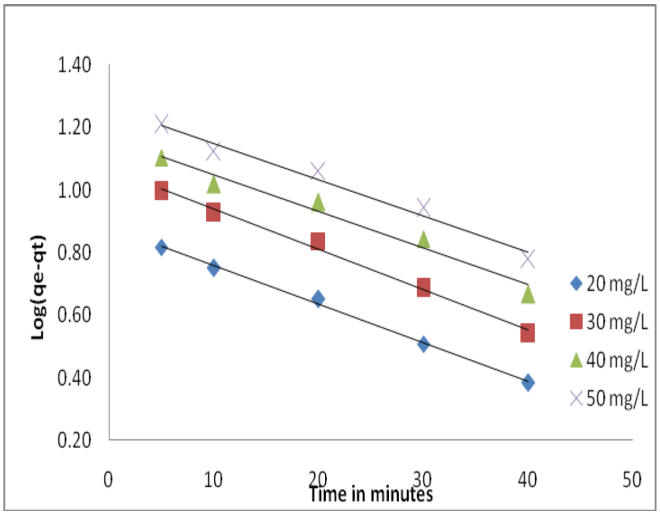

Fig. 6: Lagergren plot for RR Dye onto TPBC

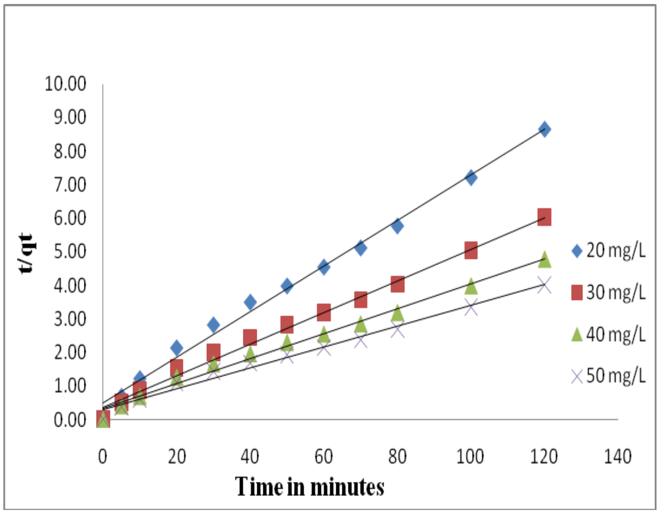

Fig. 9: Ho plot for RR Dye onto TPBC

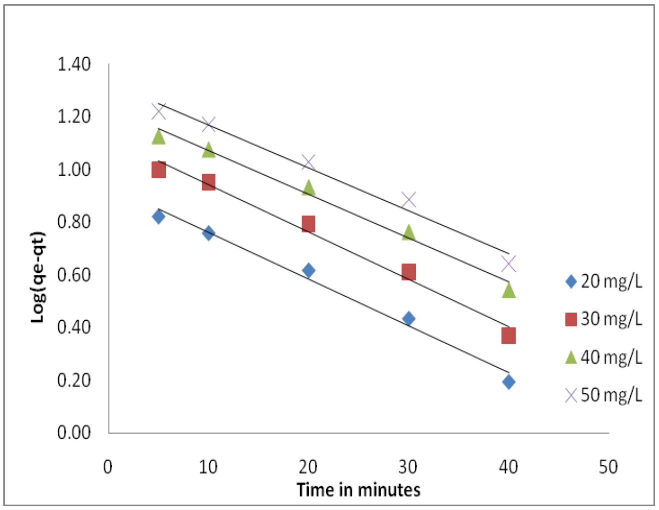

Fig. 7: Lagergren plot for RR Dye onto A20TPBC

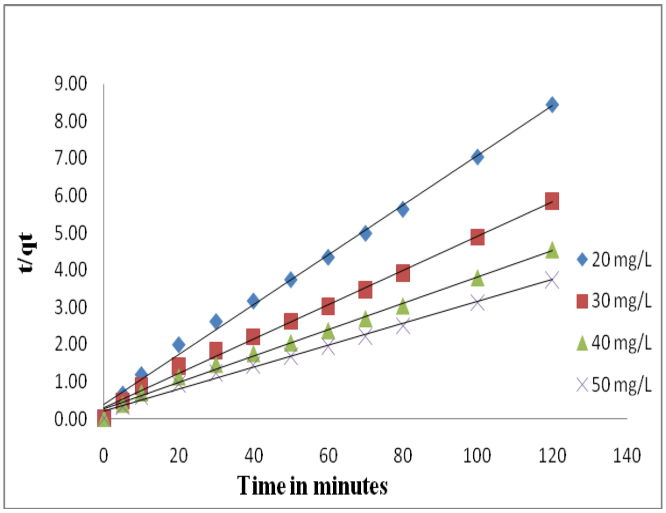

Fig. 10: Ho plot for RR Dye onto A20TPBC

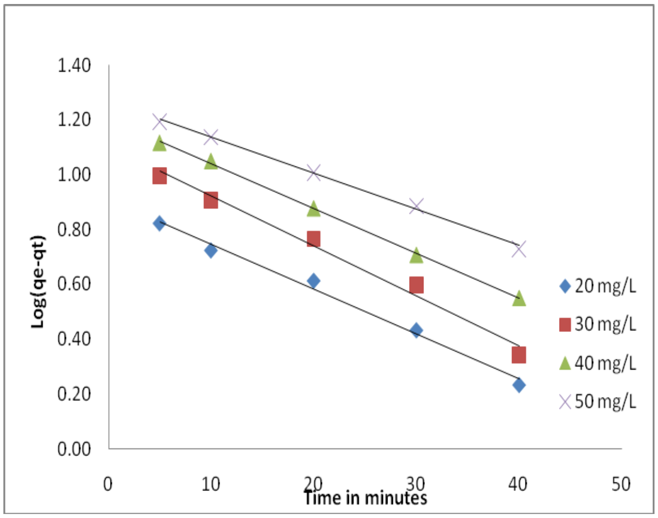

Fig. 8: Lagergren plot for RR Dye onto B20TPBC

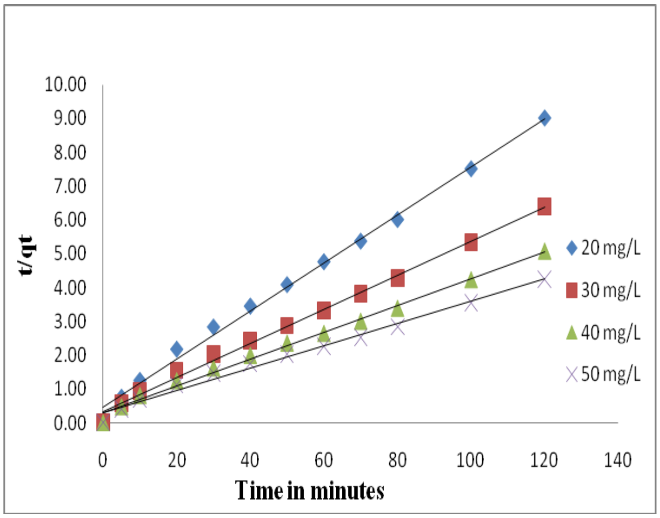

Fig. 11: Ho plot for RR Dye onto B20TPBC

Table 2: Second order Kinetic parameters for the removal of RR dye onto adsorbents

Adsorbents	Concentration mg/L	$k_2 \times 10^{-4}$ g/mg.min	q_e(Cal) mg/g	h	R^2	MSSE
TPBC	20	0.0096	14.6843	2.07	0.9926	0.82
	30	0.0061	21.2314	2.75	0.9914	
	40	0.0044	26.7380	3.15	0.9889	
	50	0.0033	32.1543	3.44	0.9868	
A20TPBC	20	0.0114	14.9701	14.20	0.9956	0.77
	30	0.0072	21.6450	20.45	0.9949	
	40	0.0051	28.0112	26.37	0.9938	
	50	0.0039	34.1297	31.96	0.9928	
B20TPBC	20	0.0109	14.0449	13.31	0.995	0.77
	30	0.0074	19.8807	18.73	0.9948	
	40	0.0051	25.2525	23.60	0.9932	
	50	0.0036	30.3951	28.18	0.989	

Between the first order and second order, second order kinetic model seems to best describe the above adsorption system as it has R^2 value which was very close to unity. Moreover, the difference between calculated adsorption capacity (qe_{cal}) and experimental adsorption capacity (qe_{exp}) values of second order is little when compared to the first order kinetic model. Statistically it is tested with the toolmean sum of error squares (MSSE) [20]. The Kp values were found to increase with an increase of RR dye concentration that reveals the rate of adsorption governed by the diffusion of adsorbed RR dye within thepores of the adsorbent, which were given in table 3 and shown in figs. 12 to 14. Present results show that pore diffusion limits the overall rate of RR dye adsorption [21].

Table 3: Intra Particle diffusion parameters for the removal of RR dye onto adsorbents

Adsorbents	Concentration mg/L	Kp (mg/ g.min)	R^2
TPBC	20	1.1938	0.994
	30	1.7887	0.9978
	40	2.2877	0.9945
	50	2.9313	0.9988
A20TPBC	20	1.2881	0.9944
	30	1.8828	0.9899
	40	2.5942	0.9975
	50	3.2844	0.9960
B20TPBC	20	1.1786	0.99901
	30	1.7755	0.9903
	40	1.9711	0.9892
	50	2.5685	0.9992

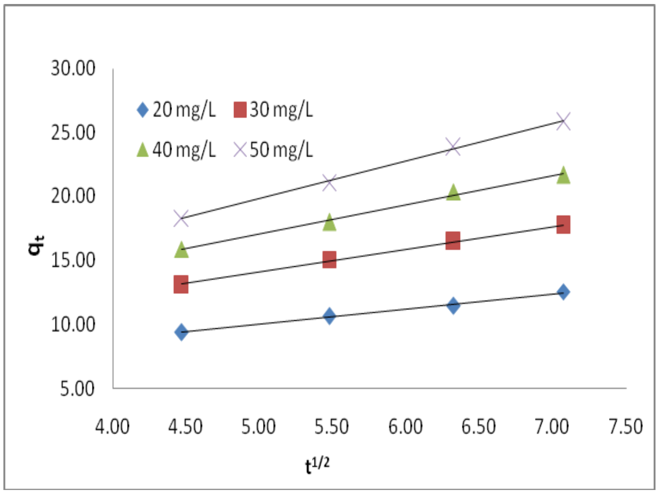

Fig. 12: Weber and Morris plot for RR Dye onto TPBC

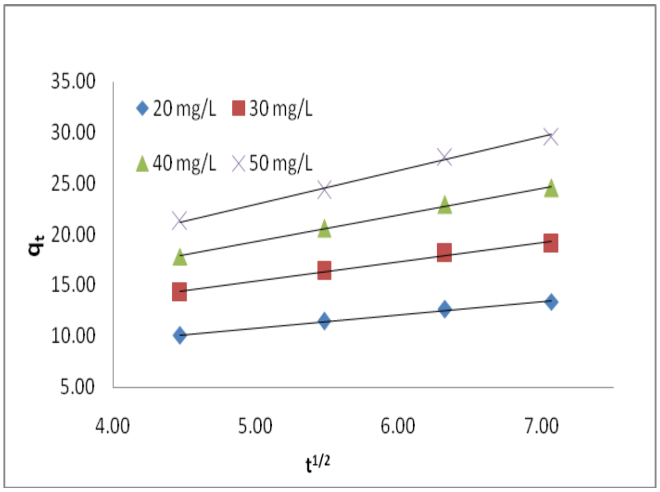

Fig. 13: Weber and Morris plot for RR Dye onto A20TPBC

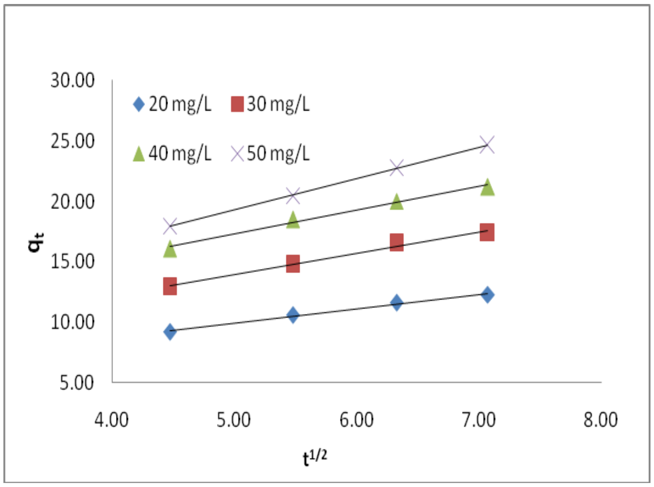

Fig. 14: Weber and Morris plot for RR Dye onto B20TPBC

4. CONCLUSION

In the present study microwave assisted Phosphoric acid activated carbon (TPBC) and acid and base surface modified carbons (A20TPBC & B20TPBC) were prepared and investigated its potential to abate chosen adsorb ate Reactive Red dye (RR dye) from aqueous solution. The adsorption of reactive red dyes onto all the three carbons were a pH-dependent process with the maximum removal efficiency at the initial pH of 4. Theoretically evaluated quantity adsorbed at equilibrium from first order and second order rate equations were compared with the quantity adsorbed at equilibrium in the actual experiments. The statistical tool 'Summation of error square test' revealed that present studied alladsorbent-adsorbate system followed second order kinetics. The variation of kp values was proportional to the initial adsorbate concentrations which indicates that the intra-particle diffusion limits the rate of the process. Then adsorption is controlled by particle diffusion and the diffusion of the dye ions to the adsorbent surface is independent of the initial concentration of the RR dye, if it is not a straight line, then it indicates that the sorption process is controlled by film- diffusion. For intra particle diffusion R^2 value nearly equal to 1 shows that the intra-particle diffusion limits the rate of the process.

Conflict of interest

None declared

5. REFERENCES

1. Sharma S, Bhattacharya A, et al. *Applied Water Science*, 2017; **7(3)**:1043-1067.
2. Raymond A, Wuana and Felix E, Okieimen, et al. *International Scholarly Research Notices*, 2011; **2011 (1):**1-20**.**
3. Shenai VA, Chemistry of dyes and Principles of dyes, 2nd ed, SevakPublications, Mumbai, India, 1983; **2**:41.
4. Dinesh Mohan, Kunwar P, Singh and Vinod K, Singh, et al. *Industrial & Engineering Chemistry Research*, 2005; **44(4):**1027-1042.
5. Ahmed I, Osman, Adel Abdel kader, Charlie Farrell, David Rooney, Kevin Morgan, et al. *Fuel Processing Technology*, 2019;**192(31):**179-202.
6. Srinivasakannan C, Mohammad El-Mootassem K, Suresh Kumar Reddy, Ahmed Al Shoaibi, et al. *Journal of Materials Science and Chemical Engineering*, 2018; **6(7)**:17.
7. Ramesh K, Rajappa A, Nandhakumar V, et al. *Z. Phys. Chem*. 2017; **231(5):**1057-1076.
8. Ramesh K, Rajappa A, Nandhakumar V, et al. *Int. J. Res. Chem. Environ*., 2014; **4(3)**:1-9.
9. Makeswariand M, Santhi T, et al. *Journal of chemistry*, 2013; **2003(1):**1-12.
10. Namasivayam C, Sangeetha D, et al. *J. Colloid and Interface Science*, 2004; **280(2)**:359-365.
11. Venkatraman BR, Hema K, Nandhakumar V, Arivoli S, et al. *J. Chem. Pharm. Res*., 2011; **3(2)**: 637-649.
12. Arvind Kumar and Hara Mohan Jena, et al. *Journal of Environmental Chemical Engineering*, 2017; **5(2)**: 2032-2041.
13. Sivakumar P, Palanisamy PN, et al. *Int. J. Chem. Tech. Res*., 2009; **1(3):**502-510.
14. ArivoliS, Nandhakumar V, Saravanan S, Sulochana Nadarajan, et al. *The Arabian Journal for Science and Engineering*, 2009; **34(1A):**1-12.
15. Palanisamy PN, Agalya A, Sivakumar P, et al. *Indian Journal of Chemical Technology*, 2011; **20:** 245-251.
16. Ho YS, McKay G, *Can. J. Chem. Eng*., 1998; **76(4):** 822-827.
17. Weber W.J. Morris JC, et al. *J. Sanit. Eng. Div. ASCE*., 1963; **89 (SA2):**31-59.
18. McKay G, Ho YS, *Processe Bio chem*., 1999; **34:**451-465.
19. Abechi ES, Gimba CE, Uzairuand A, Kagbu JA, *Arch. Appl. Sci. Res*., 2011; **3(1):**154-164.
20. Freundlich HMF, *Z. Phys. Chem*., 1906; **57A:**385-470.
21. Hameed BH, Din ATM, Ahmad AL, et al. *J. Hazard. Mater*., 2006; **28(7):**819-25.