

Capacity of Activated Carbon Derived from Agricultural Waste in the Removal of Reactive Dyes from Aqueous Solutions

Mahboobeh Manoochehri^{1,✉}, V. K. Rattan², Ameneh Khorsand³ and Homayon Ahmad Panahi¹

¹Department of chemistry, Islamic Azad University, Central Tehran branch, Tehran, Iran

²Department of chemical engineering and technology, Panjab University, Chandigarh, India.

³Member of Young Researchers Club, Islamic Azad University, Central Tehran branch, Tehran, Iran

✉e-mail: mmanooch@yahoo.com

(Received January 8, 2010; Accepted May 30, 2010)

Abstract

The study describes the results of batch experiments on the removal of Reactive Yellow 15 (RY15) and Reactive Black 5 (RB5) from synthetic textile wastewater onto Activated Carbon from Walnut shell (ACW). The experimental data were analyzed by the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) models of adsorption. The experiments were carried out as function of initial concentrations, pH, temperature (303-333), adsorbent dose and kinetics. The surface area and pore volumes of adsorbent were measured by BET and BJH methods. The findings confirm the surface area (BET) is 248.99 m²/g. The data fitted well with the Temkin and D-R isotherms for RY15 and RB5, respectively. The most favorable adsorption occurred in acidic pH. Pseudo-second order kinetic model were best in agreement with adsorption of RY15 and RB5 on ACW. The results indicate that walnut shell could be an alternative to more costly adsorbent currently being used for dyes removal.

Keywords : *Reactive dyes, BET, BJH, Walnut shell, Isotherms*

1. Introduction

Many industry-produced wastewater contains different types of organic and inorganic pollutants [1]. Generally, the wastewater from printing and dyeing units in a textile plant is rich in color, containing residue of dyes and chemicals [2,3]. Moreover, dyes used may be toxic to aquatic organisms and can be resistant to natural biological degradation [4]. Active azo dyes have double bond of nitrogen to nitrogen (-N=N-), which is bonded to an aromatic group [5,6] so, they can produce harmful health effects and it is essential to have a proper method to remove this dyes from wastewater. As a result, the removal of color from waste effluents has become environmentally important [7-9]. Many researchers use cheap and ecofriendly adsorbents to substitute the more expensive, commercially available activated carbons. Such alternatives include: biosorbents, natural materials, agricultural waste and industrial by products [10-12]. Adsorption of organic pollutants onto solid/water interfaces has been found to be an efficient and economically cheap method compared to the other purification and separation methods [13]. This paper reports on the ability of Activated Carbon from Walnut shell (ACW) to remove Reactive Yellow 15 (RY15) and Reactive Black 5 (RB5) from aqueous solutions. The effect of pH, initial dye concentrations, temperature, kinetics and dose of ACW were investigated. The Langmuir, Freundlich, Temkin

and Dubinin-Radushkevich (D-R) were used to fit the equilibrium data. Pseudo first-order and pseudo second-order kinetic models were attempted.

2. Materials and Methods

2.1. Adsorbent

The walnut shell was obtained from local natural resources. After obtained, fresh walnut shells were washed several times with distilled water to remove surface impurities and then dried at room temperature for one day. The samples were heated and burned and the charcoals were crushed by grinder and then ground to pass through a 100-mesh sieve for further experiments. It was activated to a final temperature of 500°C in muffle furnace for six hours. Some physical and chemical properties of walnut shell were showed in Table 1. This was performed by the adsorption of N₂ at 77 K using Micrometrics Surface Area Analyzer (ASAP 2010, Micromeritics Inc., USA).

2.2. Adsorbate

RY15 (Reactive Yellow 15, C.I. 11859; chemical formula, C₄₈H₄₀N₁₃NaO₁₃S₃; Mw, 1172.13 g/mol) and RB5 (Reactive

Table 1. Physicochemical Properties of ACW

Parameters	values
• Surface Area	
BET Surface Area:	249 m ² /g
Langmuir Surface Area:	400 m ² /g
Single Point Surface Area at P/P ⁰ 0.30325457:	273 m ² /g
• Pore Volume	
Single Point Total Pore Volume of pores less than 768.3726 Å Diameter at P/P ⁰ 0.97414716:	0.153 cm ³ /g
• Pore Size	
Average Pore Diameter (4V/Å by BET):	24.6 Å
BJH Adsorption Average Pore Diameter (4V/Å):	52.1 Å
BJH Desorption Average Pore Diameter (4V/Å):	53.3 Å

Black 5, C.I. 20505; chemical formula, C₂₆H₂₁N₅Na₄O₁₈S₆; Mw, 975.82 g/mol) were used as the adsorbates in this study. They were all prepared from Alvan Saabet Company in Iran and used without any further purification. The chemical structures of RY15 and RB5, shown in Fig. 1. They have a maximum visible adsorbance at wavelengths of 415 nm for RY15 and 598 nm for RB5.

2.3. Adsorption studies

Adsorption of RY15 and RB5 were carried out by a batch technique in aqueous solutions and experiments were conducted to observe the effect of various parameters effect of pH, temperature, amount of adsorbent, initial dye concentrations and kinetics. Adsorption experiments were carried out at various concentrations of dye solutions in the range of 1 × 10⁻⁵ to 5.5 × 10⁻⁵ M by adding a fixed amount of ACW (1 g) to a series of 100 mL conical flasks. The conical

flasks were then placed in room temperature for 48 h and then filtered. The final concentrations of dyes were measured at maximum wavelengths of RY15 and RB5 using a single beam UV-Vis spectrophotometer (Shimadzu, UV1101, Japan). The amount of dye adsorbed onto the adsorbent, q_e (mol/g), was calculated by equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C₀ and C_e (mol/L) are the initial and equilibrium state dye concentrations, respectively. V is the volume of the solution (L) and W is the mass of adsorbent used (g).

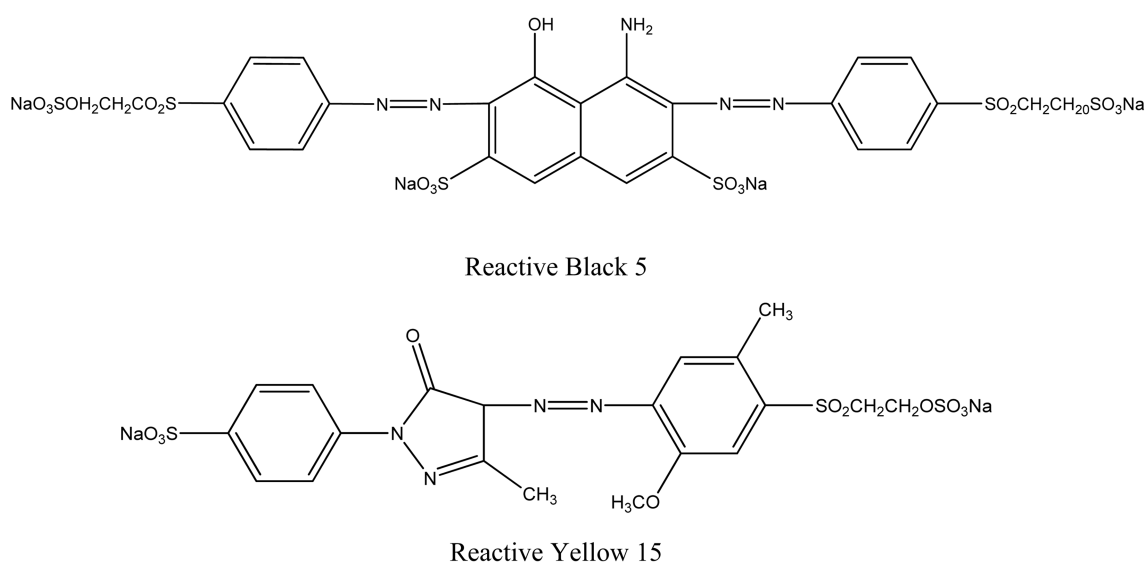
The effect of ACW dose on the amount of RY15 and RB5 adsorbed were studied by adding different amounts (0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.4 and 1.6 g) of ACW into amount of 100 mL conical flasks containing a definite volume of fixed initial concentration (3.5 × 10⁻⁵ M) of dye solutions. The flasks were placed in room temperature for 48 h and then dye concentrations were measured at equilibrium. The dye removal percentage was calculated using the following relationship:

$$\text{Removal percentage} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (2)$$

where C_i and C_f (mol/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively.

To study the effect of pH was studied by adjusting the pH of dye solutions using 1 M H₂SO₄ and 1 M NaOH solutions. The pH was measured using a pH meter (PB-11). Experiments were carried out using different initial solution pH values from 1 to 11.

To study the effect of temperature, 1 g sample of ACW was added to each 100 mL volumes of RY15 and RB5 aqueous solutions at different initial concentrations. The

**Fig. 1.** Structures of Reactive Black 5 and Reactive Yellow 15.

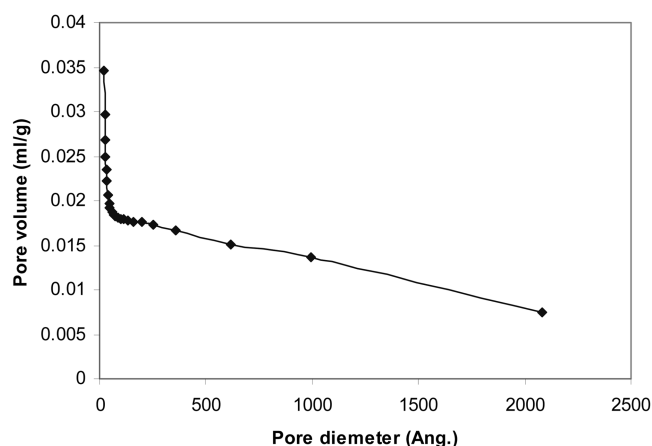


Fig. 2. Pore size distribution of ACW particles.

experiments were carried out at 303 to 333 K. Temperature control was provided by the water bath shaker units.

The kinetic studies were carried out using a mechanical stirrer. The adsorbance of all samples were determined at certain time intervals (5, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 min) during the adsorption process. The amount of adsorption at time t , q_t (mol/g) was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (3)$$

where C_t (mol/L) is the liquid-phase concentration of dye at any time.

3. Results and Discussion

3.1. Characterization of the prepared ACW

The pores in activated carbons are divided into three groups: the micropores with diameters less than 2 nm, mesopores with diameters between 2 and 50 nm, and macropores with diameters greater than 50 nm [14]. According to Table 1, the BJH results show that the pores are distributed on the ACW surface as follows: 13.64% (micropores), 77.77% (mesopores) and 8.59% (macropores). The BET surface area of the prepared ACW is 248.99 m²/g with a total pore volume of 0.153 cm³/g. Fig. 2 shows cumulative pore volume (cm³/g) vs. pore diameter (\AA). Interestingly, it becomes obvious from this figure that the pore volumes decrease as the pore diameters increase.

3.2. Effect of adsorbent dose on dyes adsorption

To optimize the adsorbent dose for the removal of RY15 and RB5 from aqueous solutions, adsorption was carried out with different adsorbent dosage at room temperature. Fig. 3 shows the effect of ACW dose on the removal percentage of

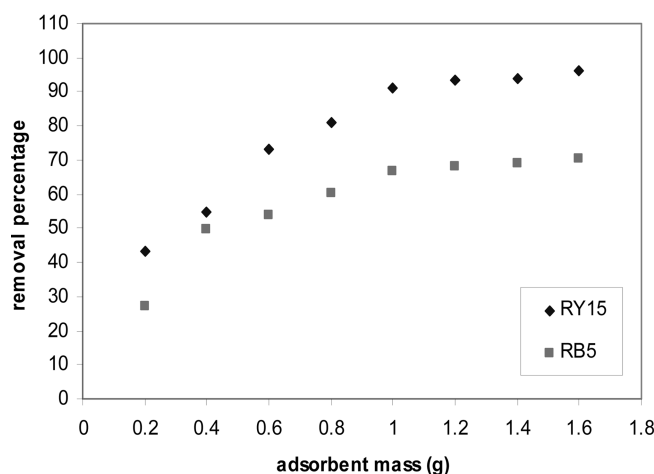


Fig. 3. Effect of adsorption dosage on adsorption of both dyes.

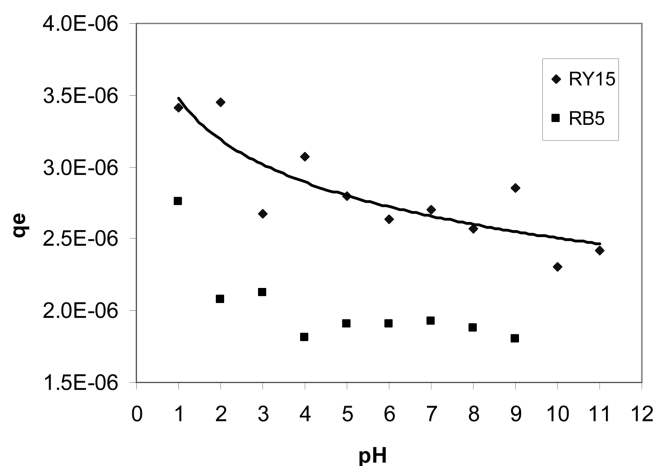


Fig. 4. Effect of pH on the adsorption of both dyes.

RY15 and RB5. It was observed that the removal of RY15 and RB5 increase up to 1 g and then it remain almost constant. The increases in colors removal percentage were duo to the increases of the available sorption surface and availability of more adsorption sites. A similar behaviour was reported for the adsorption of methylene blue on peanut hull [15].

3.3. Effect of pH

The influence of pH on adsorption of the two dyes is shown in Fig. 4 and the maximum removal was achieved at pH 1. In acidic condition, the positive charge dominates the surface of the adsorbent. Thus a significantly high electrostatic attraction exists between the positively charged surface of the adsorbent and negatively charged dye species. This attractive force increases the adsorption chances of dye species onto the surface of the adsorbent. The lower pH

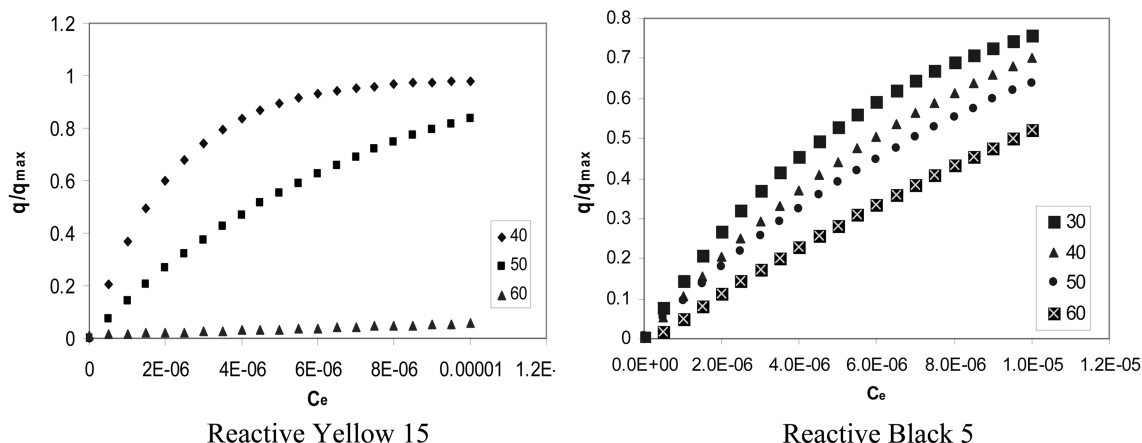


Fig. 5. Effect of temperature on the adsorption of both dyes (values in the box is in °C).

negatively charged surface site on the adsorbent did not favour the adsorption of RY15 due to electrostatic repulsion but, adsorption of RB5 shows the percent removal remained constant in pH=9-5. A similar result was observed for the adsorption of acid red 14 by soy meal hull [16] and removal of acid dyes using a biosorbent [17].

3.4. Effect of temperature

In order to observe the effect of temperature batch adsorption studies were carried out with both dyes. Adsorptions of both dyes were measured at various temperatures (303~333 K). Fig. 5 shows a decrease in adsorption with an increase in solution temperature. Therefore, adsorption of both studied dyes were exothermic and chemisorption in nature.

3.5. Isotherms modelling

The adsorption data obtained for equilibrium conditions have been analyzed by using the linear forms of the Langmuir, Freundlich, Temkin and D-R isotherms. The Langmuir adsorption isotherm (Eq. (4)), is based on the assumption [18] that adsorption takes place at specific homogeneous sites within the adsorbent and once a dye molecule occupies a site, no further adsorption take place at that site. The Freundlich isotherm (Eq. (5)), is an empirical equation employed to describe heterogeneous systems [19]. The Temkin equation (Eq. (6)), suggests a linear decrease of sorption energy as the degree of completion of the sorptional centres of an adsorbent is increased. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbent-adsorbate interactions [20]. The D-R isotherm model [21] does not assume a homogeneous surface or constant sorption potential. It was applied to estimate the porosity apparent free energy and the characteristic of adsorption and it has commonly been applied in the following form Eq. (7) and ε is the Polanyi

potential that can be calculated from Eq. (8).

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{k_L q_{\max} C_e} \quad (4)$$

$$\text{Log} q_e = \text{Log} K_F + \frac{1}{n} \text{Log} C_e \quad (5)$$

$$q_e = B \ln A + B \ln C_e \quad (6)$$

$$\ln q_e = \ln Q_m - K \varepsilon^2 \quad (7)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (8)$$

where q_e is the amount of dye adsorbed on ACW at equilibrium (mol/g), C_e the equilibrium concentration of dye solution (mol/L), K_L the Langmuir equation constant (Lit/

Table 2. Comparison of the Coefficients Isotherm Parameters by RY15 and RB5 Adsorption Onto ACW

Isotherm models	RY15	RB5
Langmuir		
q_{\max}	1×10^{-5}	2.770×10^{-6}
K_L	$1.496 \times 10^{+4}$	$1.756 \times 10^{+4}$
R^2	0.9481	0.9282
Freundlich		
K_F	1.928×10^{-3}	1.293
n	1.555	0.792
R^2	0.9230	0.9274
Temkin		
A	148.413	148.413
b	$1.238 \times 10^{+98}$	$6.193 \times 10^{+}$
R^2	0.9627	0.9807
D-R		
K	1×10^{-17}	3×10^{-17}
Q_m	2.424×10^{-6}	2.545×10^{-6}
R^2	0.9516	0.9829

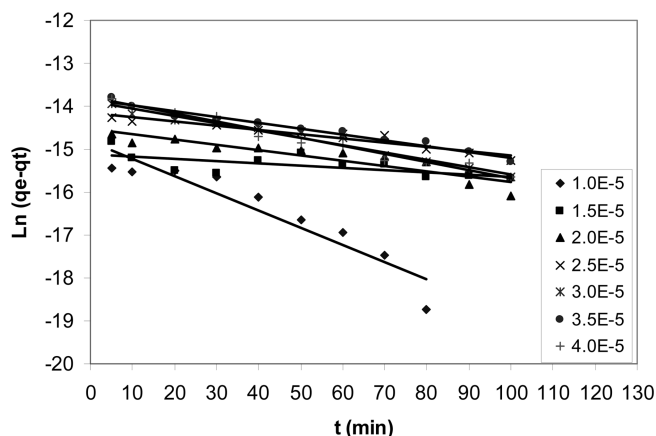


Fig. 6. Fitting of pseudo-first order model for RY15 on ACW different initial concentration.

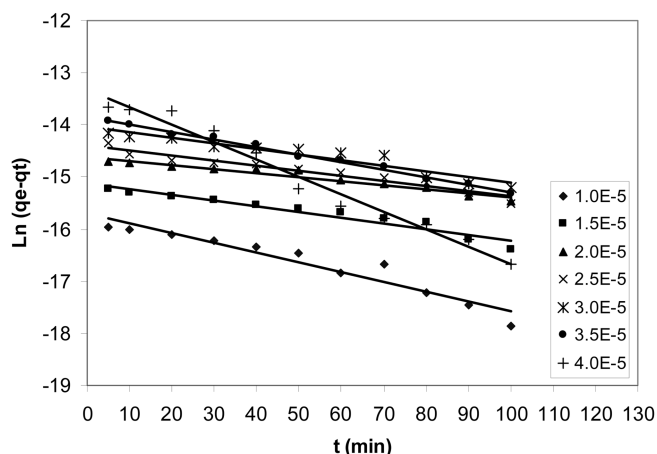


Fig. 7. Fitting of pseudo-first order model for RB5 on ACW different initial concentration.

mol), q_{\max} is the maximum adsorption capacity (mol/g), K_F is adsorption capacity unit concentration, $1/n$ is adsorption intensity, $B = \frac{RT}{b}$, R is the gas constant, b is Temkin isotherm constant, T is the absolute temperature (K), A is the Temkin isotherm constant (L/mol), K is a constant related to the adsorption energy (mol^2/J^2), Q_m is the theoretical saturation capacity (mol/g) and ε is the Polanyi potential. According to Langmuir, Freundlich, Temkin and D-R plots for both dyes, empirical constants to be determined from the intercept and slope of the linear regression. A list of the parameters obtained together with R^2 values are given in Table 2. The results indicate that the Temkin model is the best fit model for the adsorption of RY15 onto ACW and D-R model resulted into the best fit the other isotherms for RB5.

3.6. Adsorption kinetics

In order to examine the controlling mechanism of the adsorption process, pseudo-first order and pseudo-second order equations were used to test the experimental data. Pseudo-first order equation of Lagergren based on solid capacity is given by [22]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (9)$$

Where q_t is the amount of dye adsorbed (mol/g) at time t , k_1 the equilibrium rate constant of pseudo-first order kinetics (min^{-1}) and t is the constant time (min). According to Eq. (9) the plots of $\ln(q_e - q_t)$ vs. t (Figs. 6 and 7) for the

Table 3. Kinetics Constants for Pseudo-first and Pseudo-second Order Models

Dye types and		pseudo-first order			pseudo-second order		
$C_0 \times 10^5$ (M)	$q_{e, \text{exp}} \times 10^{-6}$	$K_1 \times 10^{-3}$	R^2	$k_2 \times 10^{-3}$	$q_{e, \text{cal}} \times 10^{-6}$	R^2	
RY15							
1.0	0.997	5.4	0.8863	75.88	0.586	0.9975	
1.5	1.486	9.8	0.4308	86.02	0.807	0.9973	
2.0	1.982	12.3	0.826	95.03	1.171	0.9951	
2.5	2.475	13.5	0.9228	116.0	1.487	0.9954	
3.0	2.971	17.1	0.9703	219.8	1.844	0.9963	
3.5	3.387	18.7	0.9688	481.3	1.841	0.9980	
4.0	3.648	39.8	0.9713	557.7	2.253	0.9987	
RB5							
1.0	0.402	7.80	0.9278	38.00	0.204	0.9927	
1.5	0.900	9.90	0.9386	74.57	0.525	0.9953	
2.0	1.402	10.8	0.9425	95.17	0.745	0.9950	
2.5	1.887	10.9	0.9446	157.5	1.058	0.9965	
3.0	2.360	14.5	0.9036	198.2	1.419	0.9919	
3.5	2.790	18.6	0.9934	293.3	1.615	0.9966	
4.0	3.166	33.5	0.9740	435.2	1.745	0.9945	

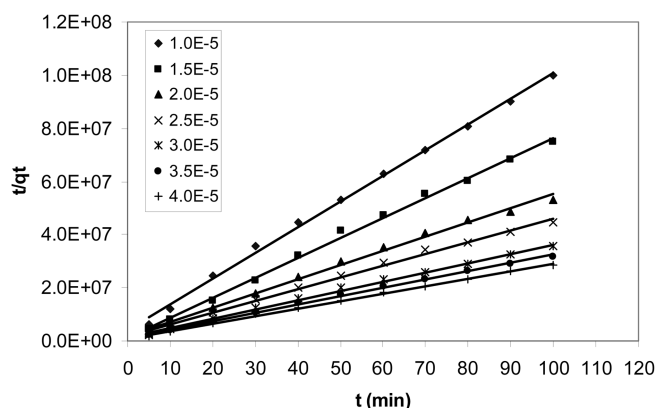


Fig. 8. Fitting of pseudo-second order model for RY15 on ACW different initial concentration.

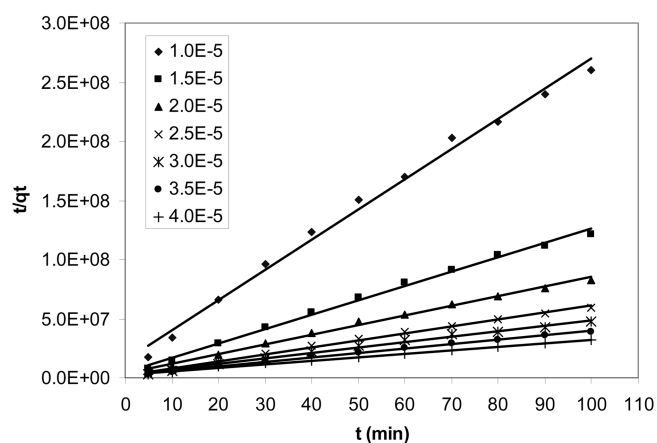


Fig. 9. Fitting of pseudo-second order model for RB5 on ACW different initial concentration.

adsorption of RY15 and RB5 onto ACW have also been tested to obtain the rate parameters. The k_1 and R^2 were calculated from these plots and are given in Table 3.

The pseudo-second order kinetic model [23] is based on adsorption equilibrium capacity and can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (10)$$

Where k_2 (g/mol min) is the rate constant for pseudo-second order adsorption. The intercept and slope of $\frac{t}{q_t}$ vs. t (Fig. 8 and 9) were used to calculate the pseudo-second order rate constant k_2 and q_e , respectively. These values are given in Table 3.

These results suggest that the adsorption of RY15 and RB5 on ACW may be best described by the pseudo-second order kinetic model with high correlation coefficients. The calculated q_e values also agreed well with the experimental data. The over all rate of the RY15 and RB5 adsorption

process are most likely to be controlled by the chemisorption process for ACW. Similar results have been observed in the adsorption of acid red 57 onto calcined alunite [24,25].

4. Conclusion

This study indicates that walnut shell was an effective adsorbent for removal of RY15 and RB5. The data indicates that the adsorption kinetics of dyes on ACW followed the pseudo-second order rate expression and the most favorable adsorption occurred in acidic pH. By comparing the correlation coefficients determined for each linear transformation of isotherm analysis, the Temkin and D-R isotherm models, which fit the experimental data reasonably well, were found to provide the best prediction for the adsorbent of RY15 and RB5. The results of the present investigation indicated that ACW, a low-cost adsorbent could be employed as an alternative to commercial activated carbon for the removal of RY15 and RB5 from aqueous solutions.

References

- [1] Bauer, C.; Jacques, P.; Kalt, A. *J. Photochem. Photobiol. A: Chem.* **2001**, *140*, 87.
- [2] Chakraborty, S.; De, S.; Basu, J. K.; DasGupta, S. *Desalination* **2005**, *174*, 73.
- [3] Crini, G. *Bioresour. Technol.* **2006**, *97*, 1061.
- [4] Hameed, B. H. *J. Hazardous Materials* **2009**, *161*, 753.
- [5] Ambrosio, S. T.; Campos Takaki, G. M. *Biores. Technol.* **2004**, *91*, 69.
- [6] Osmá, J. F.; Saravia, V.; Couto, S. R. *J. Hazardous Materials* **2007**, *147*, 900.
- [7] Gupta, V. K.; Jain, R.; Varshney, S. *J. Hazardous Materials* **2007**, *142*, 443.
- [8] Sanghi, R.; Bhattacharya, B. *Color. Technol.* **2002**, *118*, 256.
- [9] Malik, P. K. *Dyes Pigments* **2003**, *56*, 239.
- [10] Han, R.; Ding, D.; Xu, Y.; Zou, W.; Wang, Y.; Li, Y. *Bioresour. Technol.* **2008**, *99*, 2938.
- [11] Sulak, M. T.; Demirbas, E.; Kobya, M. *Bioresour. Technol.* **2007**, *98*, 2590.
- [12] Oliveira, L. S.; Franca, A. S.; Alves, T. M.; Rocha, S. D. F. *J. Hazardous Materials* **2008**, *155*, 507.
- [13] Gupta, V. K.; Mittal, A.; Jain, R.; Mathur, M.; Sikarwar, S., *J. Colloid and Interface Science* **2006**, *303*, 80.
- [14] Rouquerol, F.; Rouquerol, L.; Sing, K. "Adsorption by Powders and Porous Solids", Academic Press, 1999.
- [15] Gong, R.; Li, M.; Yang, C.; Sun, Y. *J. Hazardous Materials* **2005**, *B121*, 247.
- [16] Arami, M.; Limaee, N. Y.; Mahmoodi, N. M.; Tabrizi, N. *S. J. Hazardous Materials* **2006**, *B135*, 171.
- [17] Arami, M.; Limaee, N. Y.; Mahmoodi, N. M. *Chemical*

Engineering J. **2008**, *139*, 2.

- [18] Langmuir, I. *J. Am. Chem. Soc.* **1918**, *40*, 1361.
- [19] Freundlich, H. M. F. *J. Phys. Chem.* **1906**, *57*, 385.
- [20] Hameed, B. H. *J. Hazardous Materials* **2009**, *162*, 344.
- [21] Khaled, A.; Nemr, A. E.; El-Sikaily, A.; Abdelwahab, O. *Desalination* **2009**, *238*, 210.
- [22] Thinakaran, N.; Pulikesi, M.; Sivanesan, S. *J. Hazardous Materials* **2008**, *151*, 316.
- [23] Chairat, M.; Rattanaphani, S.; Bremner, J. B. *Dyes Pigm.* **2005**, *64*, 231.
- [24] Wu, F. C.; Tseng, R. L.; Juang, R. S. *J. Hazardous Materials* **2001**, *B81*, 167.
- [25] Ozacar, M.; Sengil, A. L. *J. Hazardous Materials*, **2003**, *9B*, 211.