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RESEARCH ARTICLE

Adsorption properties of activated almond shells for methylene blue (MB)

Ramazan Coskun[1,*], Serpil Savci[2], Ali Delibas[1]

[1] Department of Chemistry, Faculty of Science and Arts, University of Bozok, Yozgat, TURKIYE
[2] Department of Biosystems Engineering, Faculty of Engineering and Architecture, University of Bozok, Yozgat, TURKIYE

ABSTRACT

In this study, the adsorption properties of activated almond shells for methylene blue (MB) were investigated. For this aim raw almond shells (RAS) were activated with concentrated sulfuric acid. Activated almond shell (SAS) and raw almond shells (RAS) were characterized with FTIR, SEM and BET analysis. After activation, larger and deeper pores similar to chamber were formed and increase in BET surface area and adsorption rate and also new functional groups were observed. Effects of pH, initial concentration of dye and adsorbent dose on adsorption of MB were studied. Adsorption studies were fitted Langmuir isotherm and pseudo second order kinetic models. Experimental results showed that activated almond shells were not affected pH of solution and adsorption capacity were highly increased and it was calculated as 131.58 mg g^{-1} from Langmuir isotherm. It was observed that the activated almond shells could be used with high efficiency in a wide pH and concentration ranges and SASs could be desorbed and reusable without losing their activity. As a results, SAS could be used an effective adsorbent for the removal of basic dyes like MB at a wide pH and dye concentration range.

Keywords: Adsorption, methylene blue, activated almond shell, efficiently removal

1. INTRODUCTION

With developing technology inorganic and organic pollutants discarded to environment are increased day by day. Synthetic dyes have a significant effect within organic pollutants. They use in many industries such as textile, leather tanning, paper production, food technology, photo electrochemical cells, and hair colorings etc. [1-5]. Approximately 10-15% of the used dyes in industry come directly to the nature as waste [6]. As many dye and their degradation products are toxic and carcinogenic, removal of synthetic dyes from effluents have been important study in recent years for health safety [7–9]. MB dye chosen in this study is frequently used in various coloring industries such as paper, cotton, and wool. But, human health is affected adversely by MB especially ingestion of it by human resulted in respiratory illness, diarrhea, nausea, and eye burns [10]. Also, considering that it is a toxic dye, it affects the living life in the water adversely due to high solubility in the water. It is known that many different techniques such as precipitation, membrane technology, ion exchange, electro-coagulation and adsorption are used to remove both inorganic and organic pollutants from aqueous media. But, the adsorption process is the preferred method for removing organic and inorganic contaminants in water and wastewater due to ease, ease of operation and design simplicity [11-13]. To remove various types of pollutants from aquatic environment a large variety of synthetic and natural adsorbents have been used as adsorbent [14-19]. But, their use in wastewater treatment is sometimes restricted due to theirs higher cost, regeneration difficulties, inadequate adsorbent capacity, low adsorption rate and effective use weakness at wide pH and wide concentration range. Removal of dyes from textile wastewater with high efficiency is still an important problem faced by the textile industry today. To this aim, scientists are constantly exploring new, efficient and environmentally friendly materials with low cost. One of the methods used to improve the weak properties of adsorbents is modification. In the modification, acids such as carboxylic, sulphuric, phosphoric acids are generally used. It has been reported that the carboxylic, sulfonic and phosphoric

Corresponding Author: ramazan.coskun@bozok.edu.tr (Ramazan Coskun)
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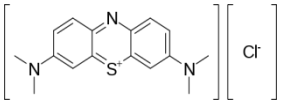
acid groups on the adsorbent are important in the removal of organic and inorganic contaminants [20 - 22]. Our aim in this study is to develop a new adsorbent, which could be quickly regenerable and it would be used at wide pH and wide concentration range effectively removal of cationic dyes such as MB.

2. MATERIAL AND METHODS

Raw almond shells (RAS) were supplied from a local farm in Yozgat, Turkey. MB was purchased from Carlo Erba Reagent. It is a cationic dyestuff (chemical formula $C_{16}H_{18}C_lN_3S$, dye purity >90%). The characteristics of this dye are presented in Table 1. The solution was prepared by dissolving MB of 1000 mg in 1 L distilled water. All the other used chemicals were Merck and used without any purification.

Table 1. Chemical structure and characteristics of methylene blue

Methylene blue	
Molecular weight (g/mol)	319.85
Color	Blue
λ_{max} (nm)	665
Dye purity	<90%
Chemical formula	$C_{16}H_{18}ClN_3S$
Structure	

2.1. Preparation of adsorbent

Firstly, the almonds were taken out from shells; secondly, they were washed and dried; lastly raw almond shells (RAS) were modificated with concentrated sulfuric acid. Certain amounts of RAS (10g/20 mL) were taken and they were shaken with concentrated sulphuric acid for 1 hour at 200 rpm at 60 0C. Then, they were filtered and washed with pure water until pH=7. Then, modificated almond shells were dried at 50 ^oC in oven and stored in desiccator. After that, activated almond shells (SAS) were used as an adsorbent for MB in adsorption studies.

2.2. Characterization of adsorbent

Functional groups, surface morphology and surface properties of the RAS, SAS and DSAS were performed with FTIR (Perkin-Elmer Spectrum 400), SEM (FEIQuanta 450 FEG), and BET (Micromeritics Gemini VII Sürfece Area and Porosity) analyses respectively. The pH measurements were made with WTW 32101 model digital pH-meters.

2.3. Adsorption studies

Adsorption studies were performed in 100 mL Erlenmeyer Flasks including 0.1 g of almond shells with 30 mL of methylene blue solution. All the adsorption experiments were performed at room temperature (25^oC) via batch method. The solution was shaken by a mechanical shaker (VWR) at the constant agitation time (200 rpm) during 24 hours. Then the supernatant was centrifuged (Elektro Mag M 815 M) at 4000 rpm for 10 minutes after the adsorption experiments. The absorbance of methylene blue was measured at maximum wavelength (λmax: 665 nm) by UV–VIS Spectrophotometer (Shimadzu UV 1208). The effect of contact time was evaluated in the time range of 0-360 minutes by using 25, 50 and 100 mg L^{-1} of initial MB concentrations and the initial dye concentration experiments were studied from 50 to 700 mgL^{-1}. For the contact time experiments were performed in 25, 50 and 100 mg L^{-1} and the initial dye concentration experiments were studied from 50 to 700 mg L^{-1}. All experiments were repeated three times. The removal percentage (R %) and adsorption amount (Q) was calculated with given equation as follow equation 1 and 2 respectively.

$$\text{Removal of dye (R)} = \frac{(C_o - C_t)100}{C_o} \quad (1)$$

$$\text{Amount of adsorption (Q)} = \frac{(C_o - C_t)V}{m} \quad (2)$$

C_o is the initial dye concentration (mg L^{-1}) whereas C_t is the dye concentration after adsorption, V dye volume (mL), m adsorbent mass (g). pH values of the medium were adjusted by addition of 0.10 M HCl or NaOH.

3. RESULTS AND DISCUSSION

3.1. Characteristics studies

3.1.1. FTIR analysis

Surface functionalities of adsorbent in adsorption process are very important. Functional groups found on its surface of almond shell were determined by FTIR analysis. Fig. 1 indicates the FTIR spectra of RAS, SAS, and DSAS saturated MB dye. As seen in RAS spectrum, the peaks at 3600-3100, 1733, 1591, 1236 and 1020 cm^{-1} belong to different functional groups which are O-H stretch of alcohols and phenols, C=O stretch of ketones and carboxyl groups, C=C stretch of aromatic ring and C-O ether stretching respectively that RAS has many functional groups. New bands were seen in spectra of SAS at 1300-1150 cm^{-1} (S=O), 1000-750 cm^{-1} (S-O) which were not appeared in RAS spectra, suggesting the conversion of ester to carboxylic acid [23]. As seen in DSAS spectra, three new bands which indicated the associated with the C–N stretch (aromatic amines) and C–H bending (CH2 and CH3), and the C–H (aromatics) after the adsorption of MB dye were observed in the DSAS spectrum at 1325 cm^{-1}, 1383cm^{-1} and 882 cm^{-1} respectively. These three distinct new bands indicate that the MB joined to SAS. Moreover, expansion in O-H bands shows that hydroxyl groups on adsorbent surface have extremely effect onto removal of MB.

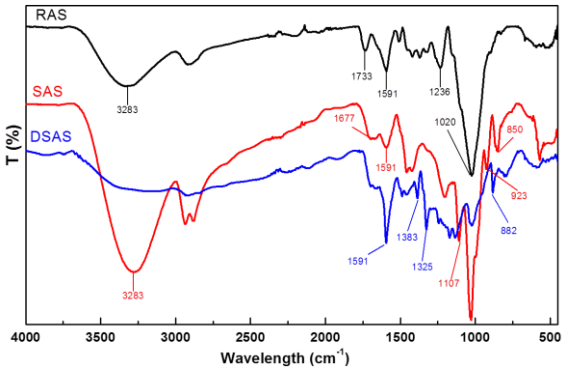


Fig 1. ATR-FTIR spectra of RAS, SAS and DSAS

3.1.2. SEM analysis

SEM images of RAS, SAS and DSAS were shown in Fig. 2. As shown in Fig. 2, while there are many micro pores in SEM image of RAS, there are many larger and deeper pores similar to chamber in SEM images of SAS. These chambers could be seen clearly in Fig. 2-c with higher magnification (x5000). These chambers can make positive effects on both the adsorption capacity of SAS and the rate of methylene blue removal of SAS. After adsorption of MB, the chambers were filled with dye evidently as seen in Fig. 2-d. The other words, it can be said that the dye molecules bind to the chamber of adsorbent. Compare to the literature it can be seen that same activator (sulphuric acid) has different effect on adsorbent surface which was used biosorbent [24].

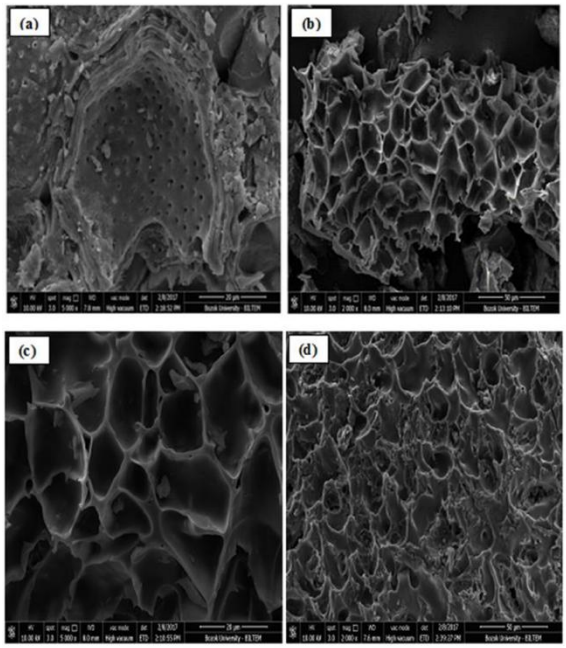


Fig 2. SEM images of a) RASx5000 b) SASx2000 c) SASx5000 d) DSASx2000

3.1.3. BET analysis

The adsorbent surface structure such as surface area and pore structure that are crucial for adsorption can be changed with used activation reagent [24-26]. BET analysis results of RAS and SAS were given in Table 2. As seen in Table 2, the surface properties of RAS which is important for adsorption substantial varied with the acid employed. Particularly, pore volume and the pore size were increased significantly.

Table 2. BET results of almond shells

Adsorbent Type	Single point surface area ($m^2\ g^{-1}$)	Pore Volume ($m^3\ g^{-1}$)	Pore Size (A^0)
RAS	0.1504	0.000564	224.8282
SAS	0.2073	0.000643	283.1749

3.2. Batch adsorption studies

3.2.1. Effect of adsorbent dose

Adsorbent dose is an important parameter for adsorption capacity. Fig. 3 shows the relationship adsorbent dose, removal (%) and adsorption capacity. As seen in Fig. 3, the amount of adsorption decreased with the increasing amount of adsorbent, while the removal percentage increased until a certain amount of adsorbent then the removal percentage remained constant further increasing the adsorbent amount. While this unchanging in adsorption amount can be interpreted by the saturation of the adsorbent, decreasing of adsorption amount can be explained by unit adsorbent. Because adsorption amount is calculated per unit of adsorbent, the amount of adsorption (Q) decreased. Similar results have been observed in some studies in the literature [27-29]. The optimum amount of adsorbent was determined to be about 3.4 g L^{-1} and this value was used in subsequent studies.

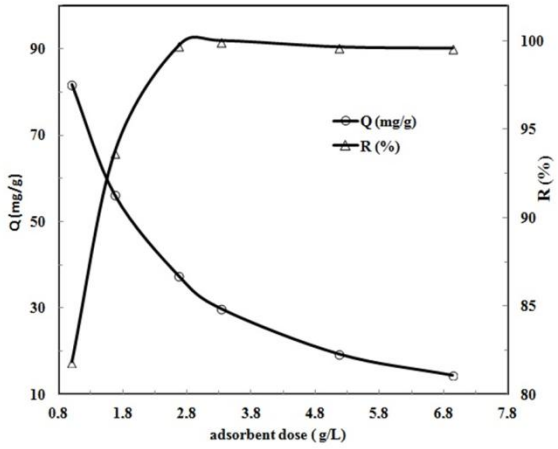


Fig 3. Effect of adsorbent dose [T = 25°C; t= 5 h; Ci = 100 ppm; pH = 10]

3.2.2. Effect of pH

The effect of pH on removal of MB onto RAS and SAS was shown in Fig. 4. As shown in Fig. 4, removal of MB by RAS increased with pH change but removal of MB by SAS was almost not changed with pH change together with high removal efficiency. Similar observations have been reported in literature for the adsorption of methylene blue on different adsorbent [30, 31]. At low pH, low adsorption of RAS can be explained due to the competitive adsorption between cationic dye and excess H^+ in the solution. Increased

pH enhances negativity of adsorbent and this situation leads to the strong attraction between the negatively charged surfaces and positively charged MB dye as a result adsorption increases. The fact that the amount of adsorption of SAS does not change with increasing pH can be explained by the decreasing pHZBC of SAS [24]. As seen in Table 3, SAS can be used a wide pH range without much change in adsorption capacity and removal efficiency compared with the given some studies in literature. In this case there is no need for pH adjustment. The use of a large pH range without pH adjustment is a great advantage over pH-sensitive adsorbents in wastewater treatment. The results indicate that the SAS can be used for dye removal in different media. Also, when compared to the other adsorbents given in Table 3, SAS has superiority with high efficiency in a wide pH range.

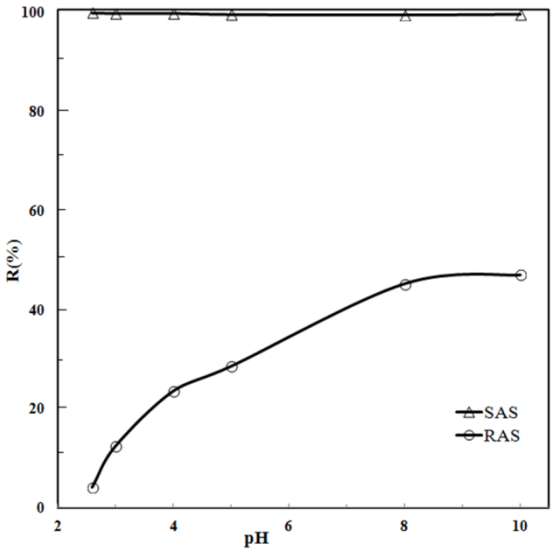


Fig 4. Effect of p [T = 25°C; t= 5 h; Ci = 100 ppm]

Table 3. Comparison of solution pH on the adsorption of MB by different adsorbents

Adsorbents	pH range	Percentage of	References
Activated-clay	2–9	60–95	[33]
Pine leaves	2–11	20–80	[34]
Pine cone	3.47–7.28	63.83–94.82	[35]
Tobacco Stem Ash	2.08–7.93	60–81	[36]
Fly ash	2–8	36–45	[37]
Activated-carbon	2–11	Increase	[38]
Modified sawdust	2–11	Increase	[39]
SALC	3 - 11	60-85	[40]
EB bio-char	4.8–11.3	53.4- 80.5	[41]
SAS	2-10	99.88-99.59	This study

3.2.3. Effect of dye concentration

The effect of the initial dye concentration on the adsorption amount and removal (%) of methylene blue on SAS is shown in Fig. 5. As shown in Fig. 5, initial dye concentration increasing from 50 to 500 mg L^{-1}, the adsorption capacity of SAS increased from 14.95 to 131 mg g^{-1} due to increased driving force [32]. While the increase in dye concentration over 500 mg L^{-1}, the adsorption capacity did not change. This phenomenon indicates that the SAS has reached saturation. Also as shown Fig. 5, high removal (%) did not change until 400 mg L^{-1}. This high removal at wide concentration range is important in industrial application. After that, dye concentration increased from 400 mg L^{-1} to 700 mg L^{-1}, removal (%) of dye decreased from 99.67 to 67.44 respectively. SAS can be an effective adsorbent for MB removal in the broad concentration range compared to the adsorbents in literatures (Table 4). As a result, it has been observed that SAS has remarkable absorptive efficiency.

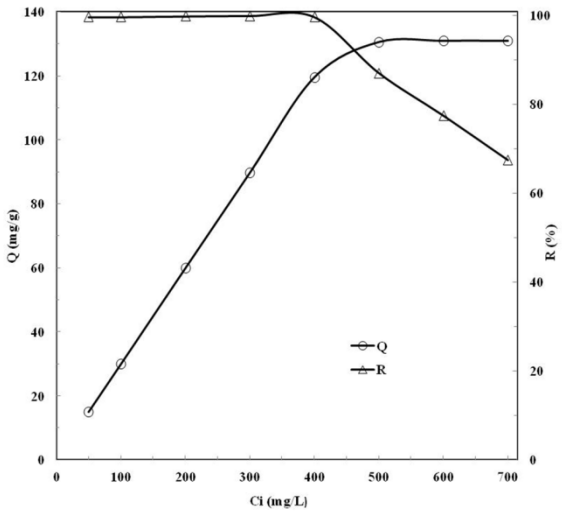


Fig 5. Effect of initial dye concentration [pH = 10; T = 25 °C; t = 5 h]

Table 4. Comparison of initial dye concentration on the adsorption of MB by different adsorbents

Adsorbents	Initial Dye Concentration range (ppm)	Percentage of removal range (%)	References
Kaolin	10-40	90–62	[42]
Modified sawdust	25-500	91.2–66.3	[39]
Raw mango seed	50-250	99.1–92.5	[43]
Modified mango seed	50-250	99.9–96.9	[43]
SALC	50-200	95-91	[40]
EB bio-char	10-100	80.5- 36.8	[41]
SAS	50-400	99.9-99.6	This study

3.2.4. Effect of time

In the adsorption studies, rapid removal for a good adsorbent is as important as high adsorption capacity. The effect of contact time on adsorption of MB onto SAS was studied at room temperature from 0 to 360 min and the obtained results were shown in Fig. 6. The adsorption of MB on the SAS was observed very quickly in the first hour for all of studied dye concentration due to initially the abundance of active sites and the increase in contact time did not

significantly increase the adsorption because of saturation of active sites on the SAS.

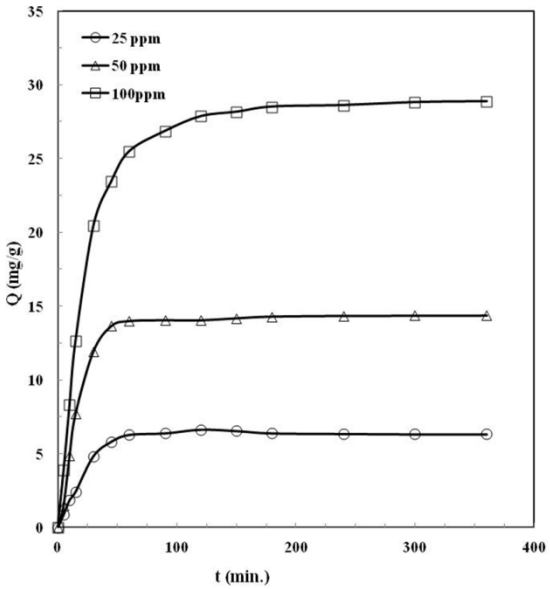


Fig 6. Effect of time [pH = 10; T = 25 °C]

3.3. Adsorption isotherms

Adsorption isotherms are necessary for understanding the surface properties of the adsorbents, for the determination of the capacities and to be able to explain the possible mechanism of adsorption. Also, they describe how the pollutants interact with the adsorbent material. The most commonly used adsorption models Langmuir and Freundlich isotherm models were used to describe the experimental data of MB adsorption onto SAS.

Langmuir model, given equation below, describes the monolayer adsorption of dye molecules on a homogeneous surface.

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \left(\frac{a_L}{K_L}\right) C_e \qquad (3)$$

where; C_e is the equilibrium concentration of adsorbate in solution after adsorption (mg L^{-1}), q_e is the equilibrium solid phase concentration (mg g^{-1}), as well as K_L (L g^{-1}) and a_L (L mg^{-1}) are the Langmuir constants.

However, the Freundlich isotherm supposes a heterogeneous surface with a non-uniform distribution and can be expressed by Eq. 4:

$$\log q_e = \log K_F + \frac{1}{n} log\ C_e \qquad (4)$$

where K_F (L g^{-1}) is the adsorption capacity at unit concentration and $1/n$ is adsorption intensity. The plot of C_e/q_e vs. C_e for Langmuir isotherm model (Fig. 7) and $log\ q_e$ vs $log\ C_e$ for Freundlich model (not given) were drawn from the experimental data given in Fig. 5. In this study, obtained isotherm parameters were shown in Table 5. As seen in the Table 5, the adsorption of methylene blue on the SAS was found to be the best fitted to the Langmuir Isotherm because of the higher correlation coefficient and closeness of q_{exp} and q_e [41]. Thus, adsorption centers on SAS are identical energetic and it can be said that methylene blue adsorption on SAS is monolayer. Found adsorption capacity of SAS was compared in Table 6 that of another adsorbents capacities given in literature. It makes clearly that the SAS has a high adsorption capacity for MB compared with other materials.

The separation factor (R_L) [40] for adsorption of MB on SAS was calculated from the Langmuir adsorption isotherm parameters and given in Fig. 8. As can see in Fig. 8, the value of R_L varies from 0.0120 to 0.0009 for the initial MB dye concentration of 100-700 mg L^{-1}. This indicates that the adsorbent prepared from the almond shell is favorable for adsorption of MB [41].

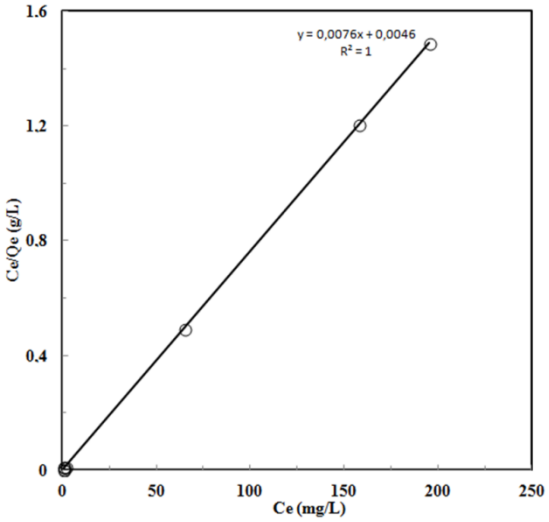


Fig 7. Langmuir isotherm plot of almond shell

Table 5. Isotherm parameters onto SAS of MB obtained from equilibrium models

Isotherm Models	Parameter (unit)	Value
Langmuir	K_L (L g^{-1})	227.272
	a_L (L mg^{-1})	1.727
	Q_{max} (mg g^{-1})	131.578
	R^2	1
Freundlich Isotherm	n_F	5.546
	K_F	57.108
	R^2	0.4934

Table 6. Comparison of found adsorption capacity of MB with various adsorbents

Adsorbent	Q (max)	References
Powdered activated carbon	91	[44]
Nut shell activated carbon	5.3	[45]
Palm tree activated carbon	128	[46]
Act. almond shell (750 °C)	1.33	[47]
Activated carbon from Walnut shell	3.53	[47]
Coir pith activated carbon	5.87	[48]
Activated carbon from Hazelnut shell	8.82	[47]
SAS	131.58	This study

3.4. Adsorption kinetics

Three kinetic models, pseudo-first order, pseudo-second order and intraparticle diffusion model which were used frequently in the adsorption studies, were used in order to investigate the adsorption mechanism of MB on SAS. Pseudo-first order [40], pseudo-second order [41–43] and intraparticle diffusion model [44–46] were given in 5, 6 and 7 equation respectively.

$$ln(Q_e - Q_t) = lnQ_e - k_1 t \quad (5)$$

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

$$Q_t = k_{id} t^{1/2} \quad (7)$$

Where, Q_t and Q_e (mg g^{-1}) are the amount of adsorption on the activated SAS at time t and equilibrium, k_1 (min^{-1}), k_2 (g $mg^{-1}min^{-1}$) and k_{id} (mg g^{-1} $min^{-1/2}$) are the rate constant for the pseudo-first-order, the pseudo-second-order and the intraparticle diffusion models respectively. For first order kinetic model the linear plot of $ln\ (Q_e - Q_t)$ vs t and for intraparticle diffusion model Q_t vs $t^{1/2}$ were drawn. But, for regulation coefficient is too low, they could not be given. The values characteristic constants of adsorption were calculated from the slope and intercept of t/Q_t vs. t (Fig. 8) and the kinetic parameters obtained for adsorption of MB on SAS were given in Table 7. Pseudo-second order kinetic model is more convenient for MB adsorption onto SAS.

3.5. Reusability of SAS

In order to investigate the reusability of the SAS, the adsorption-desorption cycle was repeated five times with the same adsorbent [17] and the results shown in Fig 9. It was observed that the adsorption capacity of SAS did not considerably change after five adsorption desorption cycles. This results shows that SAS are good reusable adsorbent for the removal of MB from aqueous environment.

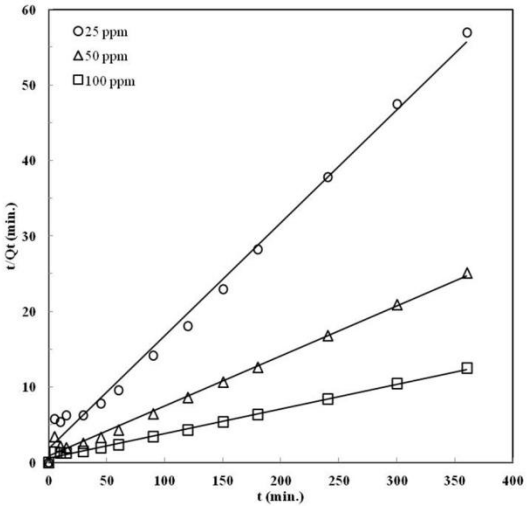


Fig 8. Pseudo-second-order plots for MB on almond shells. [pH = 10; T = 25 °C]

Table 7. Values of pseudo second order kinetic model

C_o (mg L^{-1})	$Q_{e,exp.}$ (mg g^{-1})	$Q_{e,cal.}$ (mg g^{-1})	k_2 (g $mg^{-1}min^{-1}$)	R^2
25	6.50	6.69	0.0110	0.992
50	14.36	15.06	0.0053	0.992
100	28.86	30.48	0.0020	0.995

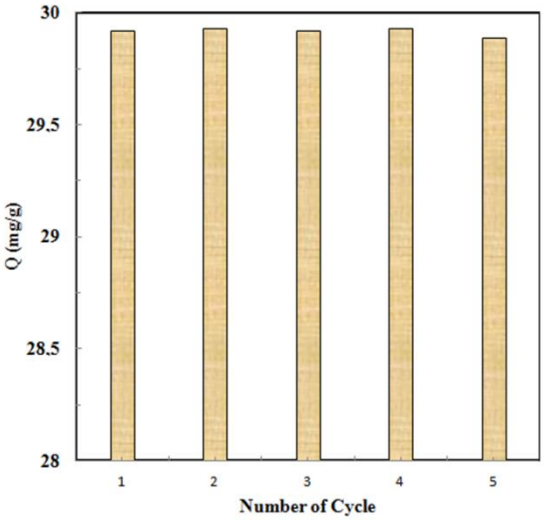


Fig 9. Reusability of SAS [pH = 10; C_i = 100 ppm; t = 3 h; T = 25 °C]

4. CONCLUSIONS

It was observed that the almond shell could be activated by a simple and easy method for increasing adsorption capacity and its the surface properties such as pore structure pore volume and surface area of the almond shells could be changed by activation. It has been determined that SAS can be used as an effective adsorbent to remove MB at a wide pH and concentration range. MB adsorption on SAS was determined to be suitable to Langmuir isotherm and second order kinetic model. Also, it was observed that SAS could be regenerated with 5 M HNO_3 and can be reusable at least five times without losing their adsorption capacity. As a result, almond shells may be an alternative adsorbent to more costly adsorbents for removing dye in wastewater treatment processes.

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