

Removal of Remazol Orange RGB from Aqueous Solution by Peanut Shell

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In this study, peanut shell was utilized as an adsorbent for the removal of remazol orange RGB from aqueous solution by adsorption technique. Adsorption experiments were conducted as a function of contact time, initial dye concentration, temperature and pH. While the amount of the dye removed by peanut shell was increasing with increasing contact time, initial dye concentration, solution temperature, it decreased with increasing solution pH. The maximum dye removal were between 82.14 and 97.42 % under all the experimental conditions studied such as concentration, pH and temperature. Adsorption kinetic was in agreement with the pseudo-second order model. Column adsorption studies were also performed and the percentage of dye adsorbed in column was between 98 and 100 % for all studied concentrations.

Key Words: Removal, Peanut shell, Remazol orange RGB, Dye, Kinetics, Column, FTIR, SEM.

INTRODUCTION

The effluent water from various industries such as textile, dying, food, cosmetic contains various type of dye which is released to the environment. Many of these dyes are toxic and even carcinogenic to human health. Therefore, before the coloured wastewaters from these industries are released to aquatic environments, it should be required to remove the dyes in effluent water. For this purpose, many methods, such as activated carbon adsorption, chemical coagulation, ion exchange, electrolysis, biological treatments, etc., have been developed for treating dye containing waste water¹⁻³. Of those methods, activated carbon adsorption is highly effective for the removal of dyes and pigments as well as other organic and inorganic pollution. However, the use of activated carbon is not suitable for developing countries because of its high cost. The use of low-cost adsorbents such as clay minerals³, peat⁴, fly ash⁵, perlite^{6,7} is more suitable. Some researchers have also extensively studied the removal of dyes by various lingocellulosic biomass such as wood⁸, orange peel⁹, rice husk¹⁰, sunflower¹¹, sawdust¹², recently. For example, Asfour et al.¹², have studied the adsorption of basic dye astrazone blue FRR 69 on hardwood (beech) sawdust. Annadurai et al.¹³ have studied the adsorption of various dyes onto cellulose-based wastes. Liversidge *et al.*¹⁴, have studied the removal of dye basic blue 41 by linseed cake. In this work, the use of peanut shells,

low-cost lignocellulosic agriculture wastes, is stuided for the adsorption of remazol orange RGB present in aqueous solution.

The amounts of peanut plant produced in the world are 18.54 million tons as an average. The amounts produced in Turkey are 70 thousand tons and the 95 % of peanut grows in the Mediterranean region of Turkey. The shells of peanut plant consist of 35 % of peanut. Hence, the potential amounts of peanut shell are approximately 6.49 million tons over the world and the amounts produced in Turkey are nearly 24.50 thousand tons¹⁵. Peanut shells are ligno-cellulosic materials with low density which is an agricultural waste. It is known that peanut shells are used in a few fields before. For example, peanut shells are used as fertilizer in the agriculture and as filler for the production of light cement as well as energy¹⁶. Moreover, they are used as a strengthening agent in producing of thermoplastic composite materials and as additive material in the producing of plastic plaque¹⁶. Moreover, it was seen that peanut shell has also been used as adsorbent for the adsorption of some dyes and metal ions in literature^{17,18}. For example, the modified peanut shells have been used as a biosorbent for the adsorption of cadmium(II), copper(II), lead(II), nickel(II) and zinc(II) ions¹⁷ and for the adsorption of some cationic and anionic dyes¹⁸. In previous work, peanut shell has been used as an adsorbent for the removal of basic red 2 which is a positively charged dye from aqueous solution¹⁹. In this study, the

use of peanut shell is studied as an adsorbent to remove the remazol orange RGB which is a negatively charged dye. In this work, peanut shell was used as an adsorbent for the adsorption of remazol orange RGB from aqueous solution. The effects of contact time, initial dye concentration, solution pH and temperature on adsorption were investigated by using batch and column system. Moreover, the isotherm and kinetic studies of the adsorption process were also performed.

EXPERIMENTAL

The peanut shell waste was provided from Osmaniye province located in the east Mediterranean region of Turkey. It was washed to remove soil and dust and then dried in an oven. Dry peanut shell was crushed into powder. The powdered peanut shell was sieved through a molecular sieve of 100-mesh. The elemental analysis and chemical component of peanut shell has been given in Tables 1 and 2, respectively¹⁹.

| TABLE-1 | | | | | | |
|------------------------------------|-------|-----|------|--|--|--|
| ELEMENTAL ANALYSIS OF PEANUT SHELL | | | | | | |
| Component | (%) | (%) | | | | |
| С | 41.53 | Ν | 2.12 | | | |
| Н | 5.55 | S | 0.24 | | | |

| TABLE-2 | | | | | | |
|-------------------------------------|-------|-----------|------|--|--|--|
| CHEMICAL COMPONENTS OF PEANUT SHELL | | | | | | |
| Component | (%) | Component | (%) | | | |
| Lignin | 32.80 | Protein | 4.90 | | | |
| Cellulose | 45.30 | Ash | 2.30 | | | |
| Hemicellulose | 8.10 | - | - | | | |

Preparation of raw material for adsorption: Raw peanut shell did not adsorb remazol orange RGB and therefore peanut shell was pretreated before experiments. Pretreated process was performed by mixturing the raw peanut shell with HCl of 0.1N on a magnetic stirrer.

Adsorbate: Remazol orange RGB, reactive orange RGB, was purchased from Dystar and was used as received without further purification. This dye is a new generation of reactive dyestuffs for medium to deep shades produced. The dye has a maximum wavelength of 478 nm on UV-VIS spectrophotometer. The absorption spectra of remazol orange RGB of various concentrations are shown Fig. 1.



Fig. 1. UV-VIS spectra of remazol orange RGB for different initial concentrations (top to bottom concentrations: 150, 100, 75, 50, 20 and 10 ppm)

Preparation of dye solutions: The stock solutions of 500-1000 mg/L of remazol orange RGB were prepared with distilled water and then they were diluted to the desired concentrations. The pH of the solutions was adjusted with 0.1N NaOH and HCl solutions using a pH meter (Elmetron pH meter).

Adsorption experiments: Adsorption experiments were carried out by shaking 0.25 g of peanut shell with 50 mL aqueous solution of remazol orange RGB in 250 mL-Erlenmayer flasks placed in a temperature-controlled shaking water bath at diffe-rent concentrations, pHs and temperatures as a function of time. After the desired contact time, the samples were withdrawn from mixture by using a micropipette and centrifuged for 5 min at 5000 rpm. After centrifuged, supernatants were analyzed for the determination of the final concentration of remazol orange RGB by using an UV-VIS spectrophotometer. The amounts of remazol orange RGB adsorbed by peanut shell, q_e were calculated using the following equation:

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

where, q_e is the amount of dye adsorbed (mg/g). C_0 and C_e are the initial and equilibrium liquid-phase concentrations of dye (mg/g), respectively. V is the volume of the dye solution (l) and W is the weight of the adsorbent used (g).

Parameters on adsorption

Concentration effect on adsorption: The initial concentrations of remazol orange RGB on sorption kinetics were selected as 10, 20, 50, 75, 100 and 150 mg/L at 40 °C, pH 3 and 130 rpm.

pH effect on adsorption: The initial pHs of remazol orange RGB solutions on adsorption were adjusted as 3, 5, 7 and 9 for the initial concentration of 50 mg/L at 40 °C and 130 rpm, respectively. The pHs of dye solutions were adjusted using 0.1N HCl and NaOH solutions by using a pH meter.

Temperature effect on adsorption: The temperatures of remazol orange RGB solutions on adsorption were selected as 20, 30, 40 and 50 °C for the initial concentration of 50 mg/L at pH 3 and 130 rpm, respectively.

Column adsorption: Column with a diameter of 1 cm and a length of 15 cm was used for continuous adsorption system. Peanut shell particles (dry weight 2.0 g) were packed between two layers of glass wool in column. Dye solutions with desired concentrations were fed through the top of the column. The flow rate of feed solutions was regulated as 0.35 mL/min (21 mL/h). The system was operated at room temperature (*ca.* 25 °C) at pH 3. The operating conditions are summarized in Table-3. The dye samples passed through column were collected from the bottom of column at specific times. The concentrations of unadsorbed dye within samples in the outlet of the column were determined as described as before.

FT-IR measurements: Peanut shell and dye-impregnated peanut shell samples after adsorption were first dried to the constant weight in an oven at 60 °C for 12 h. Afterward, 1.0 mg of the dried samples was mixed with 100 mg of KBr to make pellet. The infrared spectra of the pellets were recorded in the wave number range of 4000-650 cm⁻¹ using a Perkin-Elmer FT-IR spectrometer.

| TABLE-3 | | | | | | |
|-----------------------------|--------|--|--|--|--|--|
| COLUMN OPERATING CONDITIONS | | | | | | |
| Column diameter (cm) | 1.0 | | | | | |
| Column length (cm) | 20.0 | | | | | |
| Height of bed (cm) | 10.0 | | | | | |
| Packing size (mesh) | 100 | | | | | |
| Flow rate (mL/min) | 0.35 | | | | | |
| Concentration (mg/L) | 10-150 | | | | | |
| Temperature (°C) | 25.0 | | | | | |
| Solution (pH) | 3.0 | | | | | |

RESULTS AND DISCUSSION

Effect of contact time on adsorption: The effect of contact time on the amount of remazol orange RGB adsorbed by peanut shell was investigated under all the experiment conditions such as concentration, pH and temperature. A rapid adsorption occurs between 1-5 min and thereafter the gradual increase in adsorption maintains for 75 min except for the initial concentration of 150 mg/L. For the concentrations of 10, 20, 50, 75 and 100 mg/L, after 75 min, with the further increment in the time, the amount of dye adsorbed does not change and even from time to time, very small decreases in the amount of the dye adsorbed are observed, indicating desorption. Therefore, the time of 75 min is accepted as the optimum contact time (equilibrium time) under all conditions studied except for the initial concentration of 150 mg/L. A similar result has been reported for the adsorption of Congo red onto calcium-rich fly ash²⁰.

Effect of initial dye concentration on adsorption: Effect of initial dye concentration on adsorption was studied at six different concentrations of 10, 20, 50, 75, 100 and 150 mg/L at 40 °C at pH 3. Fig. 2 illustrates the effect of initial dye concentration on the adsorption of remazol orange RGB by peanut shell. As shown in Fig. 3, a rapid adsorption occurs within the contact time of 1-5 min for all concentrations and thereafter the gradual increase in adsorption maintains to 75 min. While the amounts of remazol orange RGB adsorbed onto peanut shell are 1.74 mg/g (87.23 %) and 3.35 mg/g (83.76 %) for the concentrations of 10 and 20 mg/L at 1 min, the maximum adsorption is found to be 1.77 mg/g (88.71 %) and 3.62 mg/g (90.63 %) at 75 min, respectively. For the concentrations of 50, 75, 100 and 150 mg/L, while the amounts of remazol orange RGB adsorbed onto peanut shell are 8.20 mg/g (82.00 %), 10.47 mg/g (69.85 %), 13.05 mg/g (65.26 %), 13.33 mg/g (44.43 %) at 1 min, the maximum adsorption is found to be 9.70 mg/g (97.07 %), 14.61 mg/g (97.42 %), 18.18 mg/g (90.92 %), 24.64 mg/g (82.14 %) at 75 min, respectively. But, for the concentration of 150 mg/L, after the 75 min the adsorption was maintained to 300 min. The maximum amount of remazol orange RGB adsorbed was 25.74 mg/g at 300 min. The fact that the high adsorption occurs for the first minutes indicates a very high interaction between functional groups on the surface of modified peanut shell and remazol orange RGB molecules. A similar result has been reported for the adsorption of basic red 2 onto peanut shell¹⁹. The very high interaction was also seen in pH and temperature studies.

Effect of pH on adsorption: The initial pH values of dye solutions affect both the chemistry of a dye molecule and an adsorbent. Herein, to investigate the effect of pH on the adsorption of remazol orange RGB from aqueous solution by



Fig. 2. Effect of initial concentration on the adsorption of remazol orange RGB by peanut shell



Fig. 3. Effect of initial solution pH on the adsorption of remazol orange RGB by peanut shell

peanut shell, the pHs of initial solutions were selected as 3, 5, 7 and 9. For the initial concentration of 50 mg/L at 40 °C, the relationship between the amounts of remazol orange RGB adsorbed at equilibrium time and the initial solution pH is shown in Fig. 3. As shown in Fig. 3, a very rapid adsorption takes place for the first minute at all the pHs and thereafter the gradual increase in adsorption prosecutes up to 75 min, maximum adsorption time. The most adsorption occurs at pH 3 and the lower adsorption occurs at pH 9. When the adsorption is 8.20 mg/g (82.00 %) and 9.707 mg/g (97.07%) at 1 and 75 min at pH 3, the adsorption is 7.912 mg/g (79.12 %) and 8.674 mg/g (86.74 %) at 1 and 75 min at pH 9, respectively.

Effect of temperature on adsorption: The effect of temperature on adsorption was studied at 20, 30, 40, 50 and 60 °C. The results obtained are showed in Fig. 4. As illustrated in the figure, a rapid adsorption is observed for the first minutes as seen in concentration and pH effects and then a gradual increase in adsorption is continued up to 75 min. While the highest adsorption occurs at 60 °C at first 10 min, after this time the most adsorption is seen at 40 °C. The lowest adsorption is resulted at 20 °C for all temperatures. For example, for the initial concentration of 50 mg/L at 40 °C, while the highest adsorption is 8.20 mg/g (82.00 %) at 1 min, the maximum



Fig. 4. Effect of solution temperature on the adsorption of remazol orange RGB by peanut shell

adsorption is 9.707 mg/g (97.07 %) at 75 min. At 20 °C, while the lowest adsorption is 5.534 mg/g (55.34 %) at 1 min, the maximum adsorption is 9.33 mg/g (93.30 %) at 75 min. The fact that the adsorption is the most at higher temperature indicates endothermic process. This may be a result of increase in the mobility of the large dye ion with increasing temperature. A similar result has been reported the adsorption of methylene blue onto perlite²¹. However, the maximum amounts of remazol orange RGB adsorbed between 20 and 60 °C are closed to each other and thus the temperature has a small effect on adsorption.

Adsorption isotherms: The adsorption equilibrium data were fitted to the Langmuir and Freundlich isotherms used commonly. Linearized the Langmuir and Freundlich adsorption isotherms can be expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{1}$$

$$\ln q_e = \ln k + \frac{1}{n} \ln C_e \tag{2}$$

where q_e is the amount of dye adsorbed at equilibrium time (mg/g), C_e is the equilibrium concentration of the dye in solution (mg/L). k and n are isotherm constants which indicate capacity and intensity of the adsorption, respectively. Q_0 and b are the Langmuir constants which indicate adsorption capacity and energy, respectively. The isotherm results indicate that the adsorption of remazol orange RGB onto peanut shell is partially consistent with only the Langmuir, but not for the Freundlich model.

Fig. 5 shows the plot of C_e/q_e against C_e at 40 °C and pH 3. The plot is partially in harmony with Langmuir model with a low correlation coefficient of 0.66. Fig. 6 illustrates the plot of ln q_e against ln C_e at 40 °C and pH 3. The plot does not obey Freundlich model due to a very low correlation coefficient of 0.55.

The values of Q_0 and b were calculated from the intercept and slope of the plot of C_o/q_e versus C_e , respectively. These constants (Q_0 and n) obtained from the Langmuir isotherms are found to be 35.33 mg/g and 0.093 g/L, respectively. The fact that the adsorption partially obeys only the Langmuir isotherm suggests that the surface of the peanut shell has not a full



Fig. 5. Langmuir isotherm of the adsorption of remazol orange RGB by peanut shell



Fig. 6. Freundlich isotherm of the adsorption of remazol orange RGB by peanut shell

homogeneous form and thus the adsorption take places randomly on the surface of the peanut shell. This situation is attributed to the fact that that various active sites on peanut shell has different affinities to remazol orange RGB molecules.

Fig. 7a-c show SEM images of raw peanut shell, peanut shell pretreated with HCl and the dye adsorbed peanut shell, respectively. It is evident from Fig. 7a that the pores within the particles of the peanut shell are highly heterogeneous. After the pretreatment of peanut shell with HCl, the some caves has taken placed on the surface of peanut shell to adsorb the dye molecule (Fig. 7b). After adsorption, peanut shell particle are remarkably covered by dye remazol orange RGB molecules, indicating a local adsorption due to heterogeneous surfaces (Fig. 7c).

Kinetics of adsorption process: Several models have been proposed to express the adsorption mechanism of solute molecules onto an adsorbent: (a) Pseudo-first order kinetic model, (b) Pseudo-second order kinetic model and (c) Intraparticle diffusion model.

A pseudo-first order kinetic model of Lagergren²² is given as:

$$\log(q_{e} - q_{t}) = \log q_{e} - \frac{k_{1}}{2.303}t$$
(3)





H Mag = 5.00 K X WD = 14 mm EHT = 20.00 kV Signal A = SE1



Fig. 7. SEM photographs of peanut shell: (a) peanut shell; (b) peanut shell pretreated with HCl (c) peanut shell adsorbed dye

A pseudo-second order kinetic model of Ho and McKay^{4,8} is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$
(4)

and an intra-particle diffusion model of Weber and Morris^{23,24} is shown as:

$$\mathbf{q}_{t} = \mathbf{k}_{i} \cdot \mathbf{t}^{1/2} + \mathbf{C} \tag{5}$$

where, k_1 is rate constant for the pseudo-first-order model, k_2 is rate constant for the pseudo-second-order model and k_i is the intra-particle diffusion rate constant. Moreover, a constant value, C, for the intra-particle diffusion in eqn. 5 has been described by Kannan and Sundaram²⁴. C is boundary layer thickness between adsorbate and adsorbent. q_e and q_t are the amount adsorbed of solute per unit adsorbent at equilibrium and any time, respectively. In eqn. 4, the initial adsorption rate is $h = k_2 q_e^2$. Various kinetic parameters for adsorption of remazol orange RGB by peanut shell at different initial dye concentration are given in Table-4.

The adsorption of remazol orange RGB on peanut shell in the present study was investigated in terms of the abovementioned kinetics models for understanding the adsorption kinetics.

Firstly, the plots of log ($q_e - q_t$) against t for the pseudofirst-order model given in eqn. 3 are drawn for all initial concentrations at 40 °C and pH 3. The plots obtained for the pseudo first-order kinetic models are showed in Fig. 8. Linear regression analysis results are given as follows:

| For 10 mg/L; y = -0.0989x - 1.4485 | $R^2 = 0.9726$ |
|---------------------------------------|----------------|
| For 20 mg/L; y = -0.2848x - 0.2330 | $R^2 = 0.9677$ |
| For 50 mg/L; $y = -0.0319x + 0.0615$ | $R^2 = 0.9219$ |
| For 75 mg/L; $y = -0.0344x + 0.4984$ | $R^2 = 0.9768$ |
| For 100 mg/L; $y = -0.0238x + 0.5776$ | $R^2 = 0.9676$ |
| For 150 mg/L; $y = -0.0319x + 0.9892$ | $R^2 = 0.9577$ |

From linear regression analysis obtained, it is determined that the values of correlation coefficients, r², obtained are 0.972, 0.967, 0.921, 0.976, 0.967 and 0.957 for the initial concentrations of 10, 20, 50, 75, 100 and 150 mg/L, respectively.

Secondly, the linear plots of t/q_t against t for the pseudosecond-order model in eqn. 4 were obtained for all initial concentrations at 40 °C and pH 3. The plots obtained for the second order models are shown in Fig. 9. Linear regression analysis results are given as follows:

| TABLE -4 | | | | | | | | | | | |
|---|-----------|-----------|-----------|----------------|-------------|-----------|-----------|------------|-----------|--------|---------|
| KINETIC PARAMETERS FOR ADSORPTION OF REMAZOL ORANGE RGB | | | | | | | | | | | |
| | | E | BY PEANUT | SHELL AT | DIFFEREN | T INITIAL | DYE CONCE | ENTRATIO | N | | |
| C_0^{a} | q_e^{b} | q_2^{c} | k_2^{d} | h ^e | $r_2^{2 f}$ | q_1^{g} | k_1^{h} | r_1^{2i} | k_j^{j} | C^k | r_i^1 |
| 10 | 1.77 | 1.77 | 20.33 | 63.69 | 0.9996 | 0.035 | 0.2277 | 0.972 | 0.0044 | 1.7372 | 0.2432 |
| 20 | 3.62 | 3.71 | 2.023 | 27.84 | 0.9998 | 0.584 | 0.6558 | 0.967 | 0.0702 | 3.2976 | 0.9440 |
| 50 | 9.70 | 9.07 | 1.293 | 106.06 | 0.9999 | 1.152 | 0.0734 | 0.921 | 0.0152 | 8.8261 | 0.6646 |
| 75 | 14.61 | 14.72 | 0.101 | 21.88 | 1.0000 | 3.150 | 0.0792 | 0.976 | 0.0441 | 12.144 | 0.6289 |
| 100 | 18.18 | 18.28 | 0.64 | 21.38 | 0.9999 | 3.780 | 0.0548 | 0.967 | 0.0557 | 14.900 | 0.6934 |
| 150 | 25.74 | 25.06 | 0.024 | 15.07 | 0.9996 | 9.754 | 0.0734 | 0.957 | 0.1244 | 17.409 | 0.6882 |

^aInitial dye concentration (mg/L). ^bEquilibrium adsorption capacity obtained as experimental (mg/g). ^cEquilibrium adsorption capacity obtained from pseudo-second-order equation (mg/g). ^dThe rate constant of pseudo-second-order reaction (g/mg min). ^eThe initial adsorption rate from pseudo-second-order kinetics (mg/g min). ^fCorrelation coefficient from pseudo-second-order equation. ^gEquilibrium adsorption capacity obtained from pseudo-first-order equation (mg/g). ^hThe rate constant of pseudo-first-order reaction (min⁻¹). ⁱCorrelation coefficient from pseudo-first-order equation. ^jIntra-particle diffusion rate constant (mg/g min^{1/2}). ^kIntercept from intra-particle diffusion equation. ⁱCorrelation coefficient from intra-particle diffusion equation.



t (min)

Fig. 8. Pseudo first-order kinetics of remazol orange RGB adsorption on peanut shell at diffrent concentration



Fig. 9. Pseudo second-order kinetics of remazol orange RGB adsorption on peanut shell at diffrent concentrations

 $\begin{array}{ll} \mbox{For 10 mg/L; } y = 0.5651x + 0.0157 & R^2 = 0.9996 \\ \mbox{For 20 mg/L; } y = 0.2695x + 0.0359 & R^2 = 0.9998 \\ \mbox{For 50 mg/L; } y = 0.1102x + 0.0094 & R^2 = 0.9999 \\ \mbox{For 75 mg/L; } y = 0.0679x + 0.0478 & R^2 = 1.0000 \\ \mbox{For 100 mg/L; } y = 0.0547x + 0.0461 & R^2 = 0.9999 \\ \mbox{For 150 mg/L; } y = 0.0399x + 0.064 & R^2 = 0.9996 \\ \end{array}$

From linear regression analysis obtained, the values of r² obtained are found to be 0.9996, 0.9998, 0.9999, 1.0000, 0.9999 and 0.99967 for the initial concentrations of 10, 20, 50, 75, 100 and 150 mg/L, respectively. Correlation coefficients from the first and pseudo-second-order models have very high values. Because the values of qe from the pseudo-first order kinetics model is not in agreement with experimental data $(q_{e(exp)})$, even correlation coefficients have high values, the adsorption does not obey this model. But the values of qe from the pseudo-second order kinetic model are in harmony with experimental data, $q_{e(exp)}$ and therefore the adsorption obeys the pseudo-second order kinetics. Similar results have been reported for the adsorption of Congo red onto fly ash²⁰ and the adsorption of methylen blue onto perlite⁶. This situation may be attributed to a chemical activation between remazol orange RGB mole-cules with the functional groups of peanut shell.

Finally, due to mass transfer effects, the plots of q_t versus $t^{1/2}$ for the intra-particle diffusion model given in eqn. 5 were

obtained for all initial dye concentrations at 40 °C and pH 3. The plots for intra-particle diffusion model are demonstrated in Fig. 10. Linear regression analysis results are given as follows:

| For 10 mg/L; $y = 0.0044x$ | + | 1.7372 | $R^2 = 0.2432$ |
|-----------------------------|---|---------|----------------|
| For 20 mg/L; $y = 0.0702x$ | + | 3.2976 | $R^2 = 0.9440$ |
| For 50 mg/L; $y = 0.0152x$ | + | 8.8261 | $R^2 = 0.6646$ |
| For 75 mg/L; $y = 0.0441x$ | + | 12.1440 | $R^2 = 0.6289$ |
| For 100 mg/L; $y = 0.0557x$ | + | 14.9000 | $R^2 = 0.6934$ |
| For 150 mg/L; $y = 0.1244x$ | + | 17.4090 | $R^2 = 0.6882$ |



Fig. 10. Intra-particle diffusion kinetics of remazol orange RGB adsorption on peanut shell at diffirent concentrations

From linear regression analysis obtained, except the initial concentration of 20 mg/L, the values of r^2 obtained were found to be 0.2432, 0.664, 0.628, 0.693 and 0.688 for the initial concentrations of 10, 50, 75, 100 and 150 mg/L, respectively. Because of the low values of correlation coefficients, it may be said that the adsorption process does not obey the intra-particle diffusion kinetic, or the adsorption is partially consistent with the intra-particle diffusion kinetic.

Column adsorption: The percentage of dye calculated from the analysis of the samples at the outlet of the column is shown in Fig. 11. As shown from this figure, a very high adsorption is seen for all initial concentrations and the maximum adsorption is found to be between 98.03 and 100 % for all initial concentrations. Furthermore, it is observed that all the outlet samples are colourless and cleared off the orange colour of remazol orange RGB. This situation indicates that a very high adsorption occurs as a result of a high affinity between the functional groups of remazol orange RGB molecules and peanut shell packed in column. Column exhaustion time is determined as 240 min.

FT-IR study of peanut shell: The broad band at 3294 cm⁻¹ indicates the existences of -OH groups of glucose and -NH groups of proteins. After treatment with HCl of peanut shell, this band is shifted to 3340 cm⁻¹. After the adsorption of the dye, this band is shifted to 3283 cm⁻¹. The strong absorption bonds at 2919 and 1737 cm⁻¹ can be assigned to -CH stretching of carboxyl groups. After treatment with HCl of peanut shell, these peaks have become more appear. These peaks, after the adsorption of the dye, are slightly shifted to 2928 and 1738 cm⁻¹, respectively. On the other hand, the intensity of band at



Fig. 11. Effect of concentration on the column adsorption of remazol orange RGB

1737 cm⁻¹ is highly increased. The absorption peaks at 1634 and 1511 cm⁻¹ can be attributed to the amide I and amide II bonds of protein peptide bonds. After treatment with HCl, the intensities of both bonds are significantly increased and these two bands are shifted to 1651 and 1510 cm⁻¹, respectively. After the adsorption of the dye, the peak at 1634 cm⁻¹ is slightly broadened and shifted to 1646 cm⁻¹ and its intensity is also decreased. Band at 1510 cm⁻¹ is diminished. The absorption peaks at around 1200-1000 cm⁻¹ indicate the existence of C-O single bond in carboxylic acids, alcohols, phenols and esters. Herein, very strong absorption peak at 1027 cm⁻¹ can be assigned to C-O bond in carboxylic and phenolic groups. After treatment with HCl, this band is increased and slightly shifted to 1023 cm^{-1} . The strong peaks at around 1417, 1369, 1230 cm^{-1} are caused by the C=O stretching band of carboxylic groups. After adsorption, the intensities of these two bands at 1369 and 1230 cm⁻¹ are highly increased and slightly shifted to 1367 and 1229 cm⁻¹, respectively. The peaks at 3500-3200 and 1540 cm⁻¹ represent the stretching vibrations of amino groups. The peak found at 1000 cm⁻¹ is finger print zone resulted from phosphate and sulphure. FT-IR result indicates that the peanut shell has characteristic bands of proteins, phenolic and carboxylic groups, polymeric compounds which are able to react with negatively charged remazol orange RGB molecules in aqueous solution. It is thought that the positively charged groups in the structure of peanut shell may react with negatively charged remazol orange RGB molecules. As a result of the interactions of the other groups in the structure of peanut shell with dye molecules, the intensities of bands belong to functional groups in structure may be slightly increased and decreased or spectral shifted.

Conclusion

Peanut shell, an agricultural waste, was used as an adsorbent for the removal of remazol orange RGB from aqueous solution by batch and column adsorption. The adsorption of remazol orange RGB was investigated as a function of initial dye concentration, pH and temperature. It was determined that the maximum adsorptions were between 82.14 and 97.42 % under all the experimental conditions studied. The values of adsorption obtained from column experiments were between 98.03 and 100 % for all concentrations. Adsorption isotherm was partially consistent with the Langmuir model. The kinetics of adsorption followed the pseudo second-order model. From the results reported it would appear that peanut shell acted as a potential adsorbent for the removal of remazol orange RGB from wastewater.

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