

Equilibrium and kinetics studies for the adsorption of direct and acid dyes from aqueous solution by soy meal hull

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Abstract

This paper deals with the application of Soy Meal Hull (SMH), an agricultural by-product, for the removal of direct and acid dyes from aqueous solutions. Four textile dyes, C.I. Direct red 80 (DR80), C.I. Direct red 81 (DR81), C.I. Acid blue 92 (AB92) and C.I. Acid red 14 (AR14) were used as model compounds. Physical characteristics of SMH such as surface area, Fourier transform infra-red (FTIR) and scanning electron microscopy (SEM) were obtained. The surface area of SMH was found to be 0.7623 m²/g and the presence of functional groups such as hydroxyl, amine and carbonyl groups were detected. The effect of initial dye concentration, pH, contact time and SMH doses were elucidated at 20 ± 1 °C. Results show that the pH value of 2 is favorable for the adsorption of all four dyes. The data evaluated for compliance with the Langmuir, Freundlich and BET isotherm models. It was found that data for DR80 and DR81 fitted well with Langmuir isotherm, for AB92, BET isotherm is preferred, while for AR14, the Freundlich isotherm is the most applicable. The adsorption capacities of SMH for DR80, DR81, AB92 and AR14 were, 178.57, 120.48, 114.94 and 109.89 mg/g of adsorbent, respectively. Also, adsorption kinetics of dyes was studied and the rates of sorption were found to conform to pseudo-second order kinetics with good correlation ($R^2 \geq 0.9977$). Maximum desorption of ≥99.8% was achieved for DR80, DR81 and AB92 and 86% for AR14 in aqueous solution at pH 10. Based on the data of present investigation, one could conclude that the SMH being a natural, eco-friendly and low-cost adsorbent with relatively large adsorption capacity might be a suitable local alternative for elimination of dyes from colored aqueous solutions.

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1. Introduction

Presence of numerous dyestuffs with various chemical properties and adverse effects in surface and underground waterways have been concern of elite section of public and government all around the world. The discharge of dye-bearing wastewater into environmental natural waterway from textile, paper, leather, tannery, plastics and cosmetics is the first contaminant that are recognized and due to being colored and turbid, are highly visible and cause damage to the aesthetic nature of the environment [1–3]. Also these dyes may drastically affect photosynthetic

phenomenon in aquatic life due to reduced light penetration [4,5]. As a result, the removal of color from waste effluents has become environmentally important [6,7]. Various methods including coagulation [8], chemical oxidation [9], photocatalysis [10,11], electrochemical [12] and adsorption techniques have been examined. Among the above mentioned methods, adsorption is considered to be relatively superior to other techniques because of low cost, simplicity of design, availability and ability to treat dyes in more concentrated form [13,14]. Activated carbon has been widely studied and proved to have high adsorption abilities to remove a large number of organic compounds. However, its use is limited mainly because of its high cost [15,16]. To find an effective and ideal adsorbent, researchers have exploited many low cost and biodegradable substitutes obtainable from natural resources for the removal of different dyes from aqueous solutions at different operating conditions (Table 1).

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Table 1
Some low cost adsorbents studied to remove dyes from aqueous solutions

Adsorbents	Dyes	Maximum monolayer adsorption capacities (mg/g)	BET surface area (m ² /g)	References
Soy meal hull	Direct re d 80	178.57	0.7623	In this work
Soy meal hull	Direct re d 81	120.48	0.7623	In this work
Soy meal hull	Acid blue 92	114.94	0.7623	In this work
Soy meal hull	Acid Red 14	109.89	0.7623	In this work
Peat	Basic blue 69	184–233	–	[17]
Peat	Acid blue 25	5–9	–	[17]
Orange peel	Direct red 23	10.72	0.8771	[18]
Orange peel	Direct re d 80	21.05	0.8771	[18]
Orange peel	Acid violet 17	19.88	–	[19]
Flyash	Methylene blue	4.48	15.6	[20]
Banana peel	Methyl orange	21.0	20.6–23.5	[21]
Banana peel	Methylene blue	20.8	20.6–23.5	[21]
Banana peel	Rhodamine B	20.6	20.6–23.5	[21]
Banana peel	Congo red	18.2	20.6–23.5	[21]
Banana peel	Methyl violet	12.2	20.6–23.5	[21]
Banana peel	Amido black 10B	6.5	20.6–23.5	[21]
Rice husk	Acid yellow 36	86.9	272.5	[7]
Eucalyptus bark	Remazol BB	90.0	–	[22]
Baggase pith	Acid blue 25	17.5 ± 0.5	–	[23]
Baggase pith	Acid red 114	20.0 ± 0.5	–	[23]
Baggase pith	Basic blue 69	152 ± 5	–	[23]
Baggase pith	Basic red 22	75 ± 2	–	[23]
Sepiolite	Reactive blue 221	3.0–17.05	250–357 (105–700 °C)	[24]
Sepiolite	Acid blue 62	3.67–8.86	250–357 (105–700 °C)	[24]
Indian Rosewood sawdust (sulphuric acid treated)	Methylene blue	24.3	98	[25]
Carbonized coir pith	Congo red	6.7	–	[26]
Fungus <i>Aspergillus niger</i>	Congo red	14.72	–	[27]

Few studies have been appeared in literature on the application of SMH for the removal of metal ions [28,29]. To our knowledge, there is not a reported research paper dealing with the dye removal from colored wastewater by SMH. In our previous study, the effects of operational parameters on the adsorption of direct dyes on orange peel were investigated [18]. The aim of the present research is to investigate the dye removal capacity and potential of SMH from colored wastewater in detail.

2. Experimental

2.1. Chemicals and methods

SMHs were obtained from Behpak Co., Behshahr, Iran. The samples were left for 24 h at room temperature and then was sieved to the particle size of <0.125 mm. Direct dyes (DR80, DR81) and acid dyes (AR14, AB92) were provided by Ciba Ltd. All dyes were used without further purification. The chemical specifications of these dyes are shown in Fig. 1. All other chemicals were of analar grade and purchased from Merck (Germany). The pH measurements were made using a pH meter (Hach). The dye solutions were centrifuged for 10 min in a Hettich EBA20 centrifuge (6000 rpm). UV–vis spectrophotometer CECIL 2021 was employed for absorbance measurements of samples. The maximum wavelength (λ_{\max}) used for determination of residual concentration of DR80, DR81, AB92 and AR14 at pH₀ 2 in supernatant solution using UV–vis spectrophotometer were 542.5, 510.5, 595.0 and 517.0 nm, respectively. Only

linear range of calibration curve is used in this research. In order to investigate the surface characteristics of SMH, FTIR (Perkin-Elmer Spectrophotometer Spectrum One) in the range 450–4000 cm⁻¹ was studied. Fig. 2 shows the FTIR spectrum of SMH. The peak positions are noticed at 3377.39, 2930.63, 1647.54, 1540.18, 1400.65, 1245.91 and 1059.12 cm⁻¹. The bands at 3377.39 are due to O–H and N–H stretching. While the band at 2930.63 represents the CH₂ asymmetric stretching vibration. The bands at 1647.54 and 1540.18 reflect the carbonyl group stretching (amide) and N–H bending, respectively. Bands at 1400.18 and 1059.12 correspond to C–N and C–O stretchings [30,31].

Scanning electron microscope of SMH and adsorbed SMH with DR80, DR81, AB92 and AR14 dyes for comparison were obtained using LEO 1455VP scanning microscope. Adsorbent samples were removed from the dye solution after equilibration and freed from the water by drying at 30 °C for 48 h in preparation for the SEM analysis. The SEM of the dried solids, were then recorded. The surface area of SMH was obtained by using the Brunauer, Emmett and Teller (BET) method with Gemini 2375 micrometrics instrument.

2.2. Sample preparation

The adsorption measurements were conducted by mixing various amounts of SMH (0.01–0.15 g) for DR80 and DR81, (0.05–0.175 g) for AR14 and AB92 in jars containing 250 mL of a dye solution (50 mg/L) at various pH₀ (2–10). The solution pH

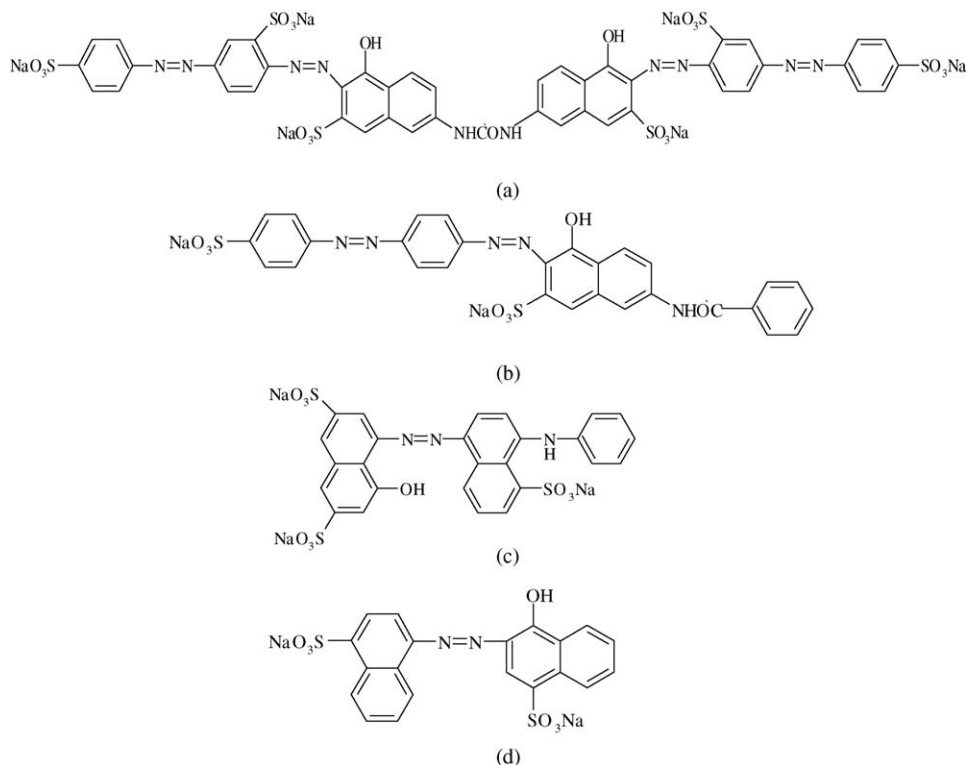


Fig. 1. Chemical structure of (a) DR80 (C.I. no.: 35780, polyazo, $\lambda_{\max} = 542.5$), (b) DR81 (C.I. no.: 28160, disazo, $\lambda_{\max} = 510.5$), (c) AB92 (C.I. no.: 13390, monoazo, $\lambda_{\max} = 595.0$) and (d) AR14 (C.I. no.: 14720, monoazo, $\lambda_{\max} = 517.0$).

was adjusted by adding a small amount of HCl or NaOH (1 M). Dye solutions were prepared using distilled water to prevent and minimize possible interferences in this study. Although in actual cases, the dye wastewater will have a different ionic strength and organics present.

Adsorption experiments were carried out at various concentrations of dye solutions (50, 75, 100, 125 and 150 mg/L) using optimum amount of SMH (0.3 g/L for DR80, 0.6 g/L for DR81 and AB92 and 0.7 g/L for AR14) at pH₀ 2, agitation speed of 200 rpm and 20 ± 1 °C for 24 h to attain the equilibrium conditions. The change on the absorbance of all samples were monitored and determined at certain time intervals (5, 10, 15, 30, 45, 60, 120, 180, 240, 300, 360, 420, 480 and 1440 min) during the adsorption process. The equilibrium was established after 5 min for DR80 and AB92, and 10 min for DR81 and AR14. At

the end of the adsorption experiments, the samples were centrifuged and the dye concentration was determined. The results were verified with the Freundlich, Langmuir and BET adsorption isotherms.

2.3. Desorption studies

The adsorbent that was used for the adsorption of 50 mg/L of dye solution was separated from solution by filtration. The filtered samples were dried and weighted for further adsorption study. It was agitated with 250 mL of distilled water at different pH₀ values (2–10) and agitation speed of 200 rpm for the predetermined equilibrium time of adsorption process. The desorbed dye was estimated as explained in Section 2.2.

3. Results and discussion

3.1. Effect of adsorbent dosage

The effect of SMH doses on the amount of dye adsorbed was investigated by contacting 250 mL of dye solution with initial dye concentration of 50 mg/L using jar test at room temperature (20 ± 1 °C) for 1440 min at a constant stirring speed of 200 rpm. Different amounts of SMH (0.2–0.36 g) for DR80, (0.04–0.6 g) for DR81, (0.2–0.6 g) for AB92 and (0.2–0.7 g) for AR14 were applied. After equilibrium, the samples were centrifuged and the concentration in the supernatant dye solution was analyzed. The plot of dye removal (%) versus adsorbent dosage (g/L) is shown in Fig. 3.

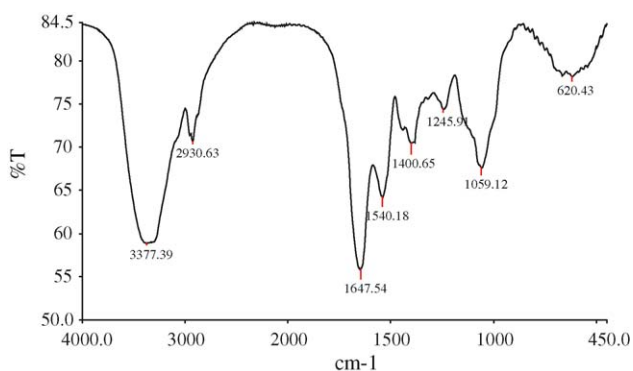


Fig. 2. Fourier transform infra-red (FTIR) spectra of SMH.

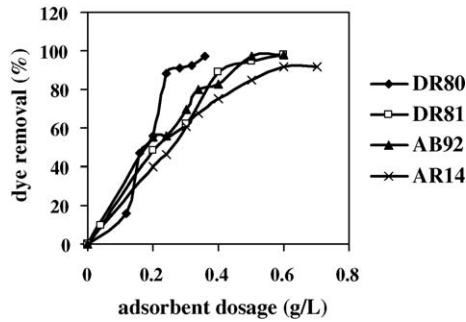


Fig. 3. Effect of adsorbent dosage on the adsorption of dyes on SMH. Conditions: pH₀ 2, T 20 ± 1 °C, S 200 rpm, 50 mg/L of dye concentration and particle size ≤ 0.125 mm.

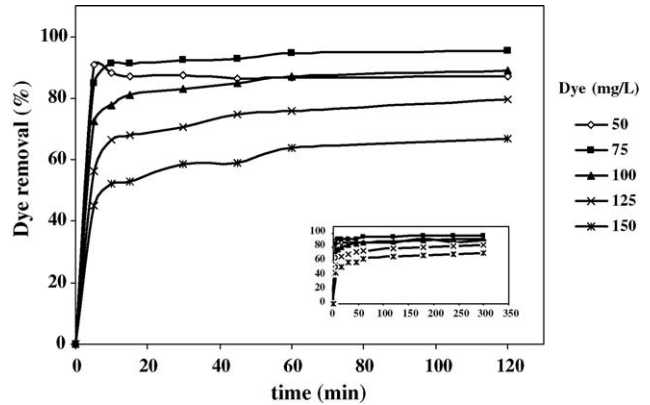


Fig. 6. Effect of time on the adsorption of AR14 on SMH. Conditions: pH₀ 2, T 20 ± 1 °C, S 200 rpm, m_s = 0.7 g/L and particle size ≤ 0.125 mm.

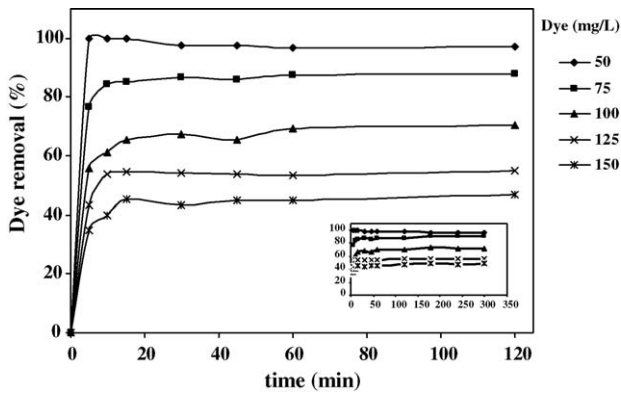


Fig. 4. Effect of time on the adsorption of DR80 on SMH. Conditions: pH₀ 2, T 20 ± 1 °C, S 200 rpm, m_s = 0.3 g/L and particle size ≤ 0.125 mm.

3.2. Effect of contact time

Adsorption is a mass transfer process that can generally be defined as the accumulation of material at the interface between two phases [32]. The adsorption efficiencies of DR80, DR81, AR14 and AB92 dyes on SMH were evaluated by determining the percentage decrease of the absorbance at 542.5, 510.5, 517 and 595 nm, respectively. The influence of varying the initial dye concentration of four dyes was assessed. The results are shown in Figs. 4–7. It is obvious that the higher the initial dye concentration, the lower the percentage of dye adsorbed.

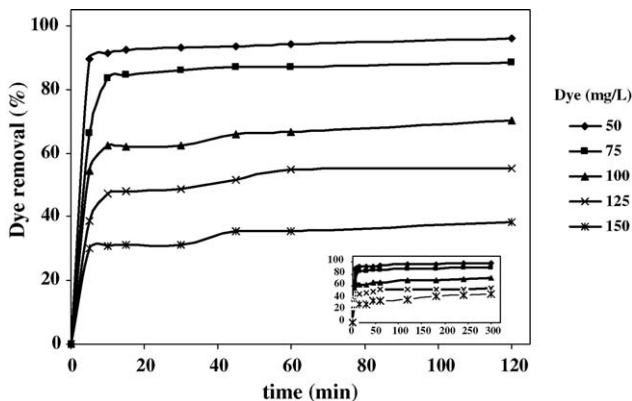


Fig. 5. Effect of time on the adsorption of DR81 on SMH. Conditions: pH₀ 2, T 20 ± 1 °C, S 200 rpm, m_s = 0.6 g/L and particle size ≤ 0.125 mm.

3.3. Adsorption isotherms

Adsorption data explain the performance of adsorbent and adsorption isotherms will describe the equilibrium distribution of solute between adsorbent and solution, which will provide the ability to estimate the adsorbent efficiency and costs.

Three most common isotherm equations namely, Langmuir, Freundlich and BET were tested in this work. The Langmuir equation can be written as follows [32–34]:

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

where q_e is the amount of dye adsorbed on SMH at equilibrium, C_e the equilibrium concentration of dye solution, K_L equilibrium constant and Q_0 is the maximum adsorption capacity.

The linear form of Langmuir equation is:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_0} + \frac{C_e}{Q_0} \tag{2}$$

the essential characteristic of the Langmuir isotherm can be expressed by the dimensionless constant called equilibrium parameter, R_L , defined by

$$R_L = \frac{1}{(1 + K_L C_0)} \tag{3}$$

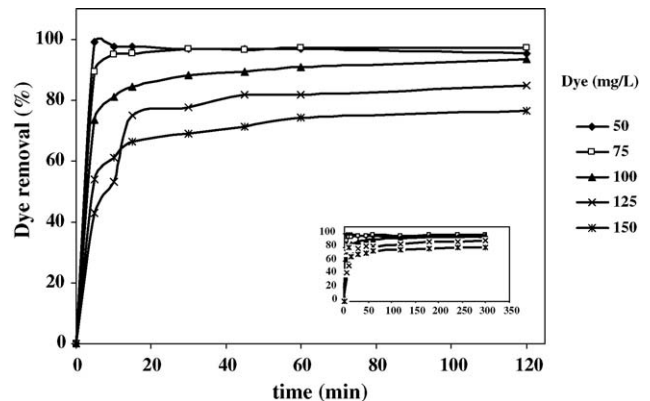


Fig. 7. Effect of time on the adsorption of AB92 on SMH. Conditions: pH₀ 2, T 20 ± 1 °C, S 200 rpm, m_s = 0.6 g/L and particle size ≤ 0.125 mm.

Table 2
Linearised isotherm coefficients for dyes

Dye type	Q_0	K_L	R_L	r_1^2	K_F	$1/n$	r_2^2	K_b	q_m	r_3^2
DR80	178.57	1.401	0.0141	0.9497	146.555	0.0534	0.914	-6.033	55.556	0.896
DR81	120.482	1.660	0.0119	0.9696	85.526	0.099	0.8271	2.863	15.387	0.2315
AB92	114.943	2.8066	7.076×10^{-3}	0.8568	87.197	0.0957	0.8539	0.9796	69.444	0.9773
AR14	109.89	0.5199	0.037	0.9681	57.823	0.192	0.9941	-40.25	62.112	0.9873

where K_L is the Langmuir constant, C_0 the initial dye concentration (mg/L), R_L values indicate the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) [18,19]. The R_L values for the adsorption of DR80, DR81, AR14 and AB92 on SMH have been shown in Table 2.

Also, Isotherm data were tested with Freundlich isotherm that can be expressed by [32–34]:

$$q_e = K_F C_e^{1/n} \quad (4)$$

where K_F is adsorption capacity at unit concentration and $1/n$ is adsorption intensity. $1/n$ values indicate the type of isotherm to be irreversible ($1/n = 0$), favorable ($0 < 1/n < 1$) and unfavorable ($1/n > 1$) [32]. Eq. (4) can be rearranged to a linear form:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (5)$$

The $1/n$ values for the Freundlich adsorption isotherm have been shown in Table 2.

Also, the BET isotherm was attempted to fit the isotherm data that can be shown in the following form [32–34]:

$$q_e = \frac{q_m K_b C_e}{(C_s - C_e) [1 + (K_b - 1) C_e / C_s]} \quad (6)$$

where q_m is amount of solute adsorbed in forming a complete monolayer (mg/g), K_b a constant expressive of the energy of interaction with the surface and C_s is saturation concentration of solute (mg/L).

The linear form of Eq. (6) can be written as follows:

$$\frac{C_e}{(C_s - C_e)q} = \frac{1}{K_b q_m} + \frac{K_b - 1}{K_b q_m} \frac{C_e}{C_s} \quad (7)$$

Fig. 8 shows the adsorption isotherms of dyes (q_e versus C_e) using SMH. The Q_0 , K_L , r_1^2 (correlation coefficient for Langmuir isotherm), K_F , n , r_2^2 (correlation coefficient for Freundlich isotherm), K_b , q_m and r_3^2 (correlation coefficient for BET isotherm) are given in Table 2. Negative values for the BET isotherm constants indicate the inadequacy of the isotherm model to explain the adsorption process, since this constant is indicative of the surface binding energy [4].

The r^2 values (goodness of fit criterion) computed by linear regression for the three types of isotherms are presented in Table 2. The data of Table 2 indicate that the best fit isotherm is a function of sorbent and sorbate considered each time. For example, the Langmuir isotherm is most appropriate for adsorption of DR80 and DR81 on SMH. The Freundlich isotherm is most suitable for adsorption of AR14 on SMH and the BET isotherm

is most appropriate for adsorption of AB92 on SMH. However, from Table 2, the adsorption capacities (Q_0) of SMH for DR80, DR81, AB92 and AR14 were found to be 178.57, 120.48, 114.94 and 109.89 mg/g of adsorbent, respectively. Superficially, one might conclude that due to the presence of large number of sulphonic groups on DR80 in comparison with other dyes the higher adsorption capacity of SMH toward DR80 might be attributed to the increased electrostatic attraction between the positively charged surface of the adsorbent and those abundant sulphonic anionic groups at pH₀ 2. In the case of AR14, although the number of sulphonic groups is low, but it looks the small size and shape of the dye molecule might play determining factor by enhancing the trapping of dye molecules into pores and cavities of the adsorbent, so increasing adsorption capacity.

3.4. Effect of pH

The results of only dye solution studies indicated that change of the initial pH (pH₀) of dye solution has negligible effect on the λ_{\max} of DR80, DR81, AR14 and AB92 dyes (pH₀ 2–10). This observation provided proofs that, at this range of pH, there is not any chemical structural change of dye molecules and in all cases no hydrolysis of dyes occurring. Based on this observation and assuming negligible dissociation of adsorbent, the pH of all dye solutions were reported as initial pH and pH control during all experiments was ignored. The maximum absorbance wavelength (λ_{\max} (nm)) of DR80, DR81, AR14 and AB92 at different pH₀ values were shown in Table 3.

The effect of pH on the adsorption of DR80, DR81, AR14 and AB92 onto SMH is shown in Fig. 9. For all dyes, the adsorp-

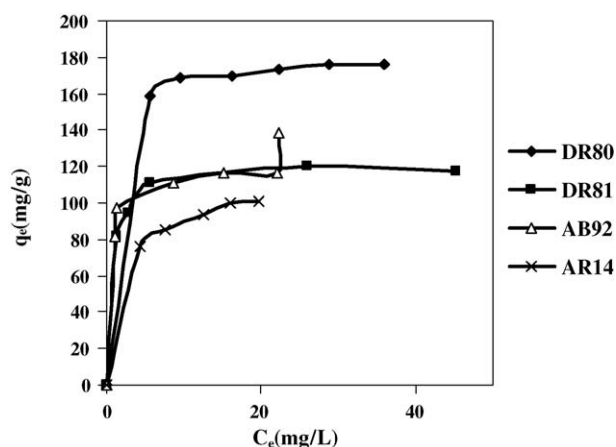


Fig. 8. Adsorption isotherms of dyes using SMH. Conditions: pH₀ 2, T 20 ± 1 °C, S 200 rpm, particle size ≤ 0.125 mm and equilibrium time = 24 h.

Table 3

The effect of initial pH of dye solutions on the maximum absorbance wavelength (λ_{\max} (nm)) of DR80, DR81, AR14 and AB92

pH	$q\lambda_{\max}$ (nm)			
	DR80	DR81	AR14	AB92
2	542.5	510.5	517.0	595.0
4	541.5	509.5	516.5	578.0
6	538.0	510.0	516.5	575.5
8	541.0	510.5	513.0	575
10	538.0	510.5	507.0	573

tion capacity increases when the pH is decreased. Maximum adsorption of direct and acid dyes occurs at acidic pH (pH_0 2). DR80, DR81, AR14 and AB92 are dissociated to polar groups (R-SO_3^-). SMH is comprised of various functional groups, such as amine, hydroxyl and carbonyl which could also be affected by the pH of solutions. Therefore, at various pH, the electrostatic attraction as well as the organic property and structure of dye molecules and SMH could play very important roles in dye adsorption on SMH. At pH_0 2, a significantly high electrostatic attraction exists between the positively charged surface of the adsorbent, due to the ionization of functional groups of adsorbent and negatively charged anionic dye. As the pH of the system increases, the number of negatively charged sites are increased. A negatively charged site on the adsorbent does not favor the adsorption of anionic dyes due to the electrostatic repulsion [26]. Also, lower adsorption of DR80, DR81, AR14 and AB92 dyes at alkaline pH is due to the presence of excess OH^- ions destabilizing anionic dyes and competing with the dye anions for the adsorption sites. The effective pH_0 was 2 and it was used in further studies. Similar results of pH effect were also reported for the adsorption of acid yellow 36 and Congo red [26,7].

3.5. Adsorption kinetics

Several models can be used to express the mechanism of solute sorption onto a sorbent. In order to investigate the mechanism of sorption, characteristic constants of sorption were determined using a pseudo-first order equation of Lagergren [35]

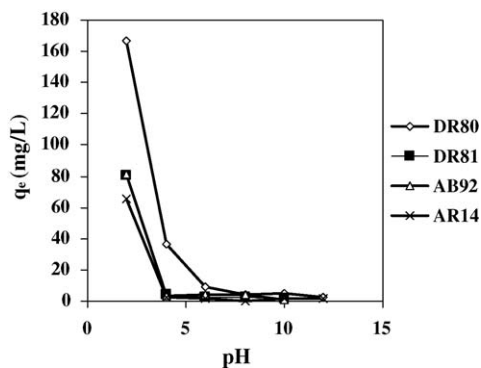


Fig. 9. Effect of pH for the adsorption of DR80, DR81, AB92 and AR14 on SMH. Conditions: T $20 \pm 1^\circ\text{C}$, S 200 rpm, particle size ≤ 0.125 mm and equilibrium time = 24 h.

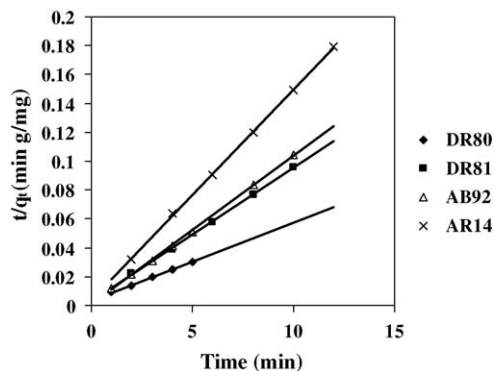


Fig. 10. Pseudo-second order sorption kinetics of DR80, DR81, AB92 and AR14 onto SMH. Conditions: pH_0 2, T $20 \pm 1^\circ\text{C}$, S 200 rpm and particle size ≤ 0.125 mm.

based on solid capacity and a pseudo-second order equation [36] based on solid phase sorption [37,38]. A linear form of pseudo-first order model [Eq. (8)] is:

$$\log(q_1 - q_t) = \log(q_1) - \frac{K_1}{2.303} t \quad (8)$$

where q_1 is the amount of dye adsorbed at equilibrium (mg/g), q_t the amount of dye adsorbed at time t (mg/g) and K_1 is the equilibrium rate constant of pseudo-first order kinetics (1/min). The linear fit between the $\log(q_1 - q_t)$ and contact time (t) under pH 2 can be approximated as pseudo-first order kinetics. Also a linear form of pseudo-second order model [Eq. (9)], Ho and MaKay's pseudo-second order model, was illustrated in Fig. 10.

$$\frac{t}{q_t} = \frac{1}{Kq_e^2} + \frac{1}{q_e} t \quad (9)$$

where q_e is amount of dye adsorbed at equilibrium (mg/g) and K is the equilibrium rate constant of pseudo-second order (g/mg min). The linear fit between the t/q_t and contact time (t) under pH_0 2 can be approximated as pseudo-second order kinetics.

The values of K_1 , K , r_4^2 (correlation coefficient for pseudo-first order sorption kinetics) and r_5^2 (correlation coefficient for pseudo-second order sorption kinetics) were calculated and shown in Table 4. From Table 4, adsorption kinetics of dyes was studied and the rates of sorption were found to conform to pseudo-second order kinetics with good correlation ($R^2 \geq 0.99$).

3.6. Desorption studies

Desorption studies help to elucidate the mechanism and recovery of the adsorbate and adsorbent. As the desorbing pH

Table 4
Kinetics constants for pseudo-first and pseudo-second order model

Dye type	K_1	q_1	r_4^2	K	q_e	r_5^2
DR80	0.775	111.249	0.9851	0.0088	185.185	0.9977
DR81	0.529	33.02	0.9952	0.053	105.26	0.9996
AB92	0.0765	13.511	0.3313	0.152	97.087	0.9996
AR14	0.3312	7.907	0.7304	0.1217	67.568	0.9995

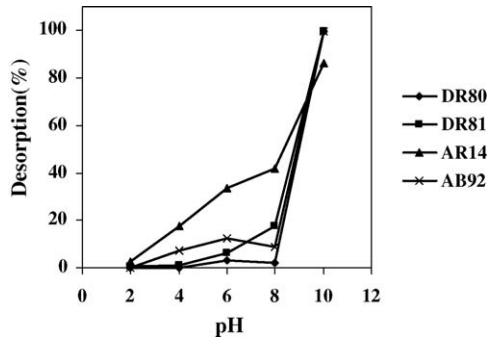


Fig. 11. Effect of pH on desorption of DR80, DR81, AB92 and AR14 on SMH Conditions: $T 20 \pm 1^\circ\text{C}$, $S 200\text{ rpm}$.

was increased, the percent desorption increased from 0 at $\text{pH}_0 2$ to ≥ 99.8 at $\text{pH}_0 10$ for DR80, DR81 and AB92 and from 2.5 at $\text{pH}_0 2$ –86 at $\text{pH}_0 10$ for AR14 at dye concentration of 50 mg/L (Fig. 11).

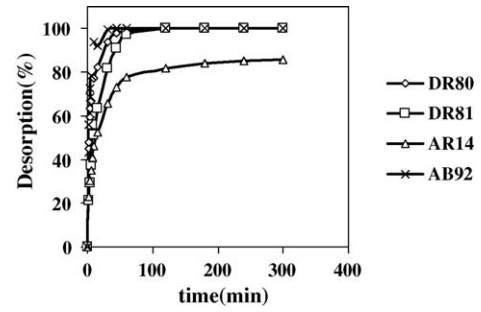


Fig. 12. Effect of time on the desorption of DR80, DR81, AR14 and AB92 from SMH adsorbent. Conditions: $\text{pH}_0 10$, $T 20 \pm 1^\circ\text{C}$, $S 200\text{ rpm}$.

As the pH of the system increases, the number of negatively charged sites increased. A negatively charged site on the adsorbent favors the desorption of dye anions due to the electrostatic repulsion [18,26,27]. At $\text{pH}_0 10$, a significantly high electrostatic repulsion exists between the negatively charged surface of the adsorbent and anionic dye.

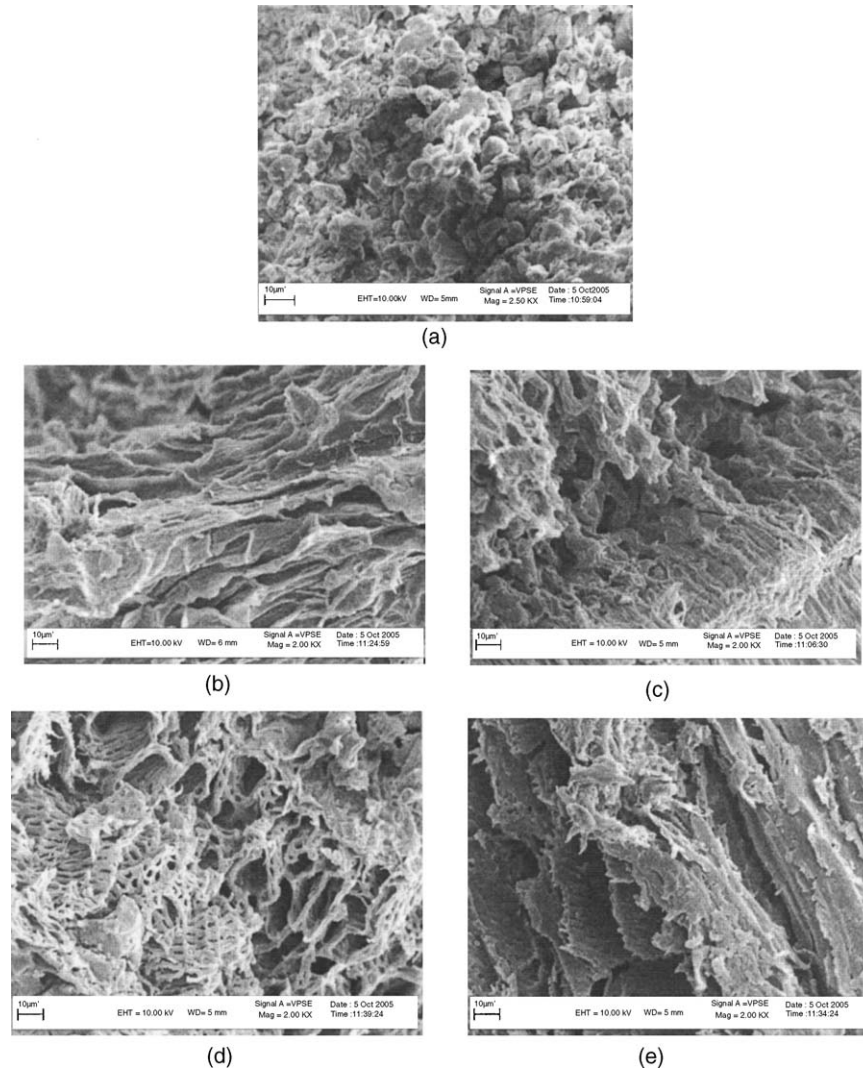


Fig. 13. Scanning electron microscope of (a) original SMH, and dye adsorbed SMH with: (b) DR80, (c) DR81, (d) AB92 and (e) AR14. Conditions: 0.3 g/L of SMH for DR80, 0.6 g/L for DR81 and AB92 and 0.7 g/L for AR14, 50 mg/L of dye concentration, equilibrium time = 24 h, $S 200\text{ rpm}$, $T 20 \pm 1^\circ\text{C}$, and particle size $\leq 0.125\text{ mm}$.

Also, the effect of time on the desorption of four dyes from SMH was investigated at pH₀ 10. Fig. 12 indicates that the maximum desorption time for DR80 and DR81 occurs after 120 min, for AB92 after 45 min and for AR14 after 180 min. These differences on the desorption time might be explained by deep study on the effect of size and charge of molecule on the formation of monolayer and multi-layer over the adsorbent. From the adsorption data, it was found that the DR80 and DR82 are following Langmuir isotherm which is indication of monolayer formation but the other two follow BET and Freundlich isotherms which are sign of multi-layer and heterogeneous adsorption formation.

3.7. SEM analysis

Scanning electron microscopy (SEM) has been a primary tool for characterising the surface morphology and fundamental physical properties of the adsorbent. It is useful for determining the particle shape, porosity and appropriate size distribution of the adsorbent. Scanning electron micrographs of SMH and adsorbed SMH with DR80, DR81, AB92 and AR14 are shown in Fig. 13. From Fig. 13, it is clear that, SMH has considerable numbers of pores where, there is a good possibility for dyes to be trapped and adsorbed into these pores. The SEM pictures of SMH samples show very distinguished dark spots which can be taken as a sign for effective adsorption of dye molecules in the cavities and pores of this adsorbent.

4. Conclusion

The results of this investigation show that SMH has suitable adsorption capacity for the removal of DR80, DR81, AR14 and AB92 from their aqueous solutions. Besides to the pores and cavities in the SMH, presence of functional groups such as hydroxyl, amine and carbonyl groups were found to be the main functional groups responsible for most of the dye adsorption. However, pores of the SMH also play an important role in dye adsorption. It was evident that pH and FTIR methods are good tools in studying the dye adsorption behaviour onto SMH. The most important factors to design and run an industrial adsorption plant are the knowledge of adsorption kinetics and isotherms. Hence, the experimental results were analyzed by using the Langmuir, Freundlich and BET equations. Adsorption obeys Langmuir isotherm for both DR80 and DR81, Freundlich isotherm for AR14 and BET isotherm for AB92. The optimal pH₀ for favorable adsorption was 2. The kinetics studies of four dyes on SMH were performed based on pseudo-first and pseudo-second order rate mechanism. The data indicate that the adsorption kinetics of each dyes on SMH follows the pseudo-second order rate expression. Desorption studies were conducted to elucidate the mechanism and recovery of the adsorbate and adsorbent. At alkaline pH a significantly high electrostatic repulsion exists between the negatively charged surface of the adsorbent and anionic dye. Very high rate of dyes desorption (≥98%) suggest an efficient recovery of the adsorbate and adsorbent which can be reused in desired process.

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