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Adsorptive performance of sunflower seed ash as a novel biosorbent for the elimination of Congo red from aqueous solution

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ABSTRACT

This study investigated the adsorption of an azo dye called Congo red from aqueous solution. Ash prepared from sunflower seed waste was used as the adsorbent. Brunauer–Emmett–Teller (BET), Scanning electron microscopy (SEM), and Fourier-Transform Infrared spectroscopy (FT-IR) analyses were performed to characterize the prepared adsorbent. Based on the results of BET, the specific active surface area was about 102 m^2/g, and the results of SEM indicated that the adsorbent surface had a very fine porosity that could be attributed to the presence of cellulosic materials in the adsorbent structure. In this study, the effect of the initial concentration of Congo red dye (10-50 mg/L), the concentration of adsorbent (1-5 g/L), and the processing time (10-240 min) on the rate of Congo red dye removal was investigated. The results showed that the highest percentage of dye removal, i.e., 92%, was achieved at a dye concentration of 50 mg/L, an adsorbent concentration of 3 g/L, and a processing time of 180 min. Under these conditions, the amount of adsorbed dye per gram of the adsorbent was 15.5 mg/g. In addition, pseudo-first order and pseudo-second order kinetic models were also used for modeling. The modeling results indicated that the pseudo-second order model had a higher level of accuracy. Finally, washing adsorbent with different solvents (one molar sodium hydroxide, double distilled water, and ethanol) was investigated, the results indicated that the adsorbent washed with one molar sodium hydroxide had a proper performance after five times of reuse.

1. Introduction

There are limited resources of freshwater on earth, and the development of industry and urbanization is leading to the release of large amounts of dyes, pollutants, organic pollutants, heavy metal ions, etc. into natural water resources [1]. Azo dyes are the main contaminants produced by industries like printing, cosmetics, textiles, and food dyes. Due to theirstrong toxicity and high level of non-biodegradability in the environment, dyes pose a serious threat to the livesof aquatic animals and

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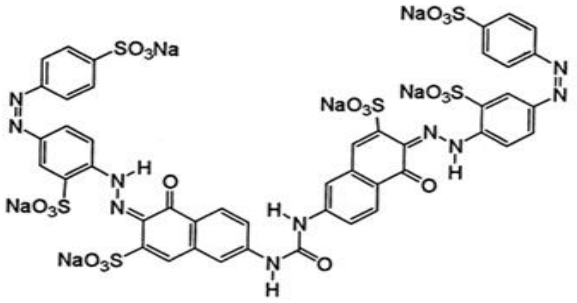
humans, even in low concentrations [2,3]. Polluted water released by industry contains highly carcinogenic and non-biodegradable dyes with Congo red. Wastewater containing Congo red dye is one of the effluent materials in the textile, printing, dyeing, paper pulp, and plastic production industries [4]. In order to reuse these polluted waters, many new and effective adsorbents have been used to remove the contaminants. Dye-contaminated water is decolorized by conventional methods such as coagulation [5], photocatalysis [6-8], and adsorption [9]. Among these, the adsorption method is very effective and efficient because it has features such as low cost, availability of various adsorbents, simplicity of the process, high efficiency, and ease of implementation [10]. The adsorption method has been used in many studies to remove Congo red from wastewater. In some studies, different adsorbents, such as composite layers made of melamine-formaldehyde and polyvinyl alcohol [11], activated carbon nanocomposites made of Guar gum [12], pineapple skin [13], synthetic FexCo3-xO4 nanoparticles [14], synthesized zeolite and ZnO particles [15], chitosan/bentonite composite [16], NiO-SiO_2 composite particles [17], and magnetic cobalt-nickel nanoparticles [18], were used as for removal Congo red from waste water. Many biosorbents have attracted the attention of many researchers due to their cost-effectiveness and good performance in removing Congo red from aqueous solutions containing this type of dye. These include paper and algae waste collected from bio-related companies [19], hydroxyapatite nanorods adsorbents synthesized from phosphogypsum wastes [20], dried powdered cabbage waste [21], Jojoba seed wastes [22], sugarcane bagasse prepared with tartaric acid [23], activated carbon from ashitaba waste and walnut shells [24], saffron stem shells [25], eucalyptus leaf powder [26], natural and modified Clinoptilolite with a surfactant [27], cetyltrimethylammonium bromide and celery residue (Apium graveolens) [28], orange peel powder [29], and activated carbon obtained from apricot kernels [30]. In many previous studies, synthetic adsorbents that have a high price and are harmful to the environment have been used; also, cheap adsorbents have been used, whose surface modifications require the use of chemicals harmful to nature and humans. Various studies have been conducted on the use of sunflower derivatives for adsorption (sunflower heads and stems as adsorbents to remove heavy metals from the aqueous environment [31], sunflower seed husks to remove Reactive Black 5 dye from aqueous solutions [32], sunflower stems for removing lead and cadmium from aqueous solution [33], and activated carbon prepared from sunflower seed husks to adsorb acid violet 17 [34]). In this work, an inexpensive and environmentally friendly adsorbent wasused to remove this coloured wastewater, which wasproduced during a simple process. The sunflower seed extract was used as an adsorbent to remove Congo red dye from an aqueous solution in a continuous fluidized bed reactor. The effects of various operational variables, such as initial dye concentration, process time, and adsorbent concentration, were investigated.

2.Materials and methods

2.1. Materials

Using Congo red dye (Merck, 98 % high purity), synthetic solutions were prepared and used as feed. Table 1 summarizes the characteristics of Congo red [23,27]. The sunflower seed pulp was obtained from local shops producing sunflower oil (Indiamart). Ethanol (Merck, 99.8%) and sodium hydroxide (NaOH) (Merck, ACS reagent, ≥97.0%, pellets) were used in the adsorbent washing step. Double distilled water was used during the experiments.

Table 1. Composition and physicochemical characteristics of Congo red [23,27].

Name	Chemical formula	Molecular structure	M, g/mol	Λ_{max}, m
Congo red	$C_{45}H_{26}N_{10}Na_6O_{21}S_6$		1323.08	**523**

2.2. Preparation of adsorbent

In the present study, ash was prepared from sunflower seed pulp, a known agricultural waste. First, the prepared sunflower seed pulp was placed in the oven, where the temperature reached 600°C at a rate of 5°C/min. It was kept at this temperature for 1 h and then reached ambient temperature. The resulting material (ash prepared from sunflower seed pulp) was then crushed and ground, and particles smaller than 45 µm were separated for testing. The resulting powder particles were stored in an insulated container. Before the experiments, no chemical operations or physical treatments were conducted on the ash.

2.3. Experimental

The schematic of the setup prepared for all experiments is presented in Figure 1. Congo red dye removal was investigated using the adsorption process in a fluidized bed reactor (the volume of the reactor is 100 mL). The fluidized bed reactor was specifically customized to investigate the adsorption of various pollutants. It had the same characteristics as a fluidized bed, in addition to establishing proper mixing to increase the contact between the adsorbent surface and pollutant molecules. This also increased the efficiency. The feed containing the dye solution made with a desired concentration and specific amounts of ash made from the sunflower seed pulp was tested at different contact times in the mentioned fluidized bed reactor. The feed solution in a container was pumped using a peristaltic pump (BT100-1F model) into the reactor from the bottom, hereby fluidizing the adsorbent. In order to increase the mixing and the adsorption efficiency, an electrical motor with a speed of 600 rpm was used to circulate two mechanical stirrers in the laboratory setup. After a specified period of time, a sample was taken out of the setup, centrifugation is carried out (to separate the adsorbent from the treated wastewater) and the solution is discarded. The Congo red dye concentration was determined using a UV-Vis spectrophotometer (PG Instruments, England, Model: T80 ++) at 497 nm and a calibration curve. The calibration curve of the device was drawn separately by preparing solutions with different concentrations of dye. The studied variables included initial dye concentration, process time, and the amount of adsorbent. The dye removal percentage and dye adsorption capacity were calculated using Equations 1 and 2, respectively:

$$\text{Dyeremoval } \% = \frac{C_i - C_t}{C_i} \times 100 \quad (1)$$

$$q_t = \frac{C_i - C_t}{M} \quad (2)$$

where C_i is the initial dye concentration in mg/L, C_t is dye concentration at residence time t in mg/L, q_t is the amount of dye adsorbed per gram of adsorbent at residence time t in mg/g, and M is the adsorbent concentration per liter of solution in g/L.

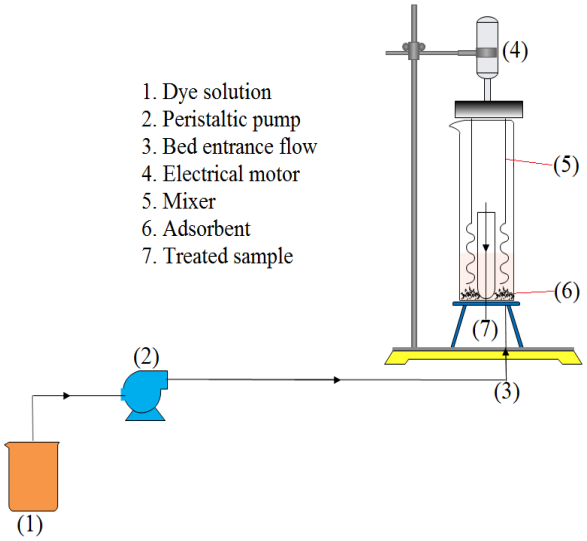


Fig.1. Schematic of the setup used in this study to remove Congo red dye using ash adsorbent obtained from sunflower seed pulp.

2.4. Characterization of the adsorbent (sunflower seed ash)

The BET, SEM, and FT-IR analyses were performed to characterize the adsorbent (ash obtained from sunflower seed pulp). The specific surface area and surface morphology and surface particle size of the samples were assessed using BET (BELSORP MINI II, N2 gas adsorption at K77) and SEM (MIRA3 TESCAN) analyses, respectively. FT-IR spectroscopy of the samples was performed using Thermo Nicolet AVATAR 360 FTIR to determine the functional groups in the samples.

2.5. Readiness of the adsorbent

The ash adsorbent obtained from sunflower seed pulp was washed with ethanol, 1 M NaOH, and double distilled water at 65°C, and the results were compared. Accordingly, the sunflower seed pulp ash collected from the experiment was stirred with 100 mL of each solvent (ethanol, 1 M NaOH, and double distilled water) for 180 min; after filtration using a filter paper and drying at an ambient temperature for 12 h, it was used again.

3. Results and discussion

3.1. Characteristic analysis of the ash obtained from sunflower seed pulp

Based on the results of BET analysis, specific surface area, total pore volume, and mean pore diameter of the ash adsorbent obtained from sunflower seed pulp ash were 102.68 m^2/g, 0.099 cm^3/g, and 3.859 nm, respectively. The results of the specific surface area of this adsorbent with other similar adsorbents are presented in Table 2.

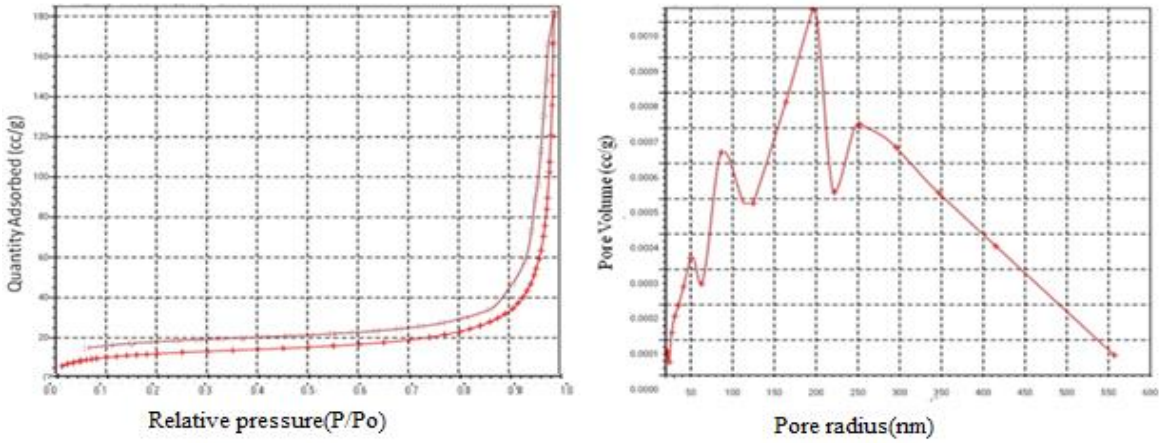


Fig. 2. BET Analysis of Sunflower seed ash

Table 2. Comparison of BET results of the used adsorbent with other studies.

Adsorbent	Specific surface area, m^2/g	Reference
natural clinoptilolite	11.93	[27]
activated carbon-sunflower seed hull	21.06	[34]
Sunflower waste–MnO_2-Fe composite	47.14	[35]
fly ash from a local power plant	7.53	[36]
sunflower seed pulp ash	102.68	this study

SEM analysis (Figure 2) was performed to study the surface variations of the sunflower seed ash employed for the adsorption process. The result showed that the bio sorbent exhibited some rough surfaces with pores of various dimensions. The pores could provide good accommodation for the pollutant dye molecules, hence affecting the adsorption process and providing the broad capability of the adsorbent for effective removal of the target dye from aqueous solutions.

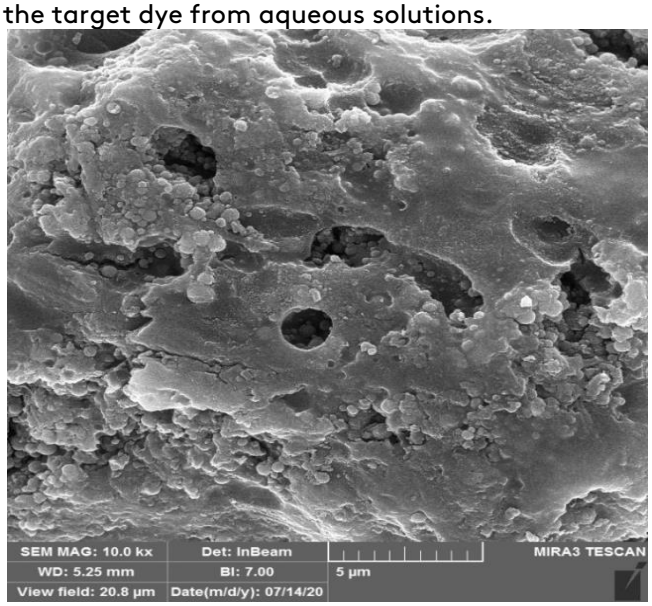


Fig. 3. Scanning electron microscopy image of the ash adsorbent.

The use of FT-IR spectra is a very important technique for determining the characteristics of functional groups as well as studying the changes of these groups in the absorbent. The FT-IR spectrum of the ash adsorbent before and after the adsorption of Congo red is presented in Figures 3-a and 3-b, respectively. Figure 3-a presents a large number of adsorption peaks that determine the composition of the substance. The presence of 3502.90 cm^{-1} and 3422.58 cm^{-1} bands indicated the tensile frequency of the hydroxyl functional group (OH) at the adsorbent surface. The peak of adsorption in the regions of 2923.47 cm^{-1} and 2856.99 cm^{-1}wasattributed to the symmetric tensile frequency of the -CH_3 group. The strong bond in the region of 1627.66 cm^{-1} indicated the tensile frequency of C=O in carboxylic acid, which bonded with intramolecular hydrogen [39]. The peak of 1387.86 cm^{-1} was caused by the symmetric curvature of -CH_3. The adsorption peak observed around 1084.54 cm^{-1}mightbe related to the frequency change at OH and the tensile frequency at C-O-C in the cellulosic structure of the adsorbent. The FT-IR results showed that the surface of ash adsorbent was abundant with different oxygen functionalities (O–H, C=O, C–O–C). These functionalities will act as active binding sites for the effective uptake of anionic dyes from the water phase [22]. As shown in Figure 3-b, after the adsorption of Congo red, the peak of tensile frequencies of the hydroxyl group and the tensile frequency of C=O in carboxylic acid with bounded intra-molecular hydrogen changed, and frequencies of 3502.90 cm^{-1} and 1627.66 cm^{-1}, respectively, were reduced to 3426.20 cm^{-1} and 1625.33 cm^{-1}. These changes all indicated the good adsorption of Congo red on the adsorbent.

3.2 Effect of operational variables on the elimination of Congo red

This study investigated the effect of different variables, including initial Congo red dye concentration, adsorbent concentration, and process time on Congo red dye removal. The values of each of these variables and their dimensions are presented in Table 3. Table 3 shows the initial concentration of the dye, the concentration of the adsorbent, and the processing time.

Table 3. Operational variables in Congo dye adsorption process and their levels.

Factor	Symbol	Unit	Levels
Congo red initial concentration	C_i	mg/L	10, 30, 50
adsorbent concentration	M	g/L	1, 3, 5
Time	t	min	10, 20, 30, 60, 90, 120, 150, 180, 240

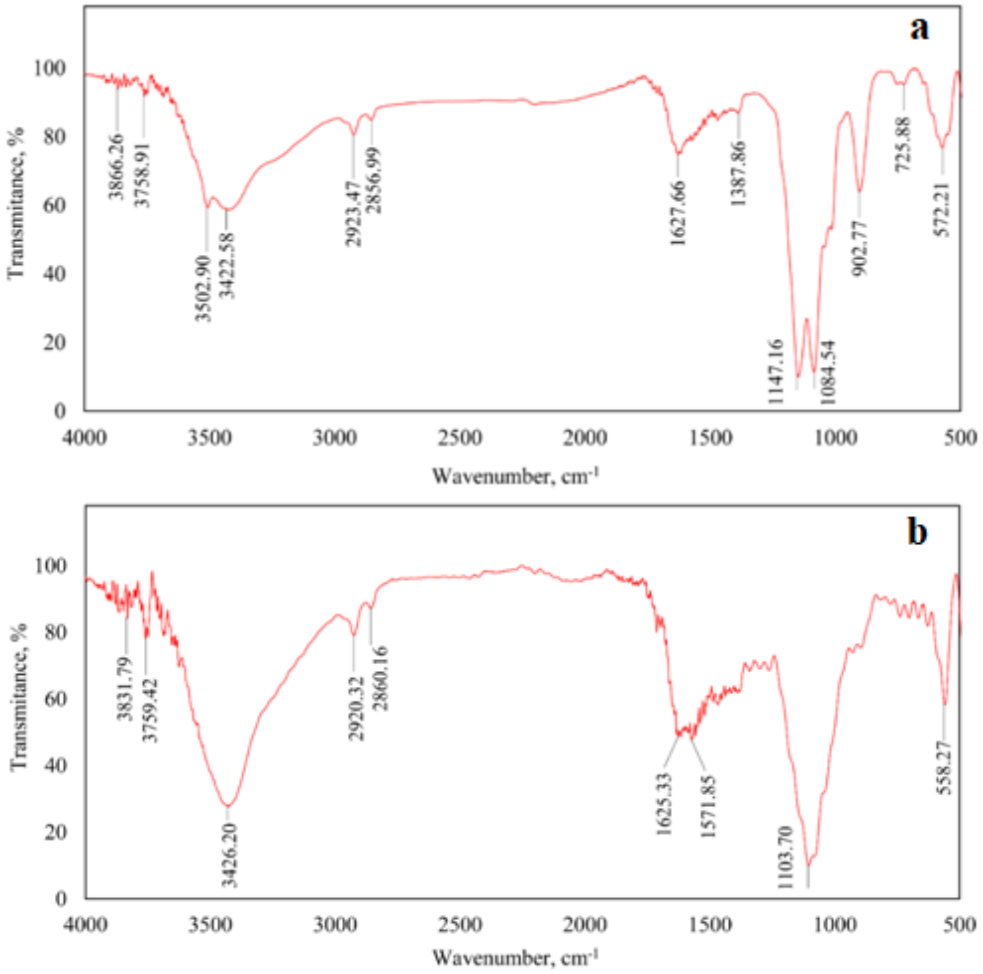


Fig.4. FT-IR spectrum of the ash adsorbent obtained from sunflower seed pulp: (a) before adsorption and (b) after adsorption.

Figure 4 presents the curves of the Congo red dye removal percentage over time at different concentrations of the ash, an adsorbent. As shown in this figure, after 10 min, more than 57% of the dye in the aqueous solution was removed. However, with further passage of time beyond 10 min, the dye removal decreased over time, but the color removal percentage still increased. At 120 min, the color removal percentage had become almost constant over time, but still the dye removal rate slightly increased until 180 min. So, the adsorption process of Congo red on the adsorbent by changing the residence time included two stages: rapid initial adsorption and slow adsorption at the end of the process. It was obvious that the initial rapid adsorption occurred due to the high affinity of Congo red and the adsorbents. Also, high adsorption sites and mass transfer gradient between the adsorbent and Congo red could be among the reasons for this fast adsorption. On the other hand, due to the saturation of the absorbent sites and reduction of the number of empty sites for adsorption, the amount of adsorption decreased in the final times [27]. As the diagrams in Figure 4 indicate, the adsorbent concentration played an important role in the percentage of Congo red dye removal. Increasing the adsorbent concentration from 1 g/L to 3 g/L showed a significant increase in Congo red dye removal percentage. With increasing the adsorbent concentration from 3 g/L to 5 g/L, the percentage of dye removal decreased slightly and remained unchanged in some cases. The diagrams in Figure 5 present the amount of dye adsorbed in grams of the adsorbent (q_t) over time. As shown in these figures, at low adsorbent concentrations (M = 1 g/L), the highest amount of adsorbed dye per gram of the adsorbent was observed, and with increasing

the adsorbent concentration to 3 g/L and then 5 g/L, the amount of adsorbed dye in grams was reduced. In other words, the more adsorbents there are, the lower the ratio of adsorbed dye per gram of the absorbent. Considering these diagrams, it is also worth noting that with increasing the adsorbent concentration, the time required to reach the final amount of adsorbed dye decreased due to the presence of more adsorbent available and the lower time of the adsorption process. Considering the results presented in Figures 4 and 5, the dye concentration of 50 mg/L, the adsorbent concentration of 3 g/L, and the time of 180 min can be introduced as the optimal operating conditions. Under these conditions, the percentage of dye removal was 91.89%, and the amount of dye absorbed per gram of the adsorbent was 15.32 mg/g.

3.3. Kinetic modeling of Congo red adsorption on ash obtained from sunflower seed pulp

In order to determine the adsorption mechanism, quantify the adsorption kinetics, and determine the limiting phase velocity, two adsorption kinetics models, i.e., pseudo-first order and pseudo-second order, were utilized [40]. Primarily, a pseudo-first order model was used to determine adsorption processes. The pseudo-first order kinetic equation or the so-called Lagergren equation assumes that the rate of uptake of adsorption sites is proportional to the number of sites not occupied [41]. This term is expressed by the following equation.

$$\frac{dq_t}{dt} = k_1(q_e - q_t)t = 0,\ \ q_t = 0 \rightarrow \ln\ln(q_e - q_t) = \ln\ln q_e + k_1 t \quad (3)$$

where q_t and q_e are the amount of dye adsorbed at the residence times of t and equilibrium, respectively, and k_1 is a pseudo-first order equation per min^{-1}.

When adsorption is consistent with the first-order model, the experimental data $\ln(q_e - q_t)$per$t$ must represent a linear relation, and the values of k_1 and q_e can be calculated using the slope and the intercept. In addition, the calculated q_e must correspond to the experimental q_e [42]. Table 4 represents the values for $q_e(\exp.), q_e(\text{calc.})$, k_1 and R^2 for the pseudo-first order model. As shown in this table, the calculated q_e values deviated from the experimental q_e despite the high correlation coefficient $(R^2 > 0.90)$ .Thus, a pseudo-first order model cannot describe the dye adsorption process. Therefore, a pseudo-second order model was used to determine the adsorption process. The second-order kinetics model was based on the assumptions of the occupancy rate of adsorption sites proportional to the square of the non-occupied sites. Moreover, the number of occupied sites was proportional to the fraction of the adsorbed dye, which is widely used in adsorption processes [41,43]. This model is expressed by Equation 4:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 t = 0,\ \ q_t = 0 \rightarrow \frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e} \quad (4)$$

where q_t and q_e are the amount of the dye adsorbed at the residence times of t and equilibrium, respectively, and k_2 is the constant adsorption rate of the pseudo-second order equation per (g/mg) (min^{-1}).

According to Equation 4, when the t/q_t diagram per t has a linear relationship, it indicates that the pseudo-second order kinetic model is suitable for adsorbing the Congo red dye on the ash adsorbent. Figure 6 shows that t/q_t had a significant linear relationship with t, which was proved by a high correlation coefficient ($R^2 \gg 0.99$). In addition, the calculated q_e values corresponded to the experimentalq_e (Table 4). These results indicated a higher correlation of the pseudo-second order equation than the first-order equation. Similar results have been observed in other studies on the adsorption of Congo red dye [23,24,26]. Also, the adsorption capacity of the sunflower seed pulp ash for Congo red removal was compared to other studies. As can be seen in Table 5, the adsorption capacity of sunflower seed pulp ash was almost near to the average of adsorption capacity of the other ash adsorbents used in previous studies to adsorb Congo red from wastewater.

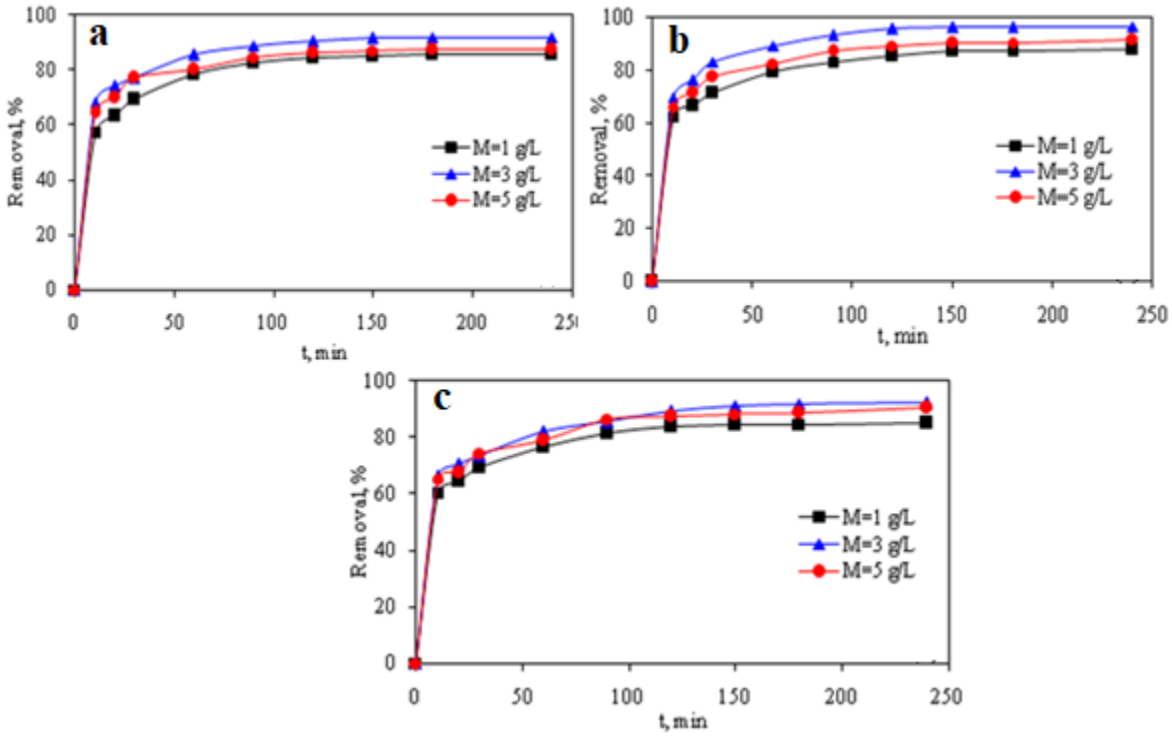


Fig.5. Effect of adsorbent load on the removal of Congo red over time at (a) initial dye concentration = 10 mg/L, (b) initial dye concentration = 30 mg/L, and (c) initial dye concentration = 50 mg/L..

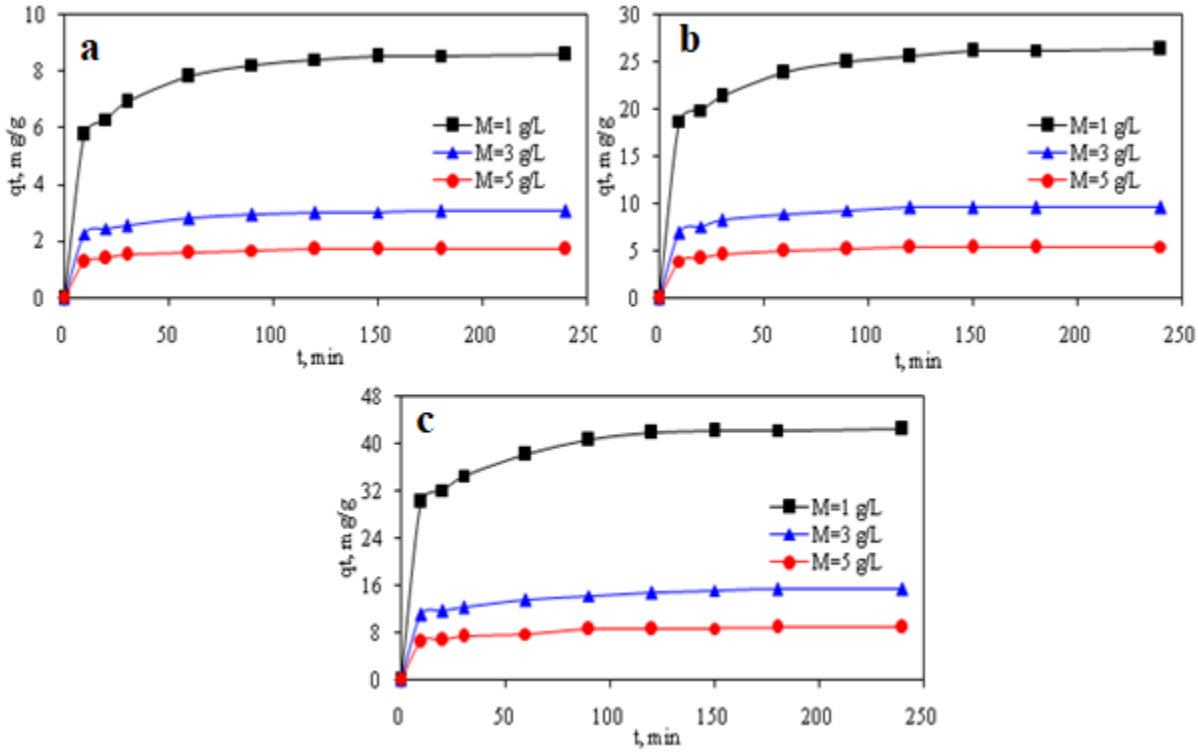


Fig.6. Adsorption capacity of the adsorbent (sunflower seed ash) at different concentrations over time under (a) initial dye concentration =10 mg/L, (b) initial dye concentration = 30 mg/L, and (c) initial dye concentration = 50 mg/L.

Table 4. Results and parameters of pseudo-first order and pseudo-second order adsorption equations.

C, mg/l	q_e (exp)mg/g	Pseudo-first order			Pseudo-second order		
		q_e (calc)mg/g	k_1, min^{-1}	R^2	q_e (calc), mg/g	k_2, (min^{-1})	R^2
10	3.06	1.76	0.0353	0.9616	3.14	0.0603	0.9999
30	9.67	5.48	0.0339	0.9821	9.92	0.0187	0.9999
50	15.34	11.48	0.0334	0.9570	15.85	0.0084	0.9995

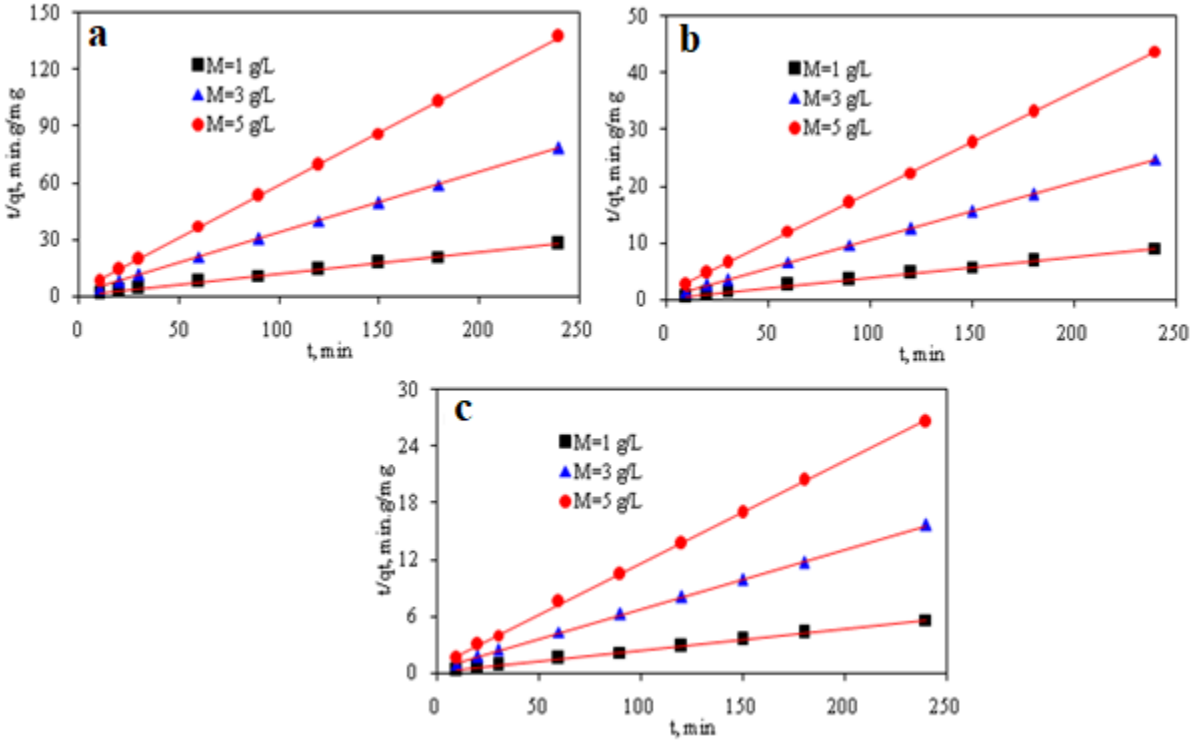


Fig. 7. Kinetic model of dye removal on pseudo-second order equations (t/q_tpert) at different concentrations of the sunflower seed ash as adsorbent under(a) initial dye concentration = 10 mg/L, (b) initial dye concentration = 30 mg/L, and (c) initial dye concentration = 50 mg/L.

Table 5. The comparison of adsorption capacity of Congo redby different adsorbents.

Adsorbent type	q_e (exp), mg/g	Reference
cationic modified orange peel powder	107.0	[29]
guava leaf-based activated carbon	47.6	[44]
Sunflower waste- manganese iron oxide composite	45.7	[35]
tea waste	32.3	[45]
activated carbon from apricot stone	23.4	[30]
fly ash from a local power plant	22.1	[36]
Antigononleptopus leaf powder	18.2	[46]
natural clinoptilolite	16.9	[27]
Pisum sativum	16.4	[47]
sunflower seed pulp ash	15.3	this study
Solanum tuberosum	6.9	[47]
pine bark	3.9	[48]

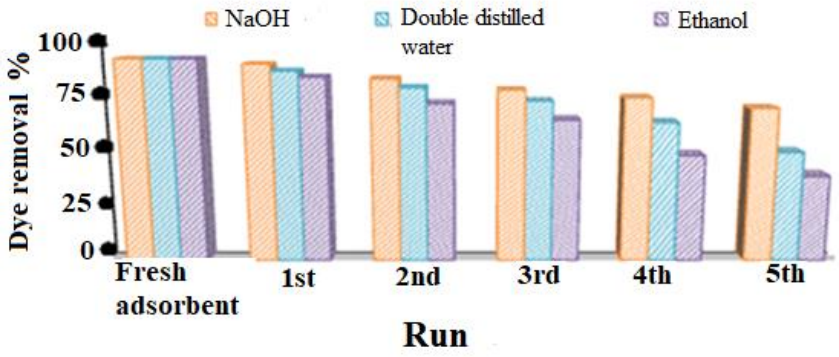


Fig. 8. Results of the washing process of the adsorbent used in this study using different solvents.

The adsorbent reusability process was performed according to the mentioned method under optimal conditions (initial dye concentration of 50 mg/L, residence time of 180 min, and the adsorbent concentration of 3 g/L). Different solvents were used to wash the adsorbent, and a 1 M NaOH solution, 65% double distilled water, and ethanol performed well in the washing process. Figure 7 summarizes the results of the washing process of the ash adsorbent obtained from sunflower seed pulp. Based on the results presented in this figure, using 1 M NaOH solution, it became possible to wash the adsorbent for five rounds of reuse while retaining the Congo red dye removal capacity. Double distilled water at 65 °C was able to wash the adsorbent well for four times. Finally, the adsorbent washing process using ethanol was performed for three rounds while maintaining the Congo red dye removal capacity.

5.Conclusion

This study used the ash adsorbent obtained from sunflower seed pulp waste to adsorb Congo red dye from an aqueous solution. The effects of initial dye concentration, adsorbent concentration, and process time were investigated. The results showed that the ash had good potential to adsorb Congo red dye. In addition, the pseudo-first order and pseudo-second order kinetic models were utilized for modeling; the results showed that the pseudo-first order model had a higher accuracy. Finally, the washing process of the adsorbent used by different solvents was investigated, and it was found that the one molar solution had a high capacity to wash the adsorbent used in this study.

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