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Adsorption of the reactive azo dyes onto NH_4Cl-induced activated carbon

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Abstract

Background: The efficacy of NH_4Cl-induced activated carbon (NAC) was examined in order to adsorb RR198, an azo reactive model dye, from an aqueous solution.
Methods: The effects of pH (3 to 10), adsorbent dose (0.1 to 1.2 g/L), dye concentration and contact time on the adsorption efficiency were investigated.
Results: The results showed that the removal of dye was highest at a solution pH of 7 and a powder dose of 1.1 g/L. The 85.9%, 72.6% and 65.4% removal of RR198 was obtained for a concentration of 25, 50 and 100 mg/L, respectively, at a relatively short contact time of 30 minutes, and at optimum pH and NAC concentrations of 1 g/L. The experimental data for kinetic analysis illustrated a best fit to the pseudo-second-order model. The study data on equilibrium were modeled using Langmuir, Freundlich and Dubinin–Radushkevich models; the Langmuir equation provided the best fit for the data.
Conclusion: Therefore, the NAC appears to be an efficient and appropriate adsorbent for the removal of reactive azo dyes from waste streams.
Keywords: Azo dye, Adsorption, Modified activated carbon, Equilibrium, Isotherm, Kinetic.
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Introduction

Wastewater generated by industries which make use of dyes to color their products contains significant concentrations of dyes (1). Synthetic dyes possess a very complex aromatic structure and are recalcitrant. Thus, they may be toxic to humans and harmful to the receiving aquatic ecosystems (2,3). In order to prevent potential adverse effects to humans and the environment, there is need to efficiently and economically remove the dyes from the contaminated effluent before being released to the environment (4).

Several physical, chemical and biological processes have been applied and/or investigated for the removal of dye from wastewater (5,6). Biological processes are known to be the most economical and environmentally accepted wastewater treatment techniques; however, dye molecules are considered non-biodegradable due to their recalcitrant nature (7), which makes the bioprocesses inefficient in treating such waste streams. Therefore, wastewater containing dyes is treated, using physical or chemical means. Although chemical processes, especially advanced oxidation processes, can often degrade and decompose the dye molecules into simple compounds and/or mineralize

them, these processes are capital intensive and difficult to operate. Physical operation remains the most commonly used method; adsorption is among the most efficient techniques for the removal of organic compounds from industrial effluents (8,9), including dyes (10). Adsorption is efficient, simple to design and operate, unaffected by toxicity, and inexpensive (11), and it is therefore an efficient and economical technique for the removal of dyes from contaminated streams.

Although many low-cost materials have been studied to date for dye removal, most of them possess relatively low adsorption capacity, resulting in the inefficiency of the process. Due to its very high specific surface area and capacity, activated carbon is the most commonly applied adsorbent for the removal of various organic compounds from contaminated streams (7,12). However, the main disadvantages of activated carbon are its high production and treatment costs (13,14). Therefore, to make the adsorption process cost-effective for dye removal, the development of more efficient adsorbents is required.

An NH_4Cl-induced activated carbon (NAC) was recently prepared and its efficiency in the removal of antibiotics (amoxicillin) and pesticides (diazinon) from contami-

nated water investigated (15,16). The results indicated a very high performance of the NAC as compared with the standard activated carbon (Merck Co.) for the removal of amoxicillin from water (16). However, to expand the application of NAC in the water industry, the understanding of its ability to remove other classes of water contaminants is crucial.

The present work was therefore planned to evaluate the capability of NAC to adsorb reactive red 198 (RR198), an azo model dye, from a synthetic aqueous solution. This work was intended to possibly introduce a new and inexpensive adsorbent for the removal of dyes from polluted streams. The influences of basic variables, including pH of the solution, adsorbent concentration, reaction time, and dye concentration, on the removal of the model dye were studied. The isotherm and kinetic properties of RR198 adsorption onto NAC were also assessed.

Methods

Materials

The adsorbent NAC is a mesoporous material, having the hydroxyl, aliphatic, carboxylic and carbonyl functional groups on its surface. The preparation method and main properties, such as fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and BET of the NAC, used in the present study are provided in details elsewhere (16). The RR198 selected for this study represents the reactive azo dye and the specification is represented in Figure 1. A 1 g/L RR198 solution was made as the stock solution. A preparation of the desired-concentration solutions of RR198 required for the adsorption experiments was made using sufficient dilution of the stock solution with distilled water.

Adsorption experiments

The adsorption studies were carried out as batch tests in 250 mL glass beakers using 100 mL dye solution as the working volume. For each test, the desired amount of adsorbent was added to the flask containing 100 mL dye solution at known concentration and pH. The suspension was then magnetically-stirred and sampled at the defined contact times. Each sample was filtered through a fiber-glass filter having 0.2 μm pore size in order to separate the particles; the filtrate was analyzed for the residual dye. The effects of initial pH (3 to 10), concentration of adsorbent (0.01 to 1.2 g/L) and dye concentration (50 to 150 mg/L) on the adsorption process were investigated. All experiments were performed at room temperature in triplicate, and about 221 samples were taken and analyzed, with the average of the results reported. The effectiveness of the prepared powder for adsorbing RR198 was evaluated based on the dye removal percentage which is calculated from the following equation:

$$Dye\ removal\ (\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{1}$$

Where C_0 (mg/L) and C_t (mg/L) represent the concentration of RR198 at initial and contact time t (min), respectively.

Kinetic experiments

Kinetic experiments were conducted as batch tests using several flasks containing 100 mL dye solution at different concentrations, ranging from 50 to 150 mg/L. The pH was regulated at the optimum value obtained from previous experiments. Each flask received 0.1 g, followed by stirring. The suspension was sampled at various time intervals between 1 and 40 minutes. The extracted samples were filtered and the filtrate was analyzed for the residual dye concentration.

Isotherm experiments

Experiments for the evaluation of the adsorption isotherm of RR198 onto the prepared adsorbent were conducted using a series of Erlenmeyer flasks containing 100 mL RR198 solution with various concentrations, ranging from 25 to 100 mg/L and optimum pH. Each flask received 0.1 g powder. The flasks were then magnetically stirred for 2 hours at a constant temperature of 25°C to ensure the attainment of equilibrium. The concentration of the remaining dye in the solution at the end of the tests was measured in the filtrate.

The adsorption capacity, $qe(mg/g)$ which is the amount of dye adsorbed onto the adsorbent was calculated based on

Properties	RR198
Chemical formula	$C_{27}H_{18}ClN_7Na_4O_{15}S_5$
Class	Azo
C.I. number	18221
Molecular weight (g mol^{-1})	967.5
Solubility in water (g L^{-1})	75
λ_{max} (nm)	518
Chemical structure	

Figure 1. The properties of RR198.

the following mass balance equation:

$$q_e = \frac{V(C_0 - C_e)}{m} \tag{2}$$

Where V is the volume of the dye solution (0.1 L), C_0 and C_e (mg/L) are initial and equilibrium dye concentrations, respectively, and m (g) is the mass of adsorbent added to the flask. The concentration of RR 198 was measured using a UV-visible spectrophotometer (UV-2100 UV/Vis Spectrophotometer – UNICO) at a maximum absorption wavelength of 518 nm.

For the determination of the pH_{pzc} (pH of the point zero charge), 250 ml of distilled water was added to a glass beaker and the pH was adjusted between 2 and 12, using 0.1 M HCl and NaOH. Then, 0.2 g of NAC was added to the solution and after 48 hours, the final pH was measured and plotted against the initial pH. Ultimately, the differences between the initial and final pH values were plotted against the initial pH. The point of intersection of the resulting curve with the horizontal axis gave the pH_{pzc} (17).

Results

In order to obtain the optimum pH for maximum adsorption of RR198 onto the NAC, the effect of the pH of dye solution, ranging from 3 to 10, was investigated under the following constant conditions: RR198 concentration of 50 mg/L, NAC concentration of 1 g/L, and contact time of 30 minutes. The adsorption experiments for each pH were conducted in triplicate, and the average results presented in Figure 2. From the figure, an increase in the pH from 3 to 7 caused corresponding increase in the percentage of RR198 adsorption from 51.5% to a maximum of 85.7%. There was a decrease in dye removal when the pH was increased to more than 8.

The influence of NAC concentration on the adsorption of RR198 was evaluated in batch experiments by the addition of various concentrations of NAC, ranging from 0.1 to 1.2 g/L into a flask containing 100 mL of 50 mg/L RR198 solution. The stirring (contact) time and pH of the solution were kept constant at 30 minutes and 7, respectively, for all batch experiments. Figure 3 illustrates the RR198 removal as a function of adsorbent quantity. As observed, the removal percentage of the target dye increased from 44.5% to 87.9% when the concentration of NAC was increased from 0.1 to 1.1 g/L. Further increase in the concentration of NAC did not affect the adsorption of RR198.

The effect of dye concentrations, ranging from 25 to 100 mg RR198/L on its removal was evaluated over a contact time of 40 minutes, using a 100 mL dye solution at constant pH and adsorbent doses of 7 and 0.1 g, respectively. Figure 4 presents the results of this phase of study in terms of removal percent. The 85.9%, 72.6% and 65.4% removal of RR198 was obtained for a concentration of 25, 50 and 100 mg/L, respectively, at a relatively short contact time of 30 minutes.

To evaluate the order and rate of the adsorption of RR198 onto the prepared adsorbent, the experimental results for equilibrium conditions were fitted with the pseudo-first
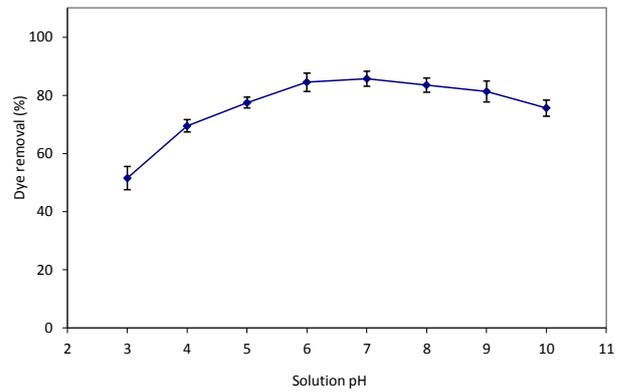

Figure 2. Influence of RR198 solution pH on dye removal (NAC concentration = 1 g/L, dye concentration = 50 mg/L, stirring time = 30 min).
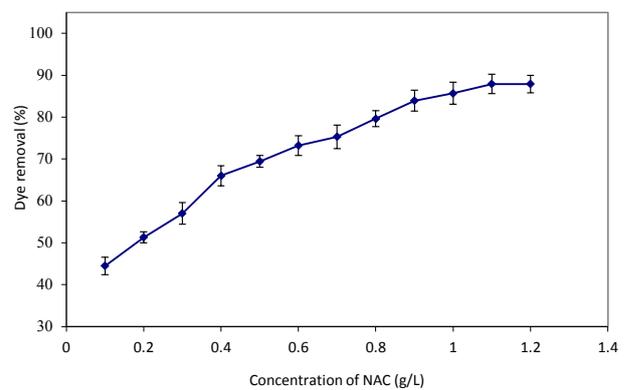

Figure 3. Influence of initial adsorbent mass on removal of RR198 (pH = 7, dye concentration = 50 mg/L, stirring time =30 min).
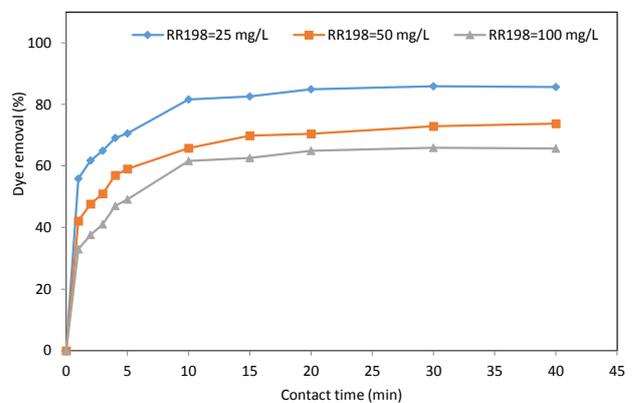

Figure 4. Influence of initial dye concentration and contact time on removal percent of RR198 (NAC concentration = 1 g/L, pH = 7, dye concentration= 25-100 mg/L, stirring time = 10-60 min).

and pseudo-second order reaction rate models, which have the following linear form (18) for boundary conditions of $q = 0$ at $t = 0$ and $q_{t} = q_e$ at $t = t_e$:

Pseudo-first order equation: $\ln(q_e - q_t) = \ln q_e - k_1 t$ (3)

Pseudo-second order equation:

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

Where k_1 and k_2 are constants of adsorption rate, q_t is the

adsorption capacity at time t, and q_e is the adsorption capacity at equilibrium conditions.

The experimental data for three concentrations of 25, 50 and 100 mg/L were fitted to these two models. It was discovered that the pseudo-second order model possessed a higher correlation ($R^2 > 0.99$) with the experimental data. The plots of the pseudo-second order model are presented in Figure 5, and the kinetic information is summarized in Table 1.

Intra-particle diffusion was checked using the Weber and Morris equation (17):

Where k_{id} is the constant of intra-particle diffusion (mg/g·min$^{0.5}$) and C is the plot intercept. The linear relationship between q_t and $t^{0.5}$ when the line extends from the plot origin indicates that intra-particle diffusion is the only step which limits the adsorption rate (3,19).

Although several isotherm models have been developed for the evaluation of equilibrium adsorption; in this study, four of the most commonly applied models, including Langmuir, Freundlich, and Dubinin–Radushkevich (D-R) models, were used to model the adsorption of RR198 onto the prepared adsorbent. The linear forms of these equations are as follows (3):

Langmuir Isotherm:

$$\frac{C_e}{q_e} = \frac{1}{b\,q_{max}} + \frac{C_e}{q_{max}} \tag{6}$$

Where q_{max} (mg/g) is the maximum adsorption capacity. The b parameter is a coefficient related to the energy of adsorption and increases with increasing strength of the adsorption bond. Values of q_{max} and b are determined from the linear regression plot of C_e/q_e versus C_e.

Freundlich Isotherm:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{7}$$

Where K_F and n are constants from the Freundlich equation. The constant K_F represents the capacity of the adsorbent for the adsorbate, and $1/n$ is the reciprocal of reaction order which is a function of the strength of adsorption. A linear regression plot of $\ln q_e$ versus $\ln C_e$ gives the K_F and n values.
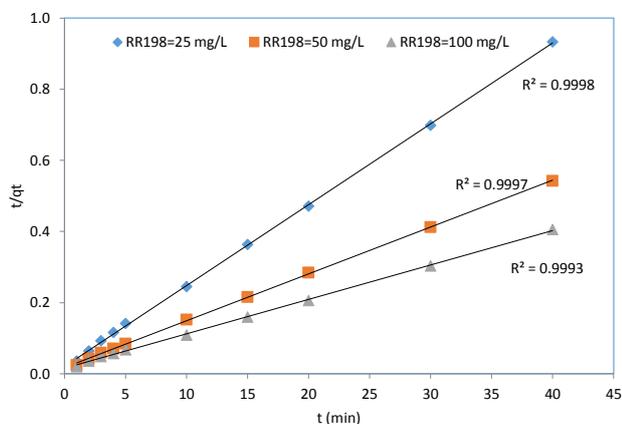
Dubinin–Radushkevich isotherm (D-R):

$$\ln q_e = \ln q_m - K_{DR}\,\varepsilon^2 \tag{8}$$

Where KDR is the D-R constant (mol2/kJ^2) and ε represents the Polanyi potential (J/mol), which is determined by:

$$\varepsilon = RT \ln[1 + 1/C_e] \tag{9}$$

K_{DR} is related to the mean of adsorption free energy E (kJ/mol) by the following equation:

$$E = \frac{1}{\sqrt{2K_{DR}}} \tag{10}$$

The results of the isotherm analysis are given in Table 2. From the table, the R^2 of the Langmuir isotherm was slightly greater than that of the other isotherms for the present adsorption system.

The favorability of RR198 adsorption onto the prepared adsorbent was further assessed by using a dimensionless parameter (R_L) derived from the Langmuir equation as follows:

$$R_L = \frac{1}{1 + b\,C_i} \tag{11}$$

Where C_i is the initial concentration of the target dye under adsorption. The adsorption process can be defined as irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$), in terms of R_L (20).

Discussion

Effect of solution pH

Solution pH is one of the most important parameters which influences the adsorption process with metal hy-

Table 1. Information regarding pseudo-second-order kinetics of RR198 adsorption onto NAC

Dye concentration (mg/L)	$q_{e,exp}$ (mg/g)	R^2	k_2 (g mg^{-1} min)	$q_{e, cal}$ (mg/g)
50	43	0.998	0.023	45.5
100	74	0.997	0.010	76.9
150	99	0.993	0.005	11.1

Table 2. Isotherm parameters of RR198 adsorption onto adsorbent

Isotherm model	Parameter	Value
Langmuir		
	q_{max} (mg/g)	188.70
	b (L/mg)	0.03
	R_L	0.17-0.39
	R^2	0.99
Freundlich		
	K_F	18.10
	N	2.40
	R^2	0.92
D–R		
	K_{DR} (mol²/kJ²)	1.60
	E (kJ/mol)	0.56
	R^2	0.70

Figure 5. Plots of second-order rates for adsorption of RR198 onto NAC.

droxide adsorbents (20). The relationship between adsorption behavior and dye solution pH can be explained by considering the pH_{pzc} of NAC (~7) and functional groups in the RR198 molecules. The surface of NAC is positively charged at a solution pH level below pH_{pzc} (~7). Therefore, an increase in the dye adsorption with a corresponding increase in the solution pH up to 7 can be related to the electrostatic interaction between the sulfonate groups of the RR198 and the positively charged sites on the NAC (21). The greater the pH level of the solution (up to pH_{pzc} of NAC), the higher is the degree of RR198 dissociation, and it thereby becomes more negatively charged (12). These anionic species are electrostatically attracted by the predominantly positively charged NAC particles. Also, the reduction in RR198 removal at pH values above 7 can be related to the formation of the negative charges on the surface of the NAC which repel the anionic RR198 molecules (22,23). Furthermore, the formation of anions, mainly hydroxides, at alkaline pH in the solution results in their competition with the dye molecules for adsorption sites (4,24), thus reducing the percentage of dye removal. The literature shows a contradictory effect of solution pH on dye adsorption onto the tested adsorbents. A conclusion can be drawn that the influence of pH and the optimum pH value for any adsorption system for eliminating dye(s) is dependent on the structure and physicochemical properties of both adsorbent and adsorbate, due to the fact that the solution pH affects both surface characteristics of the adsorbent and the structure of the dye molecule. According to Figure 2, the maximum adsorption efficiency occurred at pH value of 7. Thus, a pH of 7 was selected for use in subsequent experiments.

Effect of adsorbent concentration

Because a fixed amount of dye was used in all experiments, increasing the mass of adsorbent resulted to an increase in the adsorbent to dye ratio, which provided greater surface area and thus more sites for adsorption (25,26) and reduction of intraparticle diffusion (27). This subsequently resulted in the observed increase in dye removal with increasing adsorbent dose.

Effect of dye concentration and contact time

A critical consideration when applying the adsorption system is to provide a sufficient contact time in order to reduce the contaminant(s) in a contaminated solution with a known concentration to a desired value, by using the adsorption process under given conditions. Hence, investigating the influences of RR198 concentration and contact time on RR198 adsorption onto the prepared powder is technically important. This reveals the high affinity of prepared powder to the dye molecules and therefore shows that the powder is an effective adsorbent for dye at low concentrations. The rapid RR198 removal can be related to surface mass transfer (18,28). The observed decrease of dye removal with the increase of initial dye concentration reveals the dependency of RR198 removal on initial concentration, possibly due to limited adsorption

sites and increased intra-particle diffusion. In spite of the reduction of RR198 removal percentage with concentration increase, Figure 4 indicated an increased removal capacity with increase in initial dye concentration and contact time, reaching around 99 mg/g at equilibrium for the maximum tested dye concentration (150 mg/L). Increased removal capacity is attributed to increased collisions between dye molecules and adsorbent with increasing concentration, as well as to the increased concentration gradient and thus mass transfer driving force (26,29) which enhances RR198 molecule uptake by adsorbent particles. The figure also demonstrated further that the time to attain equilibrium and thus the adsorption mechanism (30) depended on the initial dye concentration under the range of conditions studied. Similar adsorption behavior has also been reported by other researchers, although under different experimental conditions.
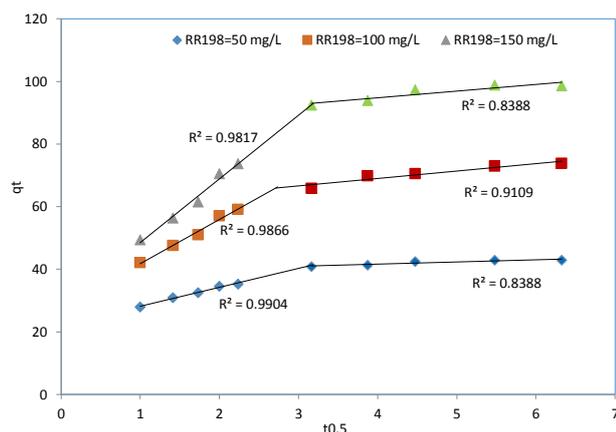
Adsorption kinetics and isotherm

The better fit of the experimental data to the pseudo-second order model than to the pseudo-first order rate revealed that both the dye and the powder affected the RR198 adsorption process under the investigated conditions (30). Also, a pseudo-second order model have been previously reported for the adsorption of RR198 on MgO nanoparticles (25). The decreasing k_2 value with increasing RR198 concentration (Table 1) verified the improvement of dye mass transfer rate with increased initial concentration. In addition, the experimental adsorption capacity ($q_{e,exp}$) value for all the tested dye concentrations was very close to the model-calculated adsorption capacity ($q_{e,cal}$) data (Table 1), thus confirming the high correlation of adsorption to the pseudo-second order model.

The adsorption of organic compounds onto an adsorbent involves five consecutive steps, including bulk solution transport, external (film) resistance to transport, internal (pore) transport, and adsorption; the slowest step limits the adsorption rate. The literature indicated that the first and last steps did not usually limit the adsorption process under experimental conditions (30). It is therefore presumed that either film resistance or diffusion into the adsorbent particles (intra-particle diffusion) is the rate limiting step. Table 3 presented a literature review about adsorption studies conducted with different adsorbent and compared with the present study. Accordingly to the table, maximum adsorption capacity in NAC was higher than other adsorbent.

The kinetic plot of intra-particle diffusion of RR198 onto the adsorbent at the initial concentrations of 50, 100 and 150 mg/L is depicted on Figure 6. According to the figure, two distinct regions were observed for three concentrations, suggesting that different mechanisms were involved in the adsorption of RR198 onto the NAC at different interval contact times. The first region of plots demonstrated that boundary layer diffusion probably limited RR198 adsorption onto NAC. The second region showed the occurrence of intra-particle diffusion as the main adsorption limiting step (4,22,24-27).

Table 3. Literature review about adsorption capacity different adsorbent for RR198 and comparison with present study

Adsorbent	q_{max} (mg/g)	Reference
Activated carbons from agricultural waste	181.9	(35)
Potamogeton crispus native	14.3	(33)
Eggshell biocomposite beads	46.9	(21)
Alumina/multi-walled carbon nanotubes	4.53	(36)
Azolla filiculoides	12.2	(37)
Waste coagulation sludge	34	(38)
NAC	188.7	Present study

Figure 6. Plot of intraparticle diffusion kinetics of RR198 adsorption onto the NAC.

Moreover, considering the slope of the regression lines for the entire range of the selected contact time, the constants of intra-particle diffusion (k_{id}) for initial RR198 concentrations of 50, 100 and 150 mg/L were found to be 2.8, 5.8 and 9.7 mg/g.min$^{0.5}$, respectively. For higher values of k_{id}, the adsorption rate was higher (31), which confirmed the improvement in adsorption capacity with increasing dye concentration. It can therefore be concluded that effect of boundary layer diffusion is more noticeable at higher dye concentrations (32).

Isotherm modeling

An isotherm describes the interaction between adsorbate and adsorbent and is a beneficial tool for optimizing an adsorption process (3). The adsorption of RR198 on the adsorbent particles was better described by the Langmuir model, which implied that RR198 adsorption occurred when a monolayer was adsorbed onto a homogenous adsorbent surface. The Langmuir model estimated a maximum RR198 adsorption capacity on the tested adsorbent of 188.7 mg/g, close to the experimental equilibrium adsorption capacity, which confirmed the precise fit of the model with the experimental data.

The calculated values of R_L for adsorption of RR198 fell between 0 and 1; therefore, the process was favorable. It is worth noting that the value of the constant n in the Freundlich model, given in Table 2, was greater than unity, which verified that the prepared powder was appropriate for use as an adsorbent for the removal of RR198 dye.

The efficiency of different adsorbents, including MgO

nanocrystals (4), modified eggshell (21), *Potamogeton crispus* biomass (33), sewage sludge char (32) and *Nostoc linckia* biomass (34) for the removal of RR198 was studied previously and the maximum adsorption capacities of 123.5, 46.9, 44.2, 25.0 and 93.5 mg/g, respectively, reported. Accordingly, the NAC attained greater adsorption capacity compared to the previously tested adsorbents for the removal of RR198. Therefore, it might be an efficient and promising adsorbent for the removal of azo dyes from the contaminated streams.

Conclusion

The present work introduced a carbon activated with NH_4Cl (NAC) as an adsorbent for dye removal from wastewater. The NAC appears to be an adsorbent with a relatively high specific surface area which is capable of efficiently removing low to moderate concentrations of reactive dyes at neutral pH conditions. The kinetic analysis indicated the high affinity of NAC to the RR198 molecules and therefore shows that the powder is an effective adsorbent for dye at low to high concentrations. The maximum RR198 adsorption capacity of NAC calculated from the Langmuir isotherm, the best fit model to the experimental data, was 188.7 mg/g, which is greater than most of the previously reported adsorbents examined for RR198 adsorption. It is therefore concluded that the NAC is an efficient and promising adsorbent for color removal from industrial wastewater.

Ethical issues
The authors certify that ethical issues (including plagiarism, data fabrication double publication and/or submission) have been completely observed by the author All data collected during the study are original and have not be published elsewhere.

Competing interests
The authors confirmed that they have no competing interest.

Authors' contributions
All authors contributed to data acquisition, analysis, interpretation, and review and approved final draft of manuscript.

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