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Effect of nitrogen functionalization on the adsorption performance of commercial charcoal activated with phosphoric acid

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ABSTRACT

This study demonstrates the impact of nitrogen modification on the adsorption properties of activated carbons toward removal of anionic polyazo dye from aqueous solutions. Commercial charcoal was activated with phosphoric acid (ACP) and then modified with mono-aminoethanol (ACP-M), EDTA (ACP-E) and chitosan (ACP-C), respectively. Surface characterizations of samples were carried out using surface pH, total acidity and basicity, zeta-potential, elemental analysis, FTIR, SEM and textural properties. Batch studies were performed to evaluate the influence of pH, contact time, initial dye concentrations and temperature toward removal of solophenyl red 3BL polyazo dye (SR) from aqueous solution. Three common adsorption isotherms including Langmuir, Freundlich and Dubinin-Radushkevich were applied to follow the adsorption process. Langmuir model was found to fit significantly the adsorption of SR dye onto the samples. Among kinetic studies, the pseudo-second-order model well-described the adsorption kinetics and intra-particle diffusion process was not be the rate controlling step. The thermodynamic study showed that the adsorption of SR dye onto activated charcoal and their corresponding modified carbons was spontaneous and endothermic. Modified samples showed better adsorption performance toward dye removal than activated carbon. The adsorption of dye is enhanced on surface of modified carbon samples as the amount of amino groups and specific surface area increased. However, the activated charcoal modified with chitosan (ACP-C) was the best adsorbent where the removal of SR dye was 85%. This result reflects the occurrence of high electrostatic attractions between positively charged surface of ACP-C and negative charges surrounded SR dye.

Keywords: Activated carbon; Nitrogen functionalization; Surface properties; Adsorption; Anionic polyazo dye

1. Introduction

Wastewater containing large amounts of dyes which colored the effluents produced from industries such as textiles, rubber, paper, plastic, cosmetics, etc., can be triggered a major risk on human health as well as livings in aquatic system [1–6]. The colored-water may transfer into drinking water and hence brings a chief threat to human health due to their toxic, mutagenic and carcinogenic effects [2]. Some of dyes cannot be easily removed by conventional wastewater treatment processes due to their complex structure and synthetic origins [3]. During the dyeing and finishing operations in the textile industry, up to 200000 tones of dyes are lost to effluents annually because of the inefficiency of dyeing processes [4]. In particular, polyazo reactive dyes such as solophenyl red 3BL dye which has large molecules are used extensively in the textile and leather industries [5]. This dye is non-biodegradable in aerobic conditions whereas it can be degraded to hazardous intermediates under aerobic environment. Purification of dye-containing wastewater has become a very important problem not only because of their adverse effect on the human health and

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aquatic environment [1]. Thus, the dye removal is emerged as an important challenge in the treatment of industrial wastewater.

Several conventional technologies for removing dyes from industrial wastewater have been used such as advanced oxidation, biological treatment, electrolysis, solvent extraction, coagulation, ion exchange, filtration, activated sludge and adsorption processes. Among these techniques, adsorption is still classified as a simple, impactful and economical method for remediation of wastewater containing dyes [1–6]. Adsorption technology utilizing activated carbon (AC) is the most promising and effective process for removing dyes from the wastewater because AC has large specific surface area and high adsorption capacity [7]. However, the micropores in its structure limit the move of bulky dye molecules from its surface into the micropores [5,8,9].

Generally, the adsorption capacity of ACs is significantly depended on the type and concentration of surface functional groups which influenced to a great extent on its efficiency [7]. The introduction of functional groups on carbon surface mainly obtained during activation process of carbonaceous precursor(s) and post-thermal/chemical treatment [10]. However, different modifications on surface of AC have been studied that include acid-base treatment, impregnation treatment, ozone treatment, surfactant treatment, plasma treatment and microwave treatment to enhance the adsorptive properties of the resulting modified activated carbons [10]. As a result of modification, different functional groups such as oxygen, nitrogen, sulfur and phosphorous are introduced on the surface or into the structure of the activated carbons and hence significantly enhance their adsorption capacity toward removal of dyes and heavy metals [6–15].

For functionalization of activated carbons with nitrogen, some recent studies have reported the coating of ACs surface with chitosan [6,11,12] and ethylene diamine tetraacetic acid (EDTA) [13,14] in order to enhance their capacity to remove heavy metals and dyes from wastewater. A previous study [5] reported that nitrogen-containing groups on amine-functionalized mesoporous carbons obtained by hard-template method impacted remarkably on adsorption of solophenyl red 3BL dye from aqueous solutions. To our knowledge's, the adsorption of solophenyl red 3BL dye onto activated commercial charcoal modified with monoamino ethanol, ethylene diamine tetraacetic acid (EDTA) and chitosan has not been investigated yet.

Therefore, the aim of this work is to study the effect of nitrogen functionalization on the adsorption performance of activated commercial charcoal with phosphoric acid toward removal of solophenyl red 3BL dye. Nitrogen modifiers such as mono-amino ethanol, ethylene diamine tetraacetic acid (EDTA) and chitosan (containing numerous of amino and hydroxyl groups) were used in the current study. Surface characterizations of samples using surface pH, total acidity and basicity, zeta-potential, elemental analysis, FTIR, SEM and textural properties were performed. Effect of pH, contact time, initial dye concentrations and temperature of the adsorption performance of prepared adsorbents was determined. Equilibrium and kinetic adsorption studies toward removal of solophenyl 3BL polyazo dye from dilute aqueous solutions were investigated.

2. Materials and methods

2.1. Materials

A commercial charcoal and ortho phosphoric acid (H_3PO_4, 85 wt. %, M_w = 98.0 g/mol) were supplied from Rasayan (Turkey). Ethylene diamine tetraacetic acid (EDTA, $(HO_2CCH_2)_2NCH_2CH_2N(CH_2CO_2H)_2$) and hydrochloric acid (HCl, 37 wt. %) were purchased from Sigma-Aldrich. Sodium hydroxide (NaOH, 98 wt%), and mono-aminoethanol ($NH_2CH_2CH_2OH$, 99 wt%) were obtained from Panreac. Chitosan ($(C_6H_{11}NO_4)_n$, M_w = 600000–800000 g/mol) was obtained from ACROS. Solophenyl red 3BL polyazo dye ($C_{45}H_{26}N_{10}Na_6O_{21}S_6$, M_w = 1673.4 g/mol) was obtained from Ciba-Geigy. A stock solution of dye (500 mg/L) was prepared without further purification. All solutions were prepared with distilled water.

2.2. Preparation of adsorbents

Phosphoric acid activation of commercial charcoal was carried out according to previous work [16]. A defined amount of commercial charcoal was impregnated firstly with 50 v/v% of H_3PO_4 under stirring for 120 min at 70°C and kept at room temperature overnight. The suspended black solid was filtered and dried at 100°C overnight. Then, the dried sample was transferred to a stainless steel reactor (60 cm of length and inner diameter of 4 cm) and admitted to a temperature controlled electric furnace. This sample was heated slowly to reach a final temperature of 500°C for 120 min without flowing of any gases. Then, the cooled product was thoroughly washed with hot water so as to remove the residual acid until the pH of filtrate becomes at ~ 6 and dried overnight at 100°C. The final product was denoted as ACP.

Three nitrogen-containing modifiers were used so as to functionalize the surface of phosphoric acid activated commercial charcoal (ACP) with mass ratio of 1/1. For modification with either mono-aminoethanol (MAE) or EDTA, about 6 g of each one added into 100 mL H_2O was mixed with the same amount of ACP under stirring and heating at 50°C for 180 min. the resulting sample was filtered, washed thoroughly with water and dried at 100°C overnight (denoted as ACP-M and ACP-E). Regarding modification with chitosan, about 6 g of this modifier was dissolved firstly in diluted acetic acid (10 v/v%) under vigorous stirring and heating at 50°C till homogeneity was obtained. Then ACP sample was added to this viscous solution and kept at the same temperature for 180 min under robust stirring. Subsequently, the solid sample was separated, washed, dried at 100°C overnight and referred as ACP-C.

2.3. Characterization of the adsorbents

The slurry or surface pH values of the finely powdered samples were measured by contacting 0.1 g of sample with 25 mL distilled water in closed flask, and left overnight under stirring and then recorded the supernatant pH liquid using a pH meter (HANNA pH 20). The total acidity and basicity amounts corresponding to surface functional groups on a carbon material were determined by using the Boehm method [17]. The acidic sites were determined by mixing small quantities (0.05 g) of each carbon material with 20 ml of different bases (0.1 M NaOH, 0.1 M Na_2CO_3 and 0.1 M $NaHCO_3$) in 25 mL beakers. The beakers were sealed and shaken for 24 h. The solutions were then filtered and titrated with 0.1 M HCl solution. Similarly, the basic sites were determined by mixing 0.05 g of each carbon material with 20 mL of 0.1 M HCl solution. The obtained solutions were titrated with 0.1 M NaOH. Zeta potential (ζ, mV) was measured by using zeta-potential analyzer (Santa Barbara, Calif., USA).

The carbon, hydrogen, oxygen, phosphorous and nitrogen contents of the obtained samples were determined automatically by a VARIO Microanalyzer System. The essential surface functional groups formed on the surface of the prepared samples were determined by Fourier transform infrared (FTIR) spectroscopy, using KBr pellets (JASCO, FT-IR-460 plus). The morphology of the prepared catalyst samples were estimated by field-emission scanning electron microscope (FE-SEM, FEI Quanta FEG-250). The textural parameters such as Brunauer-Emmett-Teller surface area (S_{BET}, m^2/g), total pore volume (V_p, cm^3/g) and average pore diameter ($\bar{r}$, Å) [18] were determined using nitrogen adsorption analysis (BEL-Sorp, Microtrac Bel Crop, Japan) at −196°C and P/P_0 = 0.005–0.999. Before N_2 adsorption analysis, samples (0.1–0.2 g) were subjected to a vacuum of 10^{-5} Torr at 250°C for 12 h in the degassing chamber.

2.4. Adsorption studies

Solophenyl red 3BL as a polyazo reactive dye having large size molecules was used to evaluate the adsorption capacity of the prepared samples. Chemical structure of dye is shown in Fig. 1. Batch adsorption experiments were carried out toward this dye to study the adsorption capacity of the activated carbon and its modified samples. About 50 mL of SR dye solutions with different initial concentrations of 20 to 300 mg/L were conducted with 50 mg of adsorbent under shaking at 200 rpm and 25°C for 24 h. The pH effect on the dye adsorption efficiency was investigated using an initial pH range of 3–10 with 50 mg of adsorbent and 100 mg/L of initial dye concentration. Influence of some factors such as initial dye concentrations and contact time was studied. Effect of temperature was carried out at 30, 40 and 50°C while initial concentration of dye, contact time and pH are fixed at 100 mg/L, 120 min and 3, respectively. Moreover, kinetic adsorption studies were performed for 50 mg of adsorbent with 100 mg/L of dye solution at 25°C, under magnetic stirrer at 200 rpm, within contact time ranging from 5 to 180 min. The dye concentrations in the filtrate were determined using a UV-visible spectrophotometer (Shimadzu Model PC-2401) with 1.0 cm length-path cell by measuring the maximum absorbance at a wavelength of 530 nm. Duplicate absorbance readings were recorded for each experiment. All absorbance results were calculated by taking the mean of two readings of absorbance and found that their relative errors were below 5%.

2.5. Adsorption calculations

The amount of adsorbed dye was calculated from the mass balance expression given by:

$$q_e = \frac{(C_o - C_e)}{m} V \quad (1)$$

where q_e is the amount of adsorbed dye by the adsorbents (mg/g), C_o initial ion concentration of SR dye (mg/L), C_e equilibrium concentration of SR dye (mg/L), m the mass of adsorbent in (mg) and V is the volume of dye solution in contact with the adsorbent (mL). Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models [19–21], as well-known adsorption isotherms; were used to analyze the adsorption of SR dye onto the investigated samples. These models are presented in the following equations:

Langmuir isotherm [19]:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q} + \frac{1}{Q} C_e \quad (2)$$

where Q is the maximum adsorption capacity (mg/ g) and K_L (L/mg) is the Langmuir adsorption equilibrium constant. Q and K_L are calculated from the slope and intercept of the isotherm plot C_e/q_e versus C_e.

The essential characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless constant called equilibrium parameter:

$$R_L = \frac{1}{1 + C_o K_L} \quad (3)$$

where C_o is the highest initial dye concentration (mg/L). The value of R_L indicates the type of isotherm to be either favorable ($0 < R_L < 1$), linear ($R_L = 1$), unfavorable ($R_L > 1$), or irreversible ($R_L = 0$).

The Gibbs free energy change of adsorption, ΔG_o (kJ/mol) can also be evaluated from the parameter K_L according to the expression; $\Delta G_o = -RT \ln K_L$.

Freundlich isotherm [20]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

where K_F is the Freundlich isotherm constant ($mg/g(mg/L)^{1/n}$), which is an indicator of the adsorptive capacity of an adsorbent for a solute, and n is a measure of the intensity of the adsorption or surface heterogeneity (a value closer to zero for $1/n$ represents a more heterogeneous surface), however, the Freundlich exponent, n, should have values lying in the range of 1 to 10 for classification as a preferable adsorption.

Dubinin–Radushkevich (DR) isotherm [21]:

$$\ln q_e = \ln Q_{DR} - \beta e^2 \quad (5)$$

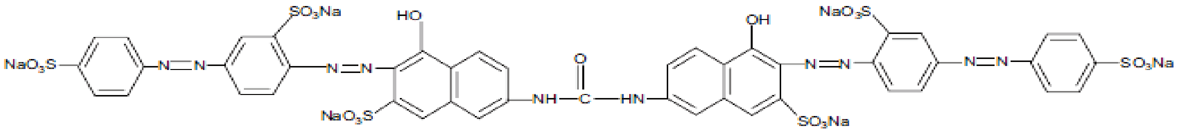

Fig. 1. Chemical structure of solophenyl red 3BL.

where Q_{DR} is the DR adsorption capacity (mg/g), β is the constant related to adsorption energy (mol^2 k/J^2). While ε is the Polanyi potential (J/mol); $\varepsilon = RT \ln(1 + 1/C_e)$, R is the universal gas constant (J/mol K) and T is the temperature (K). From the value of β, it is possible to calculate the main free energy of adsorption (E, kJ/mol); $E = \frac{1}{\sqrt{2\beta}}$.

In addition, the data of kinetic adsorption were analyzed in terms of three kinetic models such as pseudo-first order Lagergren [22], pseudo-second order [23] and intraparticle diffusion [24] which expressed in the following equations, respectively:

$$log\ (q_e - q_t) = log\ q_e - \frac{k_1 t}{2.303} \tag{7}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\ 2}} + \frac{t}{q_e} \tag{8}$$

$$q_t = k_{id}\, t^{1/2} + C \tag{9}$$

where q_e and q_t are the amounts of SR dye adsorbed (mg/g) at equilibrium and at time (t) (min), respectively. k_1 and k_2 are constants calculated from the pseudo-first adsorption rate (min^{-1}) and pseudo-second adsorption rate (g/mg·min), which can be obtained from the linear slope of $log\ (q_e - q_t)$ vs. t and t/q_t vs. t plots, respectively. Additionally, k_{id} , $t^{1/2}$ and C are the intraparticle diffusion rate constant (mg/g·$min^{1/2}$), square root of the time $(min)^{1/2}$ and intercept, respectively. In a batch reactor with rapid stirring, there is also a possibility that the transport of dye molecules from the solution into the pores of the adsorbent is the rate-controlling step.

3. Results and discussion

3.1. Surface features of the investigated samples

Table 1 describes some of surface properties of the investigated adsorbents in this study. The obtained slurry or surface pH values of these samples are in the range of 4.8–7.8. The activated commercial charcoal with phosphoric acid (ACP) has an acidic surface in nature. Otherwise, the functionalized samples with nitrogen raised the slurry pH from acidic to slight acidic and neutral pH. This affirms that the surface of ACP was modified successfully with the selected nitrogen modifiers, resulting in an enhancement in the amount of basic groups which consist of nitrogen containing basic functional surface groups as confirmed also by the data of total acidity and total basicity (Table 1). Further evidence can show the change in the nature of ACP after modification is the zeta-potential (ζ, mV). This parameter illustrates the predominant surface functional groups existed on the surface. Thus it is influenced by the type of functional groups and pH of solution. When the value of zeta-potential is negative, referring to the presence of negatively charged sites on carbon surface which produced from deprotonation of strong acidic functional groups such as carboxylic acids and vice versa in case of basic functional groups which release ^{-}OH groups in the solution. Thereof, it can be seen that the activated carbon modified with EDTA (ACP-E) showed less negatively charged sites than ACP and ACP-M, thus it is still has acidic functional groups. Conversely, the ACP modified with chitosan exhibited positively charged sites as a result of more nitrogen-containing basic surface groups (e.g. amines and amides such as –NH, $–NH_2$) as compared with that obtained upon using mono-aminoethanol and EDTA. This behavior is very useful for the adsorption of anionic dyes from dye-contaminated wastewater.

By investigating the elemental composition of those samples, it can be seen that all samples contain of carbon, oxygen, phosphorous and nitrogen contents. The content of latter element is higher in the activated carbon modified with chitosan than others. As well, it is noted that there is a considerable decrease in the content of phosphorous that offsets by a significant increasing in the amount of nitrogen after treatment of ACP with studied modifiers. The increase in percent of nitrogen reached to 95.8 and 127% as ACP was modified with EDTA and chitosan, respectively. This result may be related apparently to the large content of nitrogen (amino groups) in the chitosan. Therefore, the modification of activated commercial charcoal with the chitosan is a powerful strategy for enhancing the basic sites that required for removal of anionic dyes particularly.

The major surface functional groups on the prepared carbons were determined qualitatively using FTIR spectra and the results are depicted in Fig. 2. It can be observed that there are significant changes in the intensity of absorbance bands related to the oxygen and nitrogen-containing surface functional groups after modification of ACP with chitosan more than that obtained with mono-aminoethanol and EDTA (which contains diamine) between 3800 and 2800 cm^{-1}. However, no considerable alterations were found in FTIR spectrum of ACP-M compared to that of ACP. This result agrees with the elemental constituents where the contents of N and O elements are relatively similar in both samples.

Absorption band around 3434 cm^{-1} is attributed to the stretching vibration of H-bonded –OH groups or free

Table 1
Some surface properties of the investigated adsorbents

Adsorbents	pH of surface	Total acidity (mmol/g)	Total basicity (mmol/g)	ζ, (mV)	C %	N %	H %	P %	O %
Charcoal	5.6	0.225	0.086	–41.8	84.4	0.52	0.44	0.0	14.6
ACP	4.8	0.298	0.054	–35.6	77.1	0.55	0.27	4.30	17.8
ACP-M	6.8	0.291	0.165	–28.6	79.0	0.75	0.45	1.70	18.5
ACP-E	6.8	0.219	0.192	–6.61	78.8	0.90	0.48	1.12	18.7
ACP-C	7.8	0.285	0.484	+9.97	79.0	1.10	0.50	0.90	18.5

–OH groups. The appearance of small band around 3760 cm^{-1} conjugated with that at 3434 cm^{-1} is related also to the extension vibration of –NH groups on the surface of modified carbons [5,11–14]. In Table 1, the reference sample (ACP) contains low amount nitrogen; hence this band is appeared also in FTIR of ACP. The presence nitrogen in ACP is acquired from commercial charcoal as detected by elemental analysis in Table 1. An interesting observation is that absorption band at 3434 cm^{-1} in FTIR of ACP-C is broader than others confirming the presence of OH and NH groups with high content. Two shoulder bands at 2921 and 2850 cm^{-1} are occurred due symmetric and asymmetric C-H stretching in CH_3 group [11]. On the other hand, a shoulder band at 1634 cm^{-1} is due to N–H bending vibration of $–NH_2$ groups [5]. Other shoulder bands in the 1450–1160 cm^{-1} range are ascribed to phosphorus species (e.g. P=O, P–O–C and P=OOH), i.e., organic P–compounds [25]. Moreover, the observed bands between 1300 and 1000 cm^{-1} are ascribed to the existence of C–O single bond in carboxylic acids, alcohols, phenols, and esters. A sharp band at 1037 cm^{-1} shifted little to 1030 cm^{-1} after modification is corresponded to the C–OH (skeletal vibration) and C–O–C skeletal vibrations in pyranose ring, alcohols, ethers, epoxide and phenolic structures. After modification, a small band showed at 1170–1160 cm^{-1} is assigned to C–N stretching [5]. Other small bands appeared between 900 and 500 cm^{-1} are associated with out-of-plane bending modes of C–H as in aromatic rings.

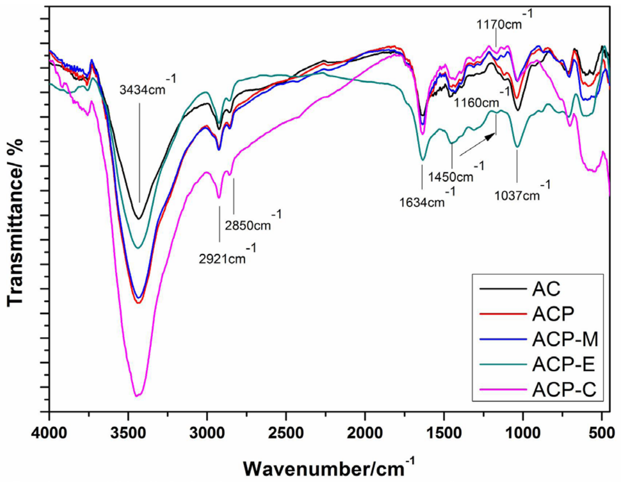

Fig. 2. FTIR spectra of the prepared adsorbents.

On the basis of the previous studies [26,27], the acidic character of carbon surface could be raised from surface oxygen groups such as carboxylic acid, lactone, phenol and lactol groups. On the other hand, the presence of basic oxygen-containing functional groups (e.g. chromene, pyrone, diketone or quinone groups), delocalized π-electrons of the polyaromatic sheets (e.g. Cπ basal planes), nitrogen-containing functional groups (e.g. pyridinic groups) and/or inorganic impurities (metal oxides) would be given basic character to carbon surface. The hereby carbons contains nitrogen and phosphorous containing oxygen functional groups which could enhance the adsorption of SR dye.

Moreover, Fig. 3 illustrates the top-view SEM images of ACP before and after modification with chitosan as an example. A rough surface of ACP is obtained with presence of irregular distribution of pores. After modification, the obtained sample (ACP-C) possesses a surface covered by a thin layer of chitosan molecules with appearing some external pores. It can be concluded that the functionalization of ACP surface with chitosan was successfully attained.

The textural properties of the reported samples are listed in Table 2. The activation of charcoal with phosphoric acid led to an increase in the internal porosity of char-

Table 2
Porous characteristics of the samples as accounted from N_2 adsorption at –196°C.

Samples	S_{BET} (m^2/g)	V_P (cm^3/g)	$\bar{r}$ (Å)	% removal of SR dye
Charcoal	837	0.674	32.2	25
ACP	891	0.945	42.2	42
ACP-M	920	0.867	37.7	52
ACP-E	937	0.787	33.6	65
ACP-C	952	0.574	24.1	85

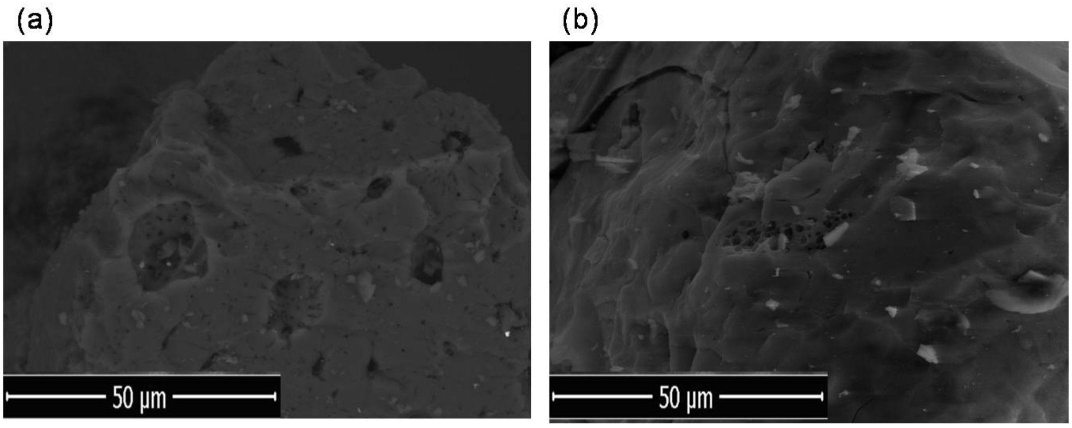

Fig. 3. SEM images of (a) ACP and (b) ACP-C samples.

coal remarkably (i.e. specific surface area, total pore volume and average pore diameter parameters are increased about ~ 6.5%, 40% and 31%, respectively). Upon modification of activated charcoal (ACP) with nitrogen-containing reagents, the specific surface area is increased from 891 to 952 m^2/g whereas other textural parameters are decreased. An increase in surface area may due to generation of new surface sites while the decrease in the total pore volume and average pore diameter results of blocking the internal pores of ACP by such molecules of modifiers. Also from this table, it can be concluded that ACP-C adsorbent exhibited the highest removal of SR dye due to its large surface area and high content of amino groups and hydroxyl groups.

3.2. Effect of pH

It is well-know that pH of dye solution might affect the adsorption capacity of the carbon adsorbent. Based on the above mentioned results, the activated carbon treated with chitosan (ACP-C) is used as a representative sample for determining the impact of pH on removal of SR dye at pHs of 3–10 as shown in Fig. 4. The removal percentage of SR dye using ACP-C decreased from 88 % to 9 % upon increasing the pH value from 3 to 10. Thus the maximum removal of dye was attained at acidic medium [11]. At pH of 3, the amino groups on the surface of modified carbon afford protonation. As the dissociated sulfonic groups of the dye are abundant at acidic pH, the modified carbon showed higher affinity to remove the SR dye than in a basic medium. Lower adsorption of the anionic SR dye at alkaline pH can be attributed to the competition between OH^- ions in water solution and SO_3^- anions of the dye for free adsorption sites on the carbon surface [5]. Thus the adsorption of SR dye onto the prepared adsorbents is governed by electrostatic interactions. Accordingly, the next adsorption experiments were run at pH of 3.

3.3. Effect of initial dye concentrations and contact time

Fig. 5a shows the relationship between the variation in initial SR dye concentrations and the adsorbed amount of dye onto the prepared samples at pH of 3 after shaking for 24 h. It was noticed that increasing initial dye concentrations from 10 to 300 mg/L led to a remarkable enhancement in the adsorbed amount of SR dye over all studied samples. It can be obviously seen that the functionalization of ACP with chitosan significantly enhanced the adsorption of SR dye. This behavior is attributed to that the chitosan can create large number of adsorptive sites on the carbon surface such as amino and hydroxyl groups, making ACP-C sample is effectively suitable for adsorption processes [5].

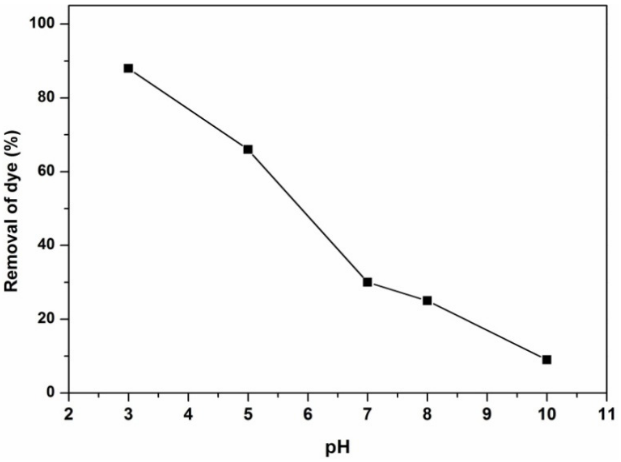

Fig. 4. Influence of pH on the removal of SR dye onto ACP-C.

Effect of contact time on the adsorption of SR dye onto the prepared samples is shown in Fig. 5b. It can be observed that the adsorption of SR dye increased rapidly within the first 40 min and then increased slowly and got equilibrium after 60 min, except for ACP-C. This finding may be taken as an evidence for the large adsorptive sites in ACP-C that generated from the functionalization of ACP by nitrogen-containing functional groups.

3.4. Effect of temperature

Influence of temperature on the adsorption of SR dye was studied at 30, 40 and 50°C (i.e. 303, 313 and 323K) as shown in Fig. 6a. This figure shows that the adsorption amounts of SR dye over all samples increase with rising in temperature from 30 to 50°C. This affirms that the adsorption process is endothermic process. Furthermore, the thermodynamic parameters such as standard Gibbs free energy (ΔG^0), enthalpy (ΔH^0) and entropy changes (ΔS^0) for the sorption process were calculated from the following equations:

$$\Delta G^0 = -RT \ln K_d \tag{10}$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{11}$$

where K_d the distribution coefficient, $K_d = q_e/C_e$ (L/g). Eq. (11) is known as Van't Hoff equation. ΔH^0 and ΔS^0 values were computed from the slope and intercept of the linear plot of $\ln K_d$ versus $1/T$ as presented in Fig. 6b and their values are listed in Table 3. Negative values of ΔG^0 confirmed that the adsorption of SR dye onto the prepared adsorbents is spontaneous. The more negative values of ΔG^0 imply a greater driving force to the adsorption process. On the other hand, positive values of ΔH^0 indicated that the adsorption process is an endothermic in nature. As well, the positive values of ΔS^0 showed that the adsorption process more likely to occur spontaneously.

3.5. Adsorption isotherms

The equilibrium adsorption data were fitted into Langmuir, Freundlich and Dubinin-Radushkevich isotherms for adsorption of SR dye onto the prepared materials at pH 3 and 20°C for 24 h. Of the three adsorption isotherms, the correlation coefficient of Langmuir isotherm model was the highest ($R^2 = 0.999$). Nevertheless, the Langmuir model fits significantly the adsorption of SR dye onto the samples, implying the surface homogeneity and monolayer coverage of dye molecules on the adsorbent surface. Also this result can be confirmed from adsorption isotherms as

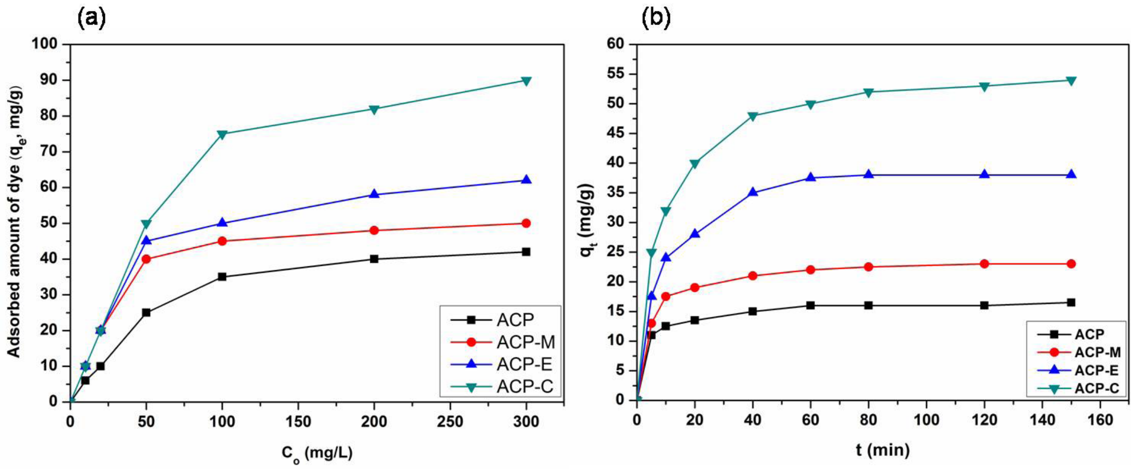

Fig. 5. (a) Effect of initial concentrations and (b) effect of contact time on the adsorption of SR dye using the prepared samples (C_o = 100 mg/L, adsorbent mass = 50 mg and pH = 3).

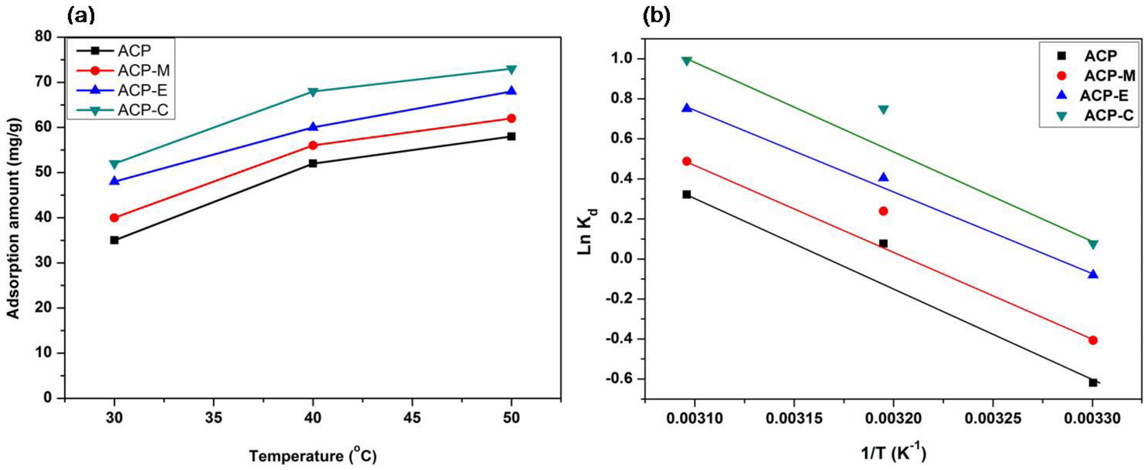

Fig. 6. (a) Effect of temperature on adsorption of SR dye and (b) Van't Hoff plots for the adsorption of SR dye onto the prepared adsorbents (C_o = 100 mg/L, adsorbent mass = 50 mg and pH = 3).

Table 3
Thermodynamic parameters for adsorption of SR dye onto the carbon adsorbents

Samples	T (K)	Thermodynamic parameters		
		ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol.K)
ACP	303	–15.8	+33.5	+111.3
	313	–18.2		
	323	–19.4		
ACP-M	303	–16.4	+36.5	+117.6
	313	–18.6		
	323	–19.9		
ACP-E	303	–17.2	+37.8	+122.1
	313	–19.3		
	323	–20.6		
ACP-C	303	–17.6	+38.4	+124.7
	313	–19.9		
	323	–21.2		

seen in Fig. 7. It was apparently found that the adsorption isotherms belong to L-type according to Giles classification [28]. Similar results were reported for the adsorption isotherms of various dyes onto different adsorbents including carbon nanotube [29], sepiolite [30] and [31].

The maximum monolayer capacities for SR dye onto ACP, ACP-M, ACP-E and ACP-C were derived to be 47, 50, 62 and 91 mg/g, respectively, as summarized in Table 4. It can be noticed that ACP-C adsorbent has the biggest adsorption capacity and enhanced the adsorption ability about two times. This finding might be attributed to its larger surface area and higher amount of nitrogen-containing basic surface groups.

R_L values were greater than 0 and less than 1, indicating that the adsorption process of SR dye occurred properly over the surface of prepared samples. The negative values of Gibbs free energy (ΔG_o) between –8.82 and –15.4 kJ/mol assess the feasibility and spontaneous nature of SR adsorption onto the investigated samples. It is worth noting that values of $1/n$ were decreased from

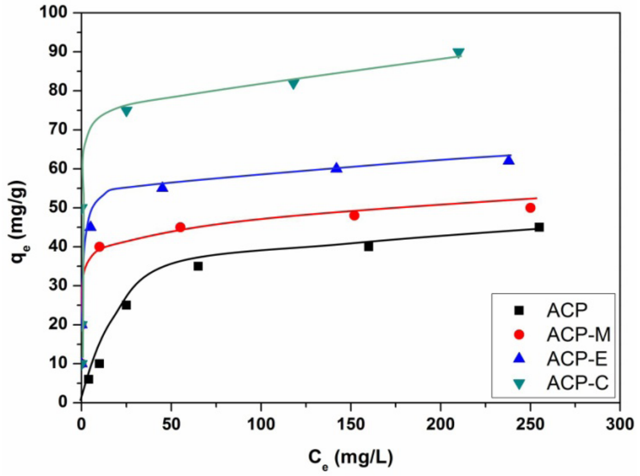

Fig. 7. Adsorption isotherms of SR dye onto the prepared adsorbents (adsorbent mass = 50 mg and pH = 3).

Table 4
Calculated parameters from Langmuir, Freundlich and Dubinin-Radushkevich isotherms for adsorption of SR dye onto the prepared materials at pH 3 and 25°C.

Models	ACP	ACP-M	ACP-E	ACP-C
Langmuir				
Q (mg/g)	47	50	62	91
K_L *(L/g)*	0.037	0.1344	0.4545	0.5494
R_L	0.0826	0.0073	0.0242	0.0061
ΔG *(kJ/mol)*	–8.82	–12.1	–14.9	–15.4
R^2	0.999	0.999	0.999	0.999
Freundlich				
K_F *((mg/g)/(L/mg)*$^{1/n}$*)*	3.38	33.5	39.8	56.5
1/n	0.541	0.088	0.082	0.072
R^2	0.962	0.954	0.959	0.958
Dubinin–Radushkevich				
Q_{DR} (mg/g)	38.5	41	49	66
β (mol²k/J²)	0.011	0.005	0.004	0.003
E (kJ/mol)	6.74	10.0	11.2	12.9
R^2	0.788	0.875	0.866	0.835

0.541 to 0.072 and became closer to zero for ACP-C and values of K_F were increased from 3.38 to 56.5 [(mg/g)/(L/mg)]$^{1/n}$, upon functionalizing the surface of ACP with chitosan. This implies that the increase in amount of nitrogen-containing basic groups leads to enhancement in the adsorption of SR dye and thus the ACP-C surface is more favorable for removing of SR dye from contaminated water. From DR model, the calculated values of main free energy of adsorption (*E*) were between 6.74 and 12.9 kJ/mol which vividly proved that the adsorption mechanism of SR dye onto the samples followed physisorption (e.g., ion-exchange, van der Waals forces or electrostatic interactions) [32].

3.6. Adsorption kinetic studies

In order to optimize the key rate-controlling steps of SR dye adsorption, the experimental data were analyzed by pseudo first-order, pseudo-second-order and intra-particle diffusion kinetic models. Kinetic plots of pseudo-second-order and intra-particle diffusion kinetic models are shown in Figs. 8a and b. As well, the calculated kinetic parameters and the correlation coefficients (R^2) from these models are presented in Table 5. The validity of each model is determined by comparing the values of R^2. Upon comparing R^2 values of the three models, it can be seen obviously that pseudo-second-order model fits better than pseudo first-order. Moreover, the calculated values of $q_{e,cal}$ from the linear plots of pseudo-second-order were very closely to those of experimental data. These results inflict that the adsorption process obeys the pseudo-second-order kinetic model. Previous studies reported similar results for the adsorption kinetics of various pollutants onto different adsorbents [33–35].

The kinetic data were further analyzed by intraparticle diffusion are displayed in Fig. 8b and their corresponding parameters are listed in Table 5. It was found that the value of k_{id} for adsorption SR dye by ACP-C is higher than those carried out by ACP, ACP-M and ACP-E adsorbents, respectively, indicating that the adsorption of dye onto ACP-C is the faster. Since the plots of $t^{1/2}$ versus q_t do not pass through origin, therefore the intra-particle diffusion may not be the rate controlling step. Fig. 8b shows two straight lines. The initial line section represents the surface or film diffusion and the second one is the intraparticle or pore diffusion. Thus the adsorption processes of SR dye onto the prepared adsorbents are governed by the film and pore diffusions.

4. Conclusions

In this study, commercial charcoal activated with phosphoric acid and their modified carbons with three nitrogen-containing modifiers such as mono-aminoethanol, EDTA and chitosan were prepared and studied as adsorbents for the removal of an anionic polyazo dye such as solophenyl red 3BL (SR) from aqueous solutions. Adsorption of SR dye was influenced by various parameters such as pH, contact time and initial dye concentrations. Amount adsorbed was increased with increasing initial dye concentration and temperature at pH = 3. Modified samples showed better adsorption performance toward dye removal than activated carbon. However, ACP-C adsorbent exhibited the highest removal of SR dye which attains about 85% than other adsorbents. This finding was attributed mainly to its large surface area and high content of amino groups. The presence of amino groups provides high electrostatic attraction between positively charged surface of ACP-C and negative charges surrounded SR dye. Furthermore, the adsorption isotherms follow the Langmuir model. The pseudo-second-order equation fitted well the adsorption kinetics of SR dye on all adsorbents. Thermodynamic parameters such as ΔG^0, ΔH^0 and ΔS^0 were calculated and their results revealed that adsorption process is spontaneous, endothermic and physical in nature.

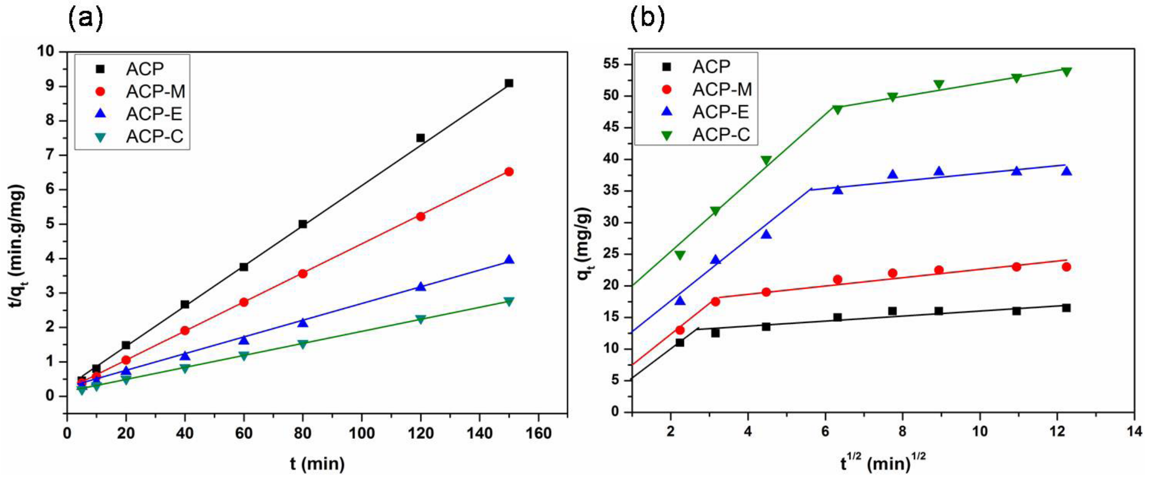

Fig. 8. (a) Pseudo-second order kinetic plots and (b) intraparticle diffusion plots for adsorption of SR dye onto the studied adsorbents (C_o = 100 mg/L, adsorbent mass = 50 mg and pH = 3).

Table 5
Kinetic adsorption parameters of pseudo-first-order, pseudo-second-order and intraparticle diffusion models for adsorption of SR dye at pH 3 and 25°C.

Adsorbents	C_o = 100 mg/L	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion		
	$q_{e\,(exp)}$ (mg/g)	k_1 (min^{-1})	$q_{e\,(cal)}$ (mg/g)	R^2	k_2 (g/mg min)	$q_{e\,(cal)}$ (mg/g)	R^2	k_{id} (mg/g min$^{1/2}$)	C	R^2
ACP	16	0.014	4.96	0.668	0.016	16	0.989	0.431	12.4	0.814
ACP-M	23	0.016	8.75	0.676	9.53×10^{-3}	21	0.999	0.617	17.3	0.842
ACP-E	40	0.021	10.3	0.742	4.08×10^{-3}	38	0.999	1.95	18.5	0.859
ACP-C	58	0.018	22.4	0.797	2.22×10^{-3}	57	0.999	2.75	24.9	0.846

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