International Journal of Minerals, Metallurgy and Materials
Volume 22, Number 7, July 2015, Page 770
DOI: 10.1007/s12613-015-1133-8

Role of the surface chemistry of activated carbons in dye removal from aqueous solution

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(Received: 1 December 2014; revised: 25 January 2015; accepted: 26 January 2015)

Abstract: Commercial activated carbons were modified by a series of chemical or physical treatments using H_2O_2, NH_3, and heating under N_2 flow without notably changing their pore structures. The resultant carbons were characterized by N_2 adsorption and Bohem titration and then used to remove Ponceau 4R, methyl orange and brilliant blue from aqueous solutions. Surface chemistry was found to play a significantly different role in removing these three compounds. The removal of anionic Ponceau 4R increases with increasing carbon surface basicity due to the predominant dispersive interaction mechanism. In contrast, surface chemistry has little effect on the removal of anionic methyl orange, which can be explained by two parallel mechanisms involving electrostatic and dispersive interactions due to the basic amine group in a dye molecule. The influence of surface chemistry on the removal of amphoteric brilliant blue dye can also be ignored due to a weak interaction between the carbons and dye molecules, which is resulted from strong cohesive energy from electrostatic forces inside amphoteric dye molecules.

Keywords: activated carbon; decolorization; dyes; modification; surface chemistry

1. Introduction

Dyes are extensively used in the textile, paper, dyeing, and printing industries and even in the food and pharmaceutical industries. Due to their high visibility and recalcitrance, effluents from these industries are often colored and cause serious visual pollution. Moreover, most of them are toxic and hazardous for human and aquatic life. Consequently, the removal of chemical dyes from industrial wastewater/water is essential. Various methods such as photodegradation [1], biodegradation [2], and adsorption [3–4] have been developed for dye removal; among these, adsorption has received increasing attention in recent years due to the chemical and biological stability of dyes.

Activated carbons (ACs) are widely used as adsorbents for dyes due to their developed pore structure and abundant surface chemical groups. Pore structure is typically characterized by surface area, pore volume, and pore size distribution. The surface chemistry depends on the quantity and variety of surface functional groups such as carboxylic, lactonic, and phenolic groups, which can be modified via physical or chemical treatment. Appropriate pore size and large pore volume are necessary for high adsorption capacity in ACs. However, surface chemistry is also an important factor that influences the adsorption capacity, in particular, the selectivity of ACs for a certain adsorbate [5–6]. For example, the study of Pereira *et al.* [7] indicated that basic surface properties of ACs are beneficial for the adsorption of anionic dyes, while acidic surface character is beneficial for the adsorption of cationic dyes. Wang and Zhu [8] confirmed that acidic surface groups result in the reduction of the adsorption of basic dyes. Yin *et al.* [9] claimed that ACs with more acidic oxygen-containing groups can effectively adsorb polar chemicals, whereas those with more basic groups exhibit high adsorption capacities for weak or non-polar substances. López *et al.* [10] suggested that the high polyphenol adsorption capacity of ACs after modification was attributed to the increased quantities of mesopores and carboxylic groups, which resulted in the formation of chemical compounds between the carboxylic groups and the

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polyphenols. These researchers studied the effects of the surface properties of ACs on the adsorption of some types of dye molecules; however, the results cannot be generalized to all dyes due to the various structures and properties of different dye molecules. For example, dyes, even those that belong to the same dye type, can contain various structures and groups such as auxochrome groups.

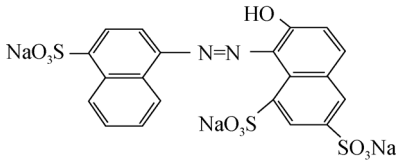
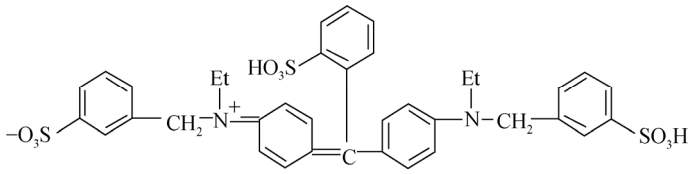
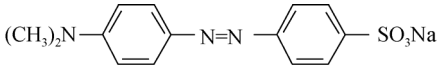
In this study, a commercial AC sample was modified by a series of treatments using the oxidant H_2O_2, NH_3 solution, and thermal treatment to attain AC samples with different surface chemistries and similar pore structures. Two anionic azo dyes with different structures (Ponceau 4R and methyl orange) along with a dye with amphoteric character (brilliant blue) were selected as adsorbates in this study because of their typical structural characteristics. The effects of AC surface chemistry on the removal of these dyes were explored and analyzed. The results significantly improve our understanding of the role of AC surface chemistry in dye removal.

2. Materials and methods

2.1. Materials

Commercial AC was obtained from SOYUM Pharmaceutical Holding Group Co. Ltd. Two types of edible pigments, Ponceau 4R (85wt% purity) and brilliant blue (85wt% purity) were obtained from Shanghai Shitou dyestuff Co., Ltd. Methyl orange and the other reagents, all of analytical purity, were purchased from Beijing Chemical Reagents Co. Ltd. The main characteristics of the three selected dyes are listed in Table 1.

Table 1. Main characteristics of the selected dyes

Dye	Structural formula	λ_{max} / nm
Ponceau 4R		509
Brilliant blue		629
Methyl orange		463

2.2. Modification

Ten portions of commercial AC samples were mixed with different mass fractions of H_2O_2 (5%, 10%, 15%, 20%, and 30%) and NH_3 (5%, 10%, 15%, 20%, and 25%) in aqueous solutions in ten conical flasks. The mixtures were placed in an oscillator at 45°C for 4 h at a rotation rate of 150 r/min. The solutions were then filtered. The filter cakes were washed with water until their pH values were ~7 and then dried. Furthermore, three batches of commercial AC samples were heated under N_2 flow for 1 h at 800, 1000, and 1100°C. The obtained samples were named as shown in Table 2.

Table 2. Nomenclature of modified AC samples

Modification method	Abbreviation
The original AC	Or-AC
H_2O_2, 5%	AC-H1
H_2O_2, 10%	AC-H2
H_2O_2, 15%	AC-H3
H_2O_2, 20%	AC-H4
H_2O_2, 30%	AC-H5
NH_3, 5%	AC-N1
NH_3, 10%	AC-N2
NH_3, 15%	AC-N3
NH_3, 20%	AC-N4
NH_3, 25%	AC-N5
Thermal treatment, 800°C	AC-R1
Thermal treatment, 1000°C	AC-R2
Thermal treatment, 1100°C	AC-R3

2.3. Characterization of adsorbents

The surface areas and pore size distributions of the AC

samples were determined using Quantchrome Autosorb-1 equipment. The AC samples were outgassed at 200°C under vacuum for 4 h prior to measurement. Their N_2 adsorption and desorption isotherms at 77 K under different partial pressures were then measured. Specific surface areas were determined by the five-point Brunauer–Emmertt–Teller (BET) method. The pore volumes were determined based on the adsorbed amounts at a relative pressure near 1. The micropore volumes were determined by the Dubinn–Radushkevic (DR) method.

The surface properties were determined using a modified Boehm titration method as follows [11–12]. 0.05 mol·L^{-1} of standard solutions (NaOH, Na_2CO_3, $NaHCO_3$, and HCl) were prepared using fresh boiled deionized water. 0.5000 g of the carbon sample was then added to a flask containing 50 mL of the standard solution. Subsequently, the flask was sealed and shaken for 24 h at room temperature, and the suspension was filtered. To eliminate the influence of dissolved CO_2 in the basic solution, 50 mL of the standard HCl solution was mixed with the NaOH, Na_2CO_3, and $NaHCO_3$ filtrate followed by boiling and cooling. The excess HCl was determined by back titration using the NaOH standard solution. The number of acidic groups was calculated based on the following assumptions: NaOH neutralizes carboxylic, lactonic, and phenolic groups; Na_2CO_3 neutralizes carboxylic and lactonic groups; and $NaHCO_3$ neutralizes only carboxylic groups. The number of basic groups was calculated according to the consumed volume of the HCl solution.

2.4. Adsorption

A series of Ponceau 4R, brilliant blue, and methyl orange solutions with different concentrations was prepared by dissolving them in deionized water without further treatment. The adsorbent (30 mg) was mixed separately with 20 mL of 0.1140 mg/mL Ponceau 4R, 0.1144 mg/mL brilliant blue, and 0.1068 mg/mL methyl orange in Erlenmeyer flasks. The suspensions were sealed and shaken in a thermostatic shaking bath at 25°C for 2 h (preliminary tests show that 2 h is sufficient to reach the adsorption equilibrium). After adsorption, the mixture was filtered. The quantity of the dye remaining in the filtrate was analyzed at its maximum adsorption wavelength in the visible range (see Table 1) using a TU-1901 UV–Vis (ultraviolet–visible) spectrophotometer. The removal ratios of pigments were calculated by

$$\text{Removal ratio} = [(c_0 - c_e)/c_0] \times 100\% \quad (1)$$

where c_0 and c_e are the initial and equilibrium concentrations of the pigment solution, respectively, mg/mL.

3. Results and discussion

3.1. Pore structure features

The isotherms of all AC samples are shown in Fig. 1. The curve shapes indicate that no significant changes in AC pore structure occurred during modification. According to International Union of Pure and Applied Chemistry (IUPAC) classification, they exhibit types I and IV isotherms and belong to micro- and meso-porous AC [13–14]. The pore structural parameters of ACs before and after modification are listed in Table 3. Compared with the original AC (Or-AC), the surface areas and micropore volumes of the modified ACs decreased slightly or remained almost unchanged, with the exception of AC-R3. The total pore volumes fluctuated to some degree. This indicates that the pore structures of most of the AC samples were only slightly changed. In contrast to the other ACs, AC-R3 presented remarkably larger surface area, total pore volume, and micropore volume, suggesting that some novel pores formed during the heating process at high temperature.

3.2. Surface chemical properties

In general, surface functional groups on ACs can be characterized by Fourier transform infrared spectroscopy (FTIR), temperature-programmed desorption (TPD), and Beohm titration. Among them, the Beohm titration method, although it is not perfect, is often used to determine the quantity of surface functional groups. The quantities of typical surface functional groups on the AC samples are shown in Table 4. The modified ACs exhibited significant differences in surface functional groups compared to the unmodified AC; H_2O_2 modification improved the surface acidity and decreased the surface basicity of AC, as previously reported [15]. With increasing H_2O_2 concentration, the quantity of carboxyl groups on AC increased, while the quantity of basic groups decreased remarkably. ACs modified by low concentrations of H_2O_2 exhibited reduced lactone content and sharply increased phenolic group content compared to the parent ACs; however, these groups presented an overall increasing trend with H_2O_2 concentration, which may have been caused by the transformation between lactones and phenolic groups under certain conditions. It is speculated that a large quantity of lactones decomposed into phenolic groups during the oxidation process at low H_2O_2 concentration, leading to the decrease in lactone quantity and the increase in the quantity of phenolic groups. When a high concentration of H_2O_2 was used, the lactone formation rate exceeded its decomposition rate, resulting in an increased quantity of lactones and a fluctuating quantity of phenolic groups. In general, the total

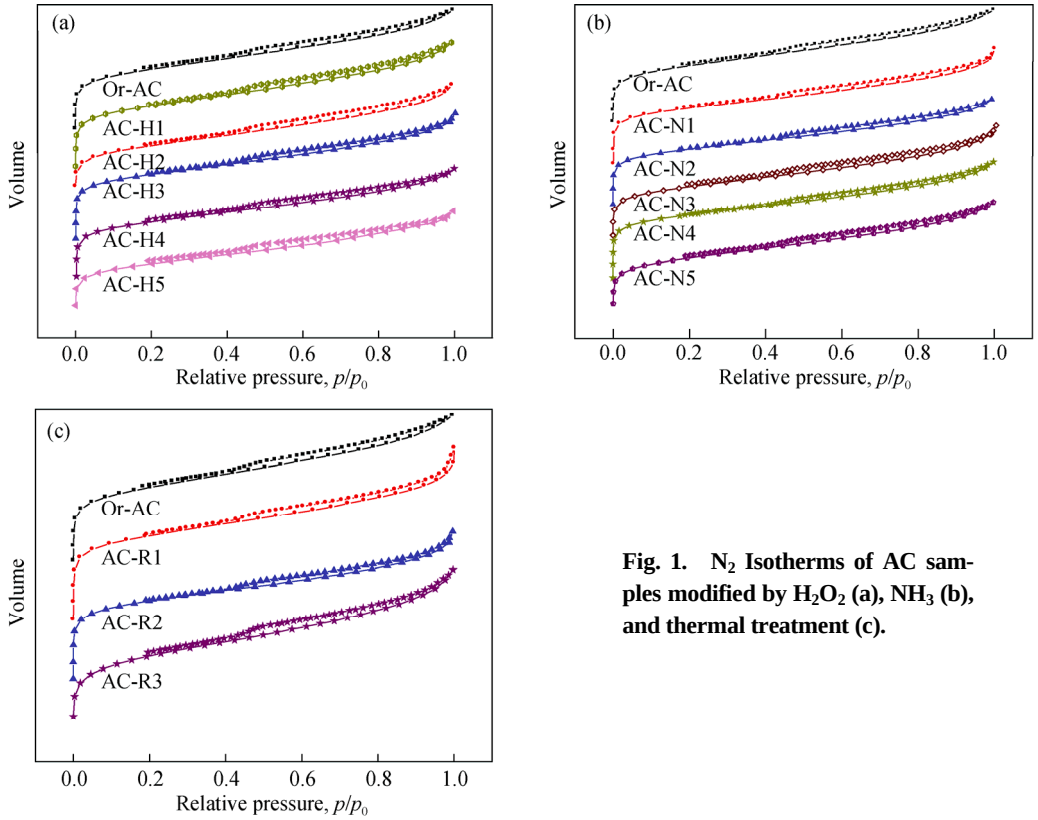


Fig. 1. N_2 Isotherms of AC samples modified by H_2O_2 (a), NH_3 (b), and thermal treatment (c).

Table 3. Pore structure parameters of ACs before and after modification

AC sample	BET surface area / ($m^2 \cdot g^{-1}$)	Total pore volume / ($mL \cdot g^{-1}$)	Average pore size / nm	Micropore volume / ($mL \cdot g^{-1}$)
Or-AC	1145	0.825	2.80	0.485
AC-H1	1071	0.797	2.89	0.468
AC-H2	1089	0.823	2.85	0.467
AC-H3	1071	0.797	2.89	0.468
AC-H4	1075	0.765	2.99	0.466
AC-H5	998	0.725	2.93	0.426
AC-N1	1084	0.871	3.29	0.475
AC-N2	1068	0.802	2.99	0.472
AC-N3	1082	0.834	3.21	0.465
AC-N4	1048	0.782	3.04	0.463
AC-N5	1138	0.834	2.83	0.492
AC-R1	1088	0.896	3.35	0.477
AC-R2	1012	0.765	3.21	0.438
AC-R3	1236	0.902	2.94	0.529

quantity of acidic oxygen-containing groups always increases with H_2O_2 concentration.

For ACs modified by NH_3 solution, the carboxyl groups and acidic groups were reduced in quantity, while the basic groups increased in quantity with increasing NH_3 concentration. The quantities of lactones and phenolic groups exhibited an overall reducing trend with a small amount of fluctuation. This indicates that the acidic groups on ACs were partly neutralized by the NH_3 solution accompanied by the formation of basic groups containing nitrogen such as amines [7]. After heating under inert atmosphere, the quantities of carboxyl groups and lactones were reduced, while

those of the phenolic and basic groups increased. With increasing heating temperature, the quantity of carboxyl groups decreased, and the quantity of basic groups increased in all cases. Overall, thermal modification reduced the amount of acidic groups and improved the surface basicity, which is mainly attributed to the formation of oxygen-free Lewis base sites on graphene layers constituting ACs [16].

Table 4. Quantities of typical surface functional groups on ACs after modification mmol·g^{-1}

Samples	Acidic groups				Basic groups
	Carboxylic groups	Lactones	Phenolic groups	Total quantity	
Or-AC	0.666	0.184	0.017	0.867	0.241
AC-H1	0.715	0.003	0.166	0.884	0.236
AC-H2	0.777	0.006	0.330	1.113	0.227
AC-H3	0.911	0.056	0.270	1.237	0.203
AC-H4	1.276	0.232	0.473	1.981	0.072
AC-H5	1.387	0.385	0.314	2.086	0.022
AC-N1	0.591	0.115	0.015	0.721	0.284
AC-N2	0.590	0.106	0.013	0.709	0.352
AC-N3	0.270	0.094	0.007	0.371	0.399
AC-N4	0.258	0.103	0.004	0.365	0.423
AC-N5	0.246	0.072	0.008	0.326	0.457
AC-R1	0.630	0.020	0.110	0.760	0.254
AC-R2	0.537	0.117	0.093	0.747	0.278
AC-R3	0.259	0.104	0.258	0.621	0.291

3.3. Removal of the dyes

The removal ratios of the dyes from the aqueous solution by AC samples modified by different methods are shown in Figs. 2–4. It is seen that the same original AC shows different adsorption capacities for Ponceau 4R, brilliant blue, and methyl orange; it has the highest adsorption capacity for Ponceau 4R and the lowest for brilliant blue. This variation can be attributed to the molecular sizes of the dyes. The effective pore size ranges of ACs are known to be different for molecules with different sizes and structures [17]. As seen in Fig. 2, the removal ratio of Ponceau 4R decreased notably with increasing H_2O_2 concentration, with the exception of a slight increase as H_2O_2 concentration increased from 20wt% to 30wt%; this can be explained by the relatively large change in the pore structure of ACs oxidized by a 30wt% H_2O_2 solution (Table 3). It is also noted that the quantities of surface carboxyl and acidic groups increased, while the quantity of basic groups decreased with increasing H_2O_2 concentration. This indicated that the carboxyl and acidic surface groups are negatively correlated with Ponceau 4R removal. However, the removal ratios achieved by the NH_3-treated and thermal-treated ACs increased with NH_3 solution concentration and treatment temperature despite their smaller ranges; this can be attributed to the high removal ratio of Ponceau 4R (~95%) by original ACs (Figs. 3 and 4). Simultaneously, both NH_3 modification and thermal treatment increased the surface basic groups of ACs. Consequently, it could be inferred that the surface basicity facilitates Ponceau 4R removal.

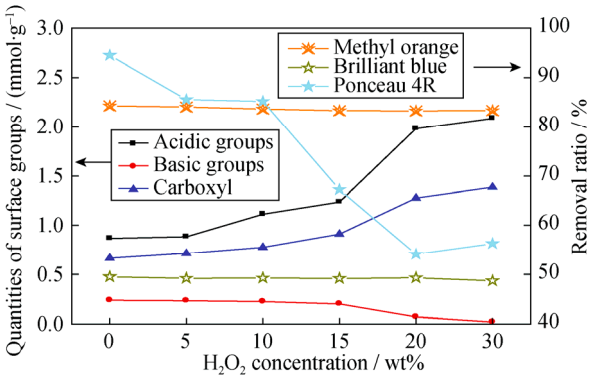


Fig. 2. Removal ratios of dyes and quantities of surface groups on modified ACs as a function of H_2O_2 concentration.

For brilliant blue and methyl orange, different performances were obtained by modified ACs. The removal ratios achieved by all modified ACs did not change remarkably compared with those of original ACs, indicating that the

surface properties of ACs have no significant effect on the removal of these two dyes. Nevertheless, there was a notable increase in the removal ratio of methyl orange by the AC (AC-R3) after heat treatment at 1100°C (Fig. 4). Considering the pore structure change in AC-R3, the increase can be mainly attributed to the large surface area and micropore volume of the AC (Table 3). In comparison to methyl orange, the molecular size of brilliant blue is large, which can explain why the same AC-R3 exhibited a different removal performance for this dye.

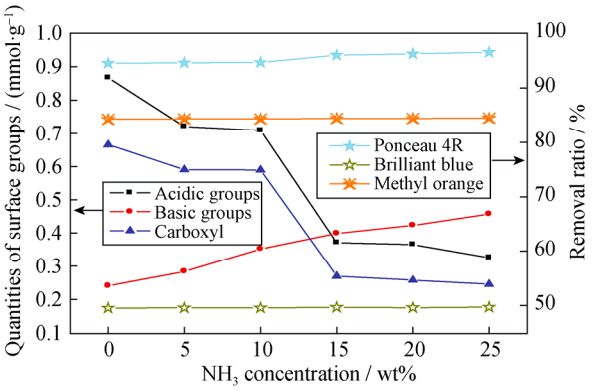


Fig. 3. Removal ratios of dyes and quantities of surface groups on modified ACs as a function of NH_3 concentration.

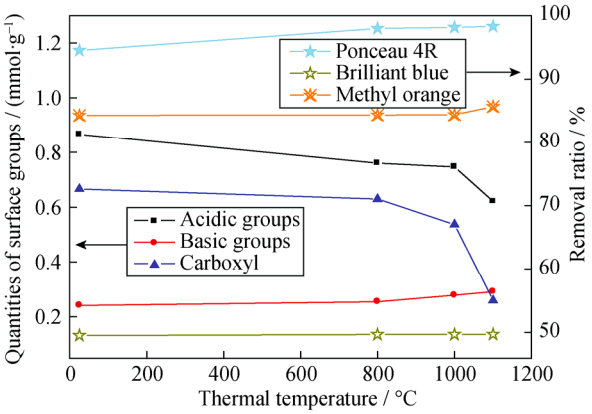


Fig. 4. Removal ratios of dyes and quantities of surface groups on modified ACs as a function of thermal temperature.

Two parallel adsorption mechanisms for dye absorption have been proposed: the first involves electrostatic interactions between dye molecules and carbon surface groups; and the second involves dispersive interactions between dye molecules and carbon surface layers [7]. Ponceau 4R is an anionic azo dye with three negatively charged sulfonate radicals, two naphthalene rings, and –N=N– bonds. Strong conjugated effects exist within this dye molecule. The removal results for Ponceau 4R show that the predominant adsorption mechanism involves dispersive interactions between delocalized π electrons on the basal planes of ACs and the free electrons of dye molecules (aromatic rings and –N=N– bonds) as well as negatively charged ions. The basic surface groups play an active role in adsorption of Ponceau 4R, contrary to what happens with the acidic groups. This is in accordance with reports on the influence of surface chemistry on anionic dyes [7,18]. The FTIR spectra of the Or-AC samples before and after adsorption of Ponceau 4R are shown in Fig. 5. Compared with the spectrum of ACs before adsorption, the spectrum after adsorption displays the characteristic peaks of Ponceau 4R. Notably, the feature peak positions are unchanged, suggesting the physical adsorption of Ponceau 4R.

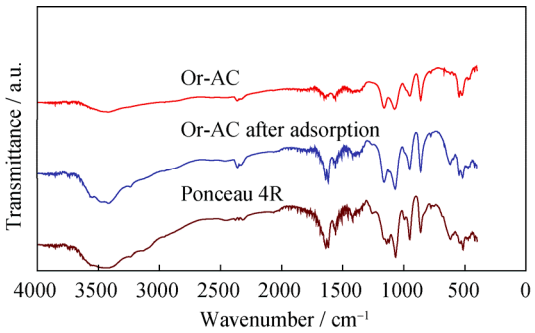


Fig. 5. FTIR spectra of original ACs before and after adsorption of Ponceau 4R.

Methyl orange is also an anionic azo dye with a negatively charged sulfonate radical and strong conjugate effects within the molecules. However, in contrast to Ponceau 4R, it has a basic tertiary amine group. The acidic surface groups of carbons (mainly carboxyls) are good anchoring sites for basic amine groups due to electrostatic interactions; thus, they play an active role in adsorption of methyl orange on ACs. Furthermore, basic surface groups facilitate adsorption by improving dispersive force between anionic azo dye molecules and carbon surface layers, as discussed above. Obviously, the adsorption involves the two parallel adsorption mechanisms. Therefore, the alteration of AC surface properties (acidity or basicity) does not significantly affect the removal of methyl orange. As for brilliant blue, the electrostatic repulsive and attractive forces between ACs and dye molecules always counteract each other due to the amphoteric character of this dye. In addition, the dispersive interactions can be very weak due to the strong cohesive energy from electrostatic interactions inside the molecule. Consequently, modification has little effect on the removal of brilliant blue. In addition, both methyl orange and brilliant blue show similar physical adsorption character on the AC samples with Ponceau 4R.

4. Conclusions

Commercial AC samples were modified by a series of chemical and physical treatments without significantly changing the pore structures. These modified ACs with different surface chemical characteristics were used to remove Ponceau 4R, methyl orange, and brilliant blue from aqueous solutions. Significant differences were observed in the influences of AC chemical character on the removal among these three dyes due to their different structures and properties. The removal of Ponceau 4R, an anionic azo dye, decreased sharply with the increase in acidic surface group quantity and the decrease in the quantity of basic surface groups on the ACs; this was attributed to the predominant adsorption mechanism involving dispersive interactions. However, the removal of anionic methyl orange and amphoteric brilliant blue was not significantly affected by the AC surface properties. For methyl orange, this can be explained by the co-existence of electrostatic and dispersive interaction mechanisms, in which all AC surface groups, both acidic and basic, are favorable for dye adsorption. For brilliant blue, the result is attributed to a weak interaction between ACs and dye molecules caused by the strong cohesive energy from electrostatic forces inside the dye molecules.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 21271022), the China National Petroleum Corporation Innovation Foundation (No. 2012D-5006-0208), the Fundamental Research Funds for the Central Universities (No. FRF-BR-13-008), and the Engineering Research Institute Foundation of University of Science and Technology Beijing (No. YJ2012-008).

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