



The use of carbon black to catalyze the reduction of nitrobenzenes by sulfides

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ABSTRACT

Using carbon black (CB) as catalyst, the reduction of nitrobenzenes (NBs) to anilines by sulfides at room temperature was studied. In the reactions, CB serves as an intermedium to accelerate the reduction of NBs by sulfides. In the presence of 0.3 g/L CB and 3.0 mM sulfides at pH 7.0 and 25 °C, our results showed that CB-catalyzed reduction of NBs were pseudo-first order. The reduction rate constant of nitrobenzene was 0.0367 h⁻¹ in the presence of CB-1, which was 10 times more than the reduction rate constant in the absence of CB-1. Other experiments of different CB samples produced by different methods and different raw materials indicated that some active oxygenated functional groups on CB surface should be the reactive sites and play the dominant role in catalyzing the reduction of NBs. The catalytic reactions of different NBs by sulfides indicated that the reduction rate constants of chloronitrobenzenes to chloroanilines were greater than those of methyl nitrobenzenes to methylanilines. And due to the effect of different substituent positions, the nitro group with *meta* substituent was reduced most easily while the nitro group with *ortho* substituent was reduced most difficulty.

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1. Introduction

Nitrobenzenes (NBs) have been discharged excessively into the environment because they are used extensively as intermediates in the manufacturing of explosives, pesticides, herbicides, dyes, pharmaceuticals, etc. [1]. They impose serious toxicities to human beings and other living organisms in a number of ways such as immunotoxicity [2], mutagenicity [3] and skin sensitization [4]. These compounds have been on the U.S. Environmental Protection Agency (US EPA) priority control list since 1970s. At present, how to reduce and eliminate the hazards of NBs attracts more and more attention from environmental researchers. NBs can be degraded by means of photodegradation [5,6], irradiation degradation [7], ultrasound degradation [8] and biodegradation [9]. For sediments contaminated by NBs, the *in situ* degradation techniques are easier and cheaper than *ex situ* techniques on dredging and disposal of the contaminated sediments [10]. In recent years, zero-valent iron has been widely applied for the *in situ* remediation of sediments contaminated by NBs. In the *in situ* remediation of sediment contaminated by nitrobenzene (NB), Fe(0)-sorbent-microorganism remediation system was applied to remediate the contaminated sediment. After NB was reduced to aniline (AN) by zero-valent iron, AN was easily degraded by microorganism in order to remove pollutants from the sediment [10]. In the anaerobic sediment

contaminated by NB, NB could be reduced rapidly by zero-valent iron that was added into the anaerobic sediment. And the degradation rate was faster than that using the anaerobic sediment or zero-valent iron alone [11]. However, other *in situ* degradation techniques of sediments contaminated by NBs has not received much attention and development by now.

It is well-known that the high sorption of NBs by sediments has great effect on their transport, transformation and bioavailability in aquatic environment [12]. There was a certain amount of carbon black (CB) in sediments and CB accounted for about 9% of the total organic carbon [13]. Subsequently CB has been recognized as an important carbonaceous geosorbent due to its mighty absorption capacity [13]. As the heterogeneous, concentrated, aromatic and carbon-rich materials, CB is derived from both natural processes and human activities by incomplete combustion of biomass and fossil fuels [14–16]. About 50–200 Tg of CB comes into the environment each year and more than 80% is from fires [17]. With the special microporous structure and high surface area, CB is able to adsorb a large number of organic pollutants including NBs, polycyclic aromatic hydrocarbons and polychlorinated biphenyls [18–25]. As a result CB in sediments should be able to accumulate most of NBs and have great influence on the transport and bioavailability of NBs [26–28]. Besides, could CB contribute directly to the transformation of NBs considering the large amount of NBs captured inside CB?

In addition to its microporous structure and high surface area, there are a lot of particular oxygenated functional groups on the surface of CB [14]. Due to the function of the particular groups,

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CB has been found to act as the catalysts in the oxidation processes of organic pollutants [29]. However, few researches have been reported about the catalytic reduction of organic contaminants in water by CB [30]. Kemper et al. [31] demonstrated that hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) could be destroyed rapidly in the presence of CB and sulfides. Xu et al. [32] designed an electro-chemical cell system in order to permit electrons to be transferred. Using this electro-chemical cell system, it was suggested that RDX was destroyed by an alternative pathway such as nucleophilic substitution, and nitroglycerin was destroyed by the reduction reactions in sulfides systems. As the intermedium of electron-transfer reaction, natural organic matter (NOM) could catalyze the reduction of NBs to anilines in aqueous solution of sulfides [33]. Because of the analogous characteristics between CB and NOM, CB might catalyze the reduction of NBs by the similar mechanism to that of NOM as the catalyst.

In anaerobic environment, there is a certain amount of sulfides produced by the microbial activities [31,34]. In this case, could CB in sediments catalyze the reduction of NBs in the presence of sulfides at room temperature? In this article, we studied the effect of CB on the reduction of NBs in aqueous solution containing sulfides at room temperature. Based on the results, the kinetics and mechanism that NBs were reduced by CB and sulfides was analyzed and discussed.

2. Experimental

2.1. Materials

Nitrobenzene (NB, 99%), 2-methylnitrobenzen (2MNb, 99%), 3-methylnitrobenzen (3MNb, 99%), 4-methylnitrobenzen (4MNb, 99%), 2-chloronitrobenzene (2CNb, 99%), 3-chloronitrobenzene (3CNb, 99%), 4-chloronitrobenzene (4CNb, 99%), aniline (AN, 99.8%), 2-methylaniline (2MAN, 99%), 3-methylaniline (3MAN, 99%), 4-methylaniline (4MAN, 99%), 2-chloroaniline (2CAN, 99%), 3-chloroaniline (3CAN, 99%) and 4-chloroaniline (4CAN, 99%) were purchased from J&K chemical and used as received. In order to elucidate the influence of different substituted groups and the substitution positions on the catalytic reaction, seven chemicals including NB, 2MNb, 3MNb, 4MNb, 2CNb, 3CNb and 4CNb were chosen as reactants to investigate the catalytic reduction under CB (0.3 g/L) and sulfides (3.0 mM) at pH 7.0 and 25 °C. The seven anilines reagents are used to obtain their respective accurate retention time on HPLC chromatogram of samples in order to analyze and determine the products of seven NBs reduced by sulfides. All other chemicals were reagent grade and used without further purification. Stock solutions of sulfides which included H₂S, S²⁻ and HS⁻ were prepared freshly by dissolving a certain amount of sodium sulfide in deoxygenated deionized water [35,36].

In order to study the effect of CB samples which are from the same raw material and prepared by different methods to the reaction of NBs and sulfides, six different CB samples prepared by red pine wood were investigated as catalysts in this study. The red pine wood from Northeast China was mechanically ground to grains less than 165 μm. CB-1 was produced under anaerobic incineration of red pine wood powders at 400 °C for 6 h. CB-2 was prepared by incubating CB-1 in a solution of 1.0 M HCl solution and stirring for 12 h to remove all soluble salts and the de-ashed residues. To remove minerals (mainly silica), the CB-2 was treated with a mixture of 10% HF solution and 1.0 M HCl solution following the same procedures using a plastic container as the receptacle. The demineralized samples were named CB-3. CB-4 was obtained by oxidizing CB-3 with 0.1 M K₂Cr₂O₇ and 2.0 M H₂SO₄ for 48 h at 55 °C [37], and CB-5 was obtained by combusting CB-3 at 375 °C for 12 h in O₂-saturated air [38]. In order to further remove the organic matters absorbed by CB, CB-5 was sequentially extracted by *n*-hexane

and the extracted samples were named CB-6. In order to study the effect of CBs which are from the different raw materials and prepared by the same method to the reaction of NBs and sulfides, nine different materials were mechanically ground to grains less than 165 μm. CB samples were produced under anaerobic incineration of charcoals powders at 400 °C for 6 h. And then all CB samples were prepared by 1.0 M HCl solution and stirred for 12 h to remove all soluble salts and the de-ashed residues. The CB samples prepared by jujube, apple wood, pine wood, oak, willow wood, coconut active carbon, wheat, corn stalks and paddy rice are hereafter referred to as DCB-1, DCB-2, DCB-3, DCB-4, DCB-5, DCB-6, DCB-7, DCB-8 and DCB-9, respectively. At last, all treated CB samples were separated from water by vacuum filtration, washed by deionized water until the filter solution became neutral and dried in the oven at 80 °C.

2.2. Characteristics of CBs

Elemental analyzes (C, H, N) of different CB samples were conducted using an Vario EI CHN elemental analyzer. The oxygen contents were determined by a mass balance. The H/C, O/C and (O+N)/C atomic ratios were calculated to evaluate the aromaticity and polarity of CB samples. The specific surface areas were measured with N₂ adsorption at 77 K by the BET method using Autosorb-1-MP surface area analyzer of American Quantachrome Company. The characteristics of different CB samples are listed in Table 1.

Oxygenated functional groups on CB surface were determined by the method proposed by Boehm [39,40]. Solutions of Na₂CO₃ (0.02 M), C₂H₅ONa (0.02 M) and HCl (0.02 M) were prepared using deionized water. A 20 mL volume of different alkali solutions was added to vials containing 0.2 g of CB samples. These samples were shaken until equilibrium. When equilibrium was reached, the CB samples were separated from the solution by decanting. The excess of base was determined by back-titration using HCl solution (0.02 M).

2.3. Theoretical calculation of Mulliken atomic charges of each atomic in substituted groups of NBs

Using the density function theory (DFT), the stable structures of several NBs were obtained by the method of B3LYP. And the Mulliken atomic charges of each atomic in substituted groups of several NBs were calculated by B3LYP method with the 6-31G* polarized basis set in the software of Gaussian 09. The Mulliken atomic charges of each atomic of substituted groups are listed in Table 2.

2.4. Experimental procedures

At pH values from 1.0 to 13.0, buffer solution was prepared with different concentrations of HCl, NaH₂PO₄, Na₂HPO₄ and NaOH solutions. All experiments were controlled by 20.0 mM buffer solution and performed in triplicate. 25.0 mL buffer solution of 20.0 mM and 3.0–5.0 mL deionized water (for dilution purposes when needed) were decanted into 50.0 mL vials containing a weighed amount of CB samples. Vials were purged with nitrogen gas for 10.0 min to remove oxygen from the solution and the headspace after they were sealed. Then aliquots (typically 0.3 mL) of 0.3 M sulfides solution were added via the syringe. And the sulfides concentration of reaction solution was usually 3 mM. However, other concentrations were used in some experiments. After adding sulfides solution, NBs were added via the syringe and the NBs concentrations of reaction solutions were acquired by the black control experiment (without CB and sulfides) using the HPLC. And the concentrations of NBs were 0.243 mM. The final aqueous volume in each vial was usually 30 mL. Finally, all vials were placed on a rotating bed at 150 rpm and 25 °C.

Table 1
Elemental compositions, atomic ratios, BET-N₂ specific surface area (SA) and the amount of AOFG of all CB samples.

Sample	C (%)	H (%)	N (%)	O (%)	H/C	O/C	(O+N)/C	SA (m ² /g)	AOFG (10 ⁻³ mM/m ²)
CB-1	66.82	15.37	3.16	14.65	2.760	0.164	0.205	96.62	9.837
CB-2	71.32	13.56	3.27	11.85	2.282	0.125	0.162	105.28	8.816
CB-3	75.37	9.49	2.84	12.30	1.511	0.122	0.155	115.67	8.461
CB-4	79.52	4.64	1.73	14.11	0.700	0.133	0.151	128.69	8.265
CB-5	82.80	5.36	1.87	9.97	0.776	0.090	0.110	120.57	7.844
CB-6	81.62	5.83	2.05	10.50	0.857	0.096	0.118	126.68	7.519
DCB-1	81.38	13.93	2.83	1.86	2.054	0.017	0.046	356.35	2.695
DCB-2	71.32	12.56	3.81	12.31	2.113	0.129	0.175	255.22	2.704
DCB-3	73.18	11.69	3.03	12.1	1.917	0.124	0.159	105.23	8.815
DCB-4	78.88	10.65	3.21	7.26	1.620	0.069	0.103	214.25	4.105
DCB-5	82.67	6.02	2.93	8.38	0.873	0.076	0.106	703.65	1.358
DCB-6	86.67	5.23	4.02	4.08	0.724	0.035	0.075	1474.12	0.602
DCB-7	65.73	15.82	1.05	17.4	2.888	0.198	0.212	38.51	24.700
DCB-8	70.38	16.23	2.71	10.68	2.767	0.113	0.146	78.95	10.880
DCB-9	61.27	13.29	1.52	23.92	2.603	0.292	0.314	21.86	28.741

Table 2
The Mulliken atomic charges of each atomic in substituted groups of different NBs.

Samples	Mulliken atomic charges NO ₂			CH ₃				Cl
	N	O-1	O-2	C	H-1	H-2	H-3	
NB	+0.3806	-0.3935	-0.3935					
2MNB	+0.3708	-0.3994	-0.3932	-0.5020	+0.1808	+0.1884	+0.1478	
3MNB	+0.3796	-0.3953	-0.3947	-0.5310	+0.1678	+0.1744	+0.1665	
4MNB	+0.3776	-0.3973	-0.3973	-0.5333	+0.1668	+0.1780	+0.1668	
2CNB	+0.3574	-0.3632	-0.3790					+0.0513
3CNB	+0.3860	-0.3875	-0.3878					+0.0069
4CNB	+0.3820	-0.3917	-0.3917					+0.0101

In order to overcome the impact of CB adsorption and ensure a high recovery of NBs and their products, reaction solutions were separated by vacuum filtration and CB samples sequentially extracted three times by 5 mL methanol before being analyzed. Using these processing methods, the recovery test of seven NBs and seven anilines indicated that the recovery of NBs and anilines were 85–92% and 90–95%, respectively. At last, all centrifugal solution including reaction aqueous solution and extracted solution were transferred to the same reagent bottles waiting to be analyzed. And the concentrations of NBs were the quotients of the total quantities of NBs (including reaction aqueous solution and extracted solution) and the volume of reaction aqueous solution. All NBs and anilines were analyzed using an Agilent 1100GC HPLC equipped with a Diomand C-18 column (200 mm × 4.6 mm, 5 μm). Mobile phase was the mixture of acetonitrile and water (65/35, v/v). The wavelength of UV detector was adjusted from 230 to 280 nm depending on different types of NBs and anilines. The flow rate of mobile phase was 1.0 mL/min and the injection volume of the sample was 20.0 μL.

3. Results and discussion

3.1. Catalytic reduction of NB

From Fig. 1, when there is only NB and CB-1, about 7% of NB disappeared. Even so, NB was not reduced by CB-1 because NB was hard to be fully recovered as the result of the adsorption of CB-1 to NB (the recovery of NB was more than 90%). And the reduction rate of NB was very slow when NB was only mixed with 3.0 mM sulfides without addition of CB-1. However, as illustrated in Fig. 1 NB was reduced rapidly in the presence of 0.3 g/L CB-1 and 3.0 mM sulfides, which demonstrated that CB-1 could accelerate the reduction of NB in the presence of sulfides. There are some oxygenated functional groups on CB surface [14]. Because some oxygenated functional groups are easy to accept or lose electrons, carbon materials which

are rich in oxygenated functional groups are usually used as catalysts [30]. In the reductive reaction, carbon materials serves not only as an adsorbent but also as an electrical conductor to enable the reduction of NB using hydrazine as a reducing agent [41]. In addition, one previous research [32] has proved that nitroglycerin was destroyed by the reduction reactions in sulfides systems in the presence of CB. Therefore, it was speculated that some oxygenated functional groups on CB surface might accept the electrons of

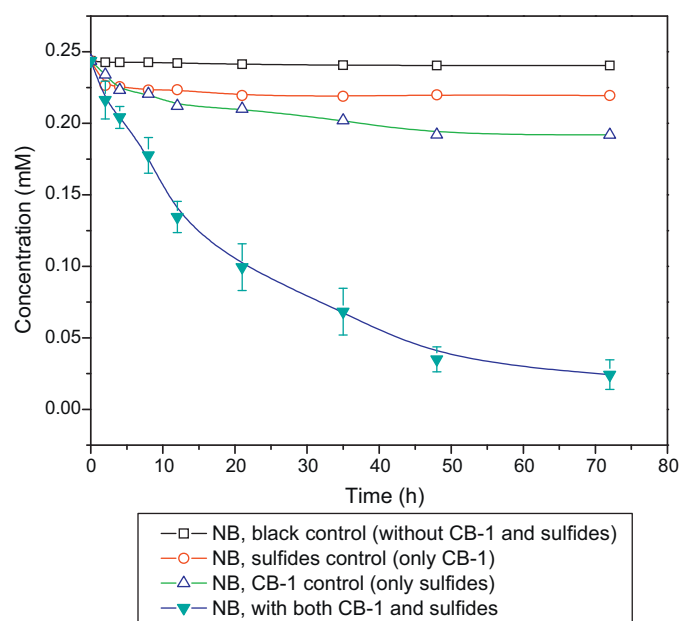


Fig. 1. The reduction of NB by sulfides (3.0 mM) in the presence of CB-1 (0.3 g/L) at pH 7.0 and 25 °C.

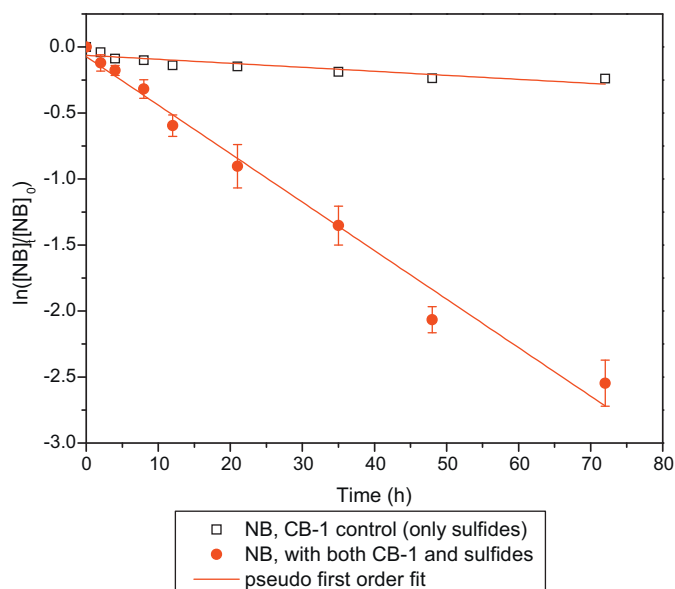


Fig. 2. Plot of $\ln([NB]_t/[NB]_0)$ versus time for the reduction of NB by CB-1 (0.3 g/L) and sulfides (3.0 mM) at pH 7.0 and 25 °C.

sulfides and provide these electrons to accelerate the reduction of NB in this experiment.

Fig. 2 is the plot of $\ln([NB]_t/[NB]_0)$ versus time, $[NB]_t$ and $[NB]_0$ were NB concentrations at the t time and the initial time, respectively. The plot indicated that the CB-1 mediated reaction was pseudo-first order in the presence of CB-1 (0.3 g/L) and sulfides (3.0 mM) at pH 7.0 and 25 °C. The reduction rate constant was calculated by the equation of $\ln([NB]_t/[NB]_0) = -k_{obs}t$, where k_{obs} was the reduction rate constant. Based on this equation, k_{obs} value was 0.00304 h^{-1} when NB was only mixed with 3.0 mM sulfides without addition of CB-1. However, in the presence of CB-1 (0.3 g/L) and sulfides (3.0 mM), the k_{obs} value of 0.0367 h^{-1} could be obtained from the equation, which was 10 times more than k_{obs} value in the absence of CB-1. And other k_{obs} values of our experiments were also calculated by the equation. In the catalytic reduction of NB, NB was reduced via two-electron reduction [12] and transformed to the final product of AN (Fig. 3). The compound analysis showed that the contents of intermediates including nitrosobenzene and phenylhydroxylamine were very low throughout the reaction and more than 93% NB was transformed to AN by sulfides in the presence of CB-1 after 3 days (Fig. 4).

3.2. The influence of sulfides and pH on catalytic reaction

Fig. 5 is the plot of k_{obs} versus the concentrations of sulfides in the presence of CB-1 (0.3 g/L) at pH 7.0 and 25 °C. The plot indicated that the k_{obs} values of NB were correlated positively with the concentrations of sulfides in the range of 1.0–5.0 mM. However, the catalytic reaction was not observed significantly when the concentration of sulfides was less than 1.0 mM. From Fig. 3, the reduction

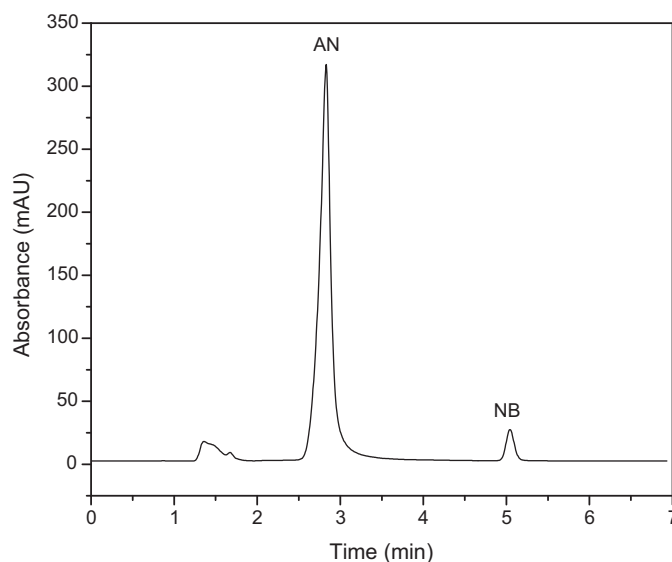


Fig. 4. The HPLC spectrogram of catalytic reduction of NB after 3 days.

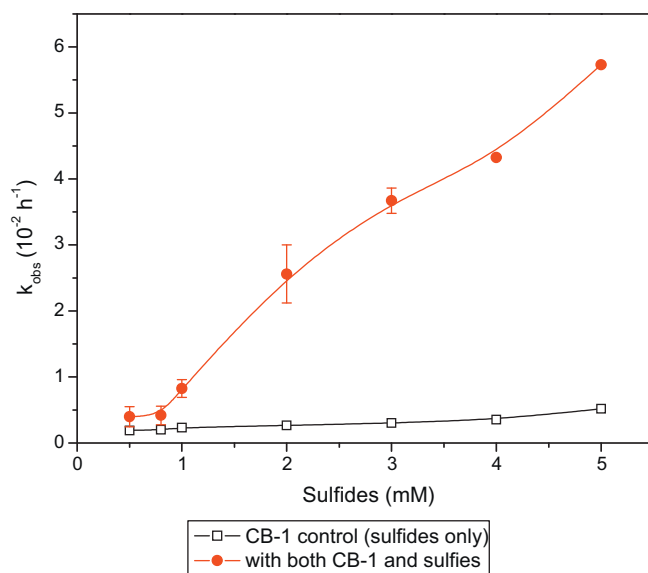


Fig. 5. The k_{obs} values of NB by sulfides in the presence of CB-1 (0.3 g/L) at pH 7.0 and 25 °C.

of NB was a two-electron reduction, and sulfides could also be oxidized to elemental sulfur undergo similar two-electron oxidation [12]. So it was speculated that a two-electron reduction of NB by sulfides formed some unstable intermediate, such as nitrosobenzene and phenylhydroxylamine, which could be rapidly reduced to final product of AN in the presence of CB-1.

From Fig. 6, it was observed that NB was not reduced by CB-1 from pH 1.0 to pH 13.0 in the absence of sulfides. And only with

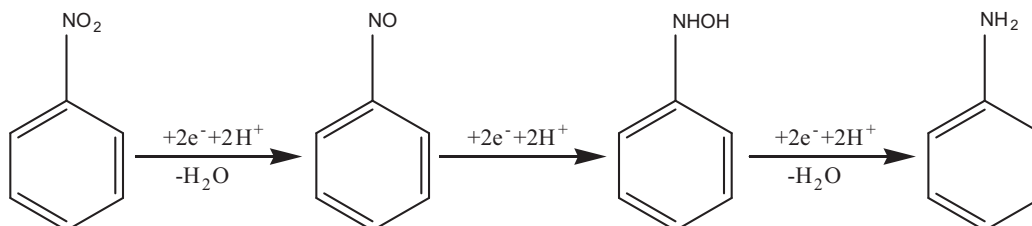


Fig. 3. The electron addition and protonation steps of the reduction reaction of NB.

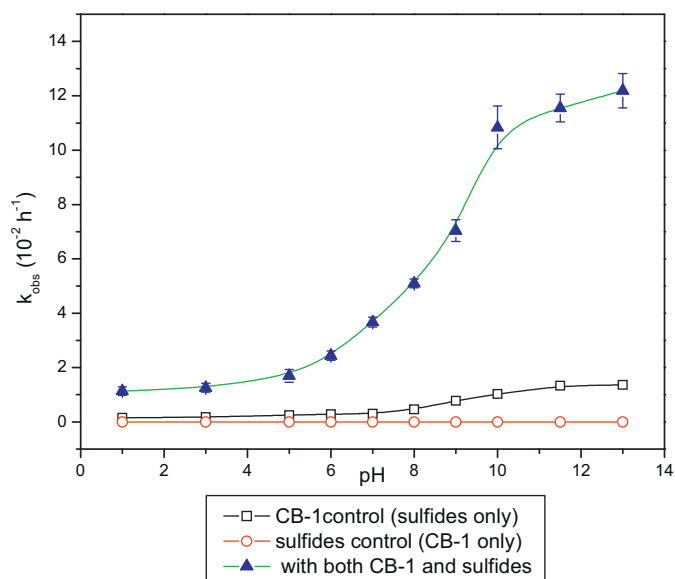


Fig. 6. The relationship of k_{obs} values of NB and different pH values in the presence of sulfides (3.0 mM) and CB-1 (0.3 g/L) at 25 °C.

3.0 mM sulfides and NB, the k_{obs} values of NB increased slowly with pH values increasing. Generally the reducing rate of NB increased accordingly with pH values from 1.0 to 13.0 in the presence of sulfides and CB-1. And the k_{obs} values of NBs catalyzed by CBs and sulfides increased from $0.0113 h^{-1}$ to $0.1219 h^{-1}$ with pH values from 1.0 to 13.0. However, there was no significant catalytic effect when the pH value was less than 3.0. When the pH value was over 10.0, NB was reduced rapidly by sulfides in the presence of CB-1. With pH values in the range of 5.0–9.0, the k_{obs} values of NB were correlated positively with the pH values increasing. Based on the results, it was found that the k_{obs} values of NB catalyzed by CB-1 significantly increased with pH values increasing, which demonstrated that the catalytic ability of CB-1 improved with pH values increasing. It is well-known that there are a certain number of phenolic groups on CB surface [14]. Previous research has proved that the quinone functional groups are the important active sites for carbon materials used in the reduction of nitro compounds [30]. With pH values increasing, the amount of quinone functional groups that were regarded as main active groups for the reduction of NB also increased because of the deprotonation of phenolic groups [31]. As a result, the catalytic ability of CB-1 for the reduction of NB by sulfides increased with pH values increasing so that the k_{obs} values of NB increased rapidly with pH values increasing.

3.3. The effect of different CB samples on catalytic reaction

As the heterogeneous, concentrated, aromatic and carbon-rich materials, CB derives from incomplete combustion of biomass and fossil fuels. And the properties of CB samples are decided by not only raw materials but also the method of preparation. In order to study the effect of CB samples which are from the same raw material and prepared by different methods to the reaction of NBs and sulfides, the reactions that CB-1, CB-2, CB-3, CB-4, CB-5 and CB-6 mediated the reduction of NB by sulfides at 25 °C were studied. CB-2 and CB-3 was prepared from CB-1 after treated by HCl solution (1.0 M), HCl (1.0 M) and HFl (10%) solution, respectively. After the inorganic carbon and minerals mixed with CB were eliminated, the specific surface areas of CB samples increased significantly. After the organic materials were removed by the oxidation of $K_2Cr_2O_7$ (0.1 M) (CB-4) or the combustion at 375 °C in O_2 -saturated air (CB-5), the surface areas of CB samples also increased. In order to

eliminate the influence of some organic materials adsorbed by CB on the catalytic reaction, the organic materials adsorbed by CB-5 were extracted to prepare CB-6 by *n*-hexane. Besides, in order to study the effect of CB samples which are from the different raw materials and prepared by the same method to the reaction of NBs and sulfides, we studied the reduction catalyzed by nine CB samples prepared from different raw materials (DCB-1, DCB-2, DCB-3, DCB-4, DCB-5, DCB-6, DCB-7, DCB-8 and DCB-9), which were significant difference in structures and surface characteristics. The properties of all CB samples were listed in Table 1.

The elemental compositions and atomic ratios of all CB samples were listed in Table 1. H/C ratio more than 1.0 suggests that CB contains original organic residues such as fatty acid, aromatic core and fractions [42]. On the contrary, H/C ratio less than 1.0 indicates that CB is highly carbonized and exhibits a highly aromatic structure. The low O/C ratio indicates that CB becomes less hydrophilic and the number of functional groups decreases with the (O+N)/C ratio decreasing [43]. Carboxylic and lactone groups on carbon material are a certain stability and difficult to participate the reduction of nitro compounds [30]. According to Boehm [39,40], Na_2CO_3 neutralizes carboxylic and lactone groups, and C_2H_5ONa neutralizes all oxygenated functional groups on CB surface. Subsequently the content of the relative active oxygenated functional groups (AOFG) on CB surface, which included all oxygenated functional groups on CB surface except carboxylic acids and lactones, could be achieved by calculating the consumption of different alkalis. The amount of AOFG was listed in Table 1.

Because the reduction of NB and sulfides in the presence of CB was a surface reaction, the masses of CB samples were chosen to give approximately the same BET surface area to attain the desirable sorption extent of NB in the experiments. The surface area normalized reduction rate constants (k_{SA}) of NB were acquired by the equation of $k_{SA} = k_{obs}/(\text{surface area of CB})$ in the presence of sulfides (3.0 mM) at pH 7.0 and 25 °C. For studying the influence of AOFG on CB surface to the reduction of NB by sulfides, the relationship of AOFG on different CB surface and k_{SA} of NB catalyzed by different CB samples was observed in the presence of sulfides (3.0 mM) at pH 7.0 and 25 °C. Although the properties of CB samples were obvious differences for CB samples prepared by two methods, it was found that there was some relevance of k_{SA} and the amount of AOFG.

For the CB samples (CB-1, CB-2, CB-3, CB-4, CB-5 and CB-6) which are from the same material and prepared by different methods, it was found that the values of k_{SA} increased with the amount of AOFG (Fig. 7). For other CB samples (DCB-1, DCB-2, DCB-3, DCB-4, DCB-5, DCB-6, DCB-7, DCB-8 and DCB-9) which are from the different raw materials and prepared by the same method, the k_{SA} values also increased with the amount of AOFG (Fig. 8). AOFG were the oxygenated functional groups on CB surface except carboxylic acids and lactones, such as phenolic, carbonyl and other quinone functional groups, which had been proved to be the important active sites for carbon materials used in the reduction of nitro compounds [30]. Therefore, it was concluded that AOFG on CB surface were as the main active site and played the dominant role in catalyzing the reduction of NB in the presence of sulfides.

3.4. Catalytic reduction of different NBs

There are different substituted groups of different NBs, such as methyl, halogen, amino and so on. These substituted groups are located at the different substituent positions of benzene ring. Therefore, the electron cloud densities of carbon atoms of benzene ring make prominent difference owing to the conjugation effect and inductive effect of the substituted groups. Furthermore, the chemical dissociation energies of some bonds change largely with the conjugation effect and inductive effect.

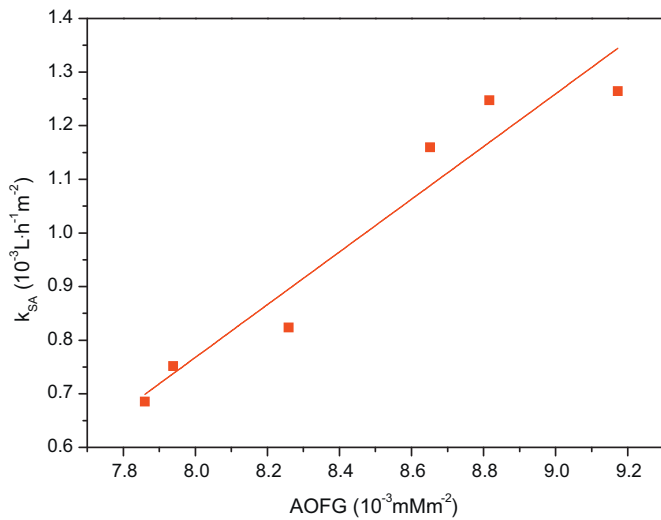


Fig. 7. The relationship of the amount of AOFG and k_{SA} values of NB catalyzed by six CB samples prepared by the same raw material and different methods in presence of sulfides (3.0 mM) at pH 7.0 and 25 °C.

In these experiments of different NBs in the presence of CB-1 (0.3 g/L) and sulfides (3.0 mM), it was found that all of these NBs could be reduced by sulfides. Although there was some difference in their reduction rates of NBs, more than 90% of NBs were finally reduced to anilines. However, it was not found the dechlorination phenomenon of chloronitrobenzenes in our experiments. And the product of 2CNB, 3CNB and 4CNB reduced by sulfides was 2CAN, 3CAN and 4CAN, respectively. In Fig. 9, it was found that the k_{obs} values of chloronitrobenzenes were greater than those of methylnitrobenzenes. With chlorine atom attaching to benzene ring, chlorine-group can strongly attract electron and further reduce the electron cloud density of carbon atom connecting with nitro-group. Then nitro-group becomes poor-electron and is easy to capture electrons to be reduced. Contrarily, methyl group attaching to benzene ring is able to increase the electron cloud density of carbon atom connecting with nitro-group, which makes nitro-group rich-electron and is difficult to capture electrons. Therefore, chloronitrobenzenes could be reduced faster than methylnitrobenzenes by sulfides in the presence of CB-1.

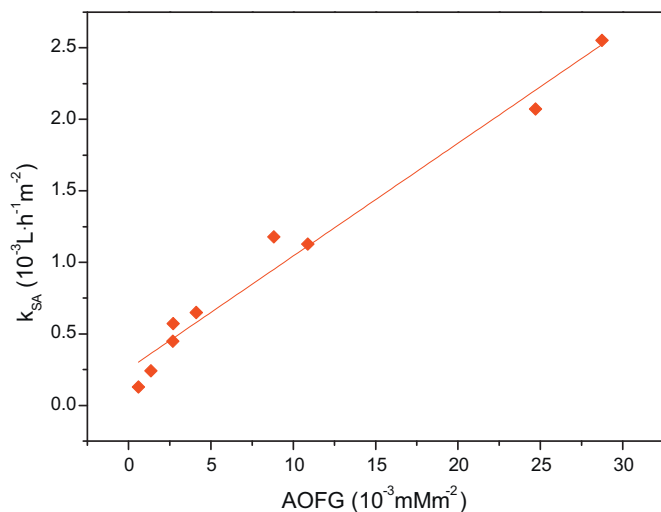


Fig. 8. The relationship of the amount of AOFG and k_{SA} values of NB catalyzed by nine CB samples prepared by the different raw materials and the same method in presence of sulfides (3.0 mM) at pH 7.0 and 25 °C.

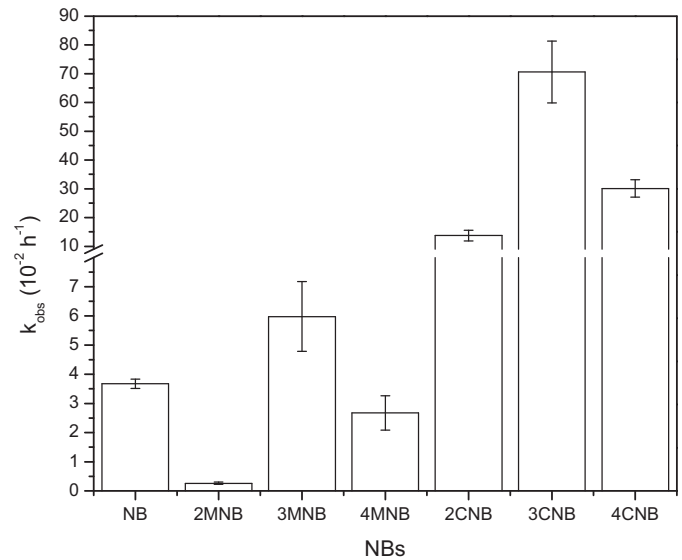


Fig. 9. The k_{obs} values of NBs in the presence of CB-1 (0.3 g/L) and sulfides (3.0 mM) at pH 7.0 and 25 °C.

In addition, the sequences of k_{obs} values of chloronitrobenzenes and methylnitrobenzenes were as follows: $k_{obs}(3\text{CNB}) > k_{obs}(4\text{CNB}) > k_{obs}(2\text{CNB})$, $k_{obs}(3\text{MNB}) > k_{obs}(4\text{MNB}) > k_{obs}(2\text{MNB})$ (Fig. 9). Due to the different substituent position of chloro and methyl group, there is a significant difference for the Mulliken atomic charge of N atomic in nitro group of different chloronitrobenzenes and methylnitrobenzenes. Based on Table 2, it was found that the Mulliken atomic charges of N atomic were all positive and as follows: $3\text{CNB} > 4\text{CNB} > 2\text{CNB}$ and $3\text{MNB} > 4\text{MNB} > 2\text{MNB}$. With the Mulliken atomic charge of N atomic increasing, nitro group is easier to be reduced. Therefore, the nitro group with *meta* substituent was reduced most easily while the nitro group with *ortho* substituent was reduced most difficultly owing to the effect of different substituent positions.

4. Conclusions

Our study clearly demonstrated that CB was able to effectively mediate the reduction reactions of NBs in the presence of sulfides at room temperature. CB serves not only as an adsorbent but also as an intermedium to accelerate the reduction of NBs. The CB catalyzed reduction reactions of NBs were pseudo-first order in the presence of 3.0 mM sulfides at pH 7.0 and 25 °C. AOFG on CB surface should be the reactive sites and play the dominant role in catalyzing the reduction of NBs in the presence of sulfides. The k_{obs} values of NBs increased with pH values increasing from 1.0 to 13.0. Both the type of substituent and the position of substituent could affect the reduction of NBs and the final products of NBs are amino compounds. Accordingly, we must pay more attention to that CB is able to involve in the transformation of NBs in the aquatic system and sediments. Due to considerably high toxicity, amino compounds should be given greater concern in comparison with the parent compounds. In addition, an *in situ* remediation technique using CB as catalyst for the degradation of NBs in sediments should be researched and developed.

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