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Short communication

Removal of ammonium ions from aqueous solutions with coal-based activated carbons modified by oxidation

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ABSTRACT

The main purpose of this work is to study the possibilities for removal of ammonium ions from aqueous solutions by the two coal-based activated carbons (one obtained from Bulgarian lignite from the Chukurovo deposit, and the second, available as commercial product) and their oxidized modifications. The porous texture and surface chemistry of the adsorbents were characterized. Adsorption of NH_4^+ ions was investigated using solutions with different concentrations in the range 35–280 mg l^{-1} in a static mode. Equilibrium modeling data were fitted to linear Langmuir's and Freundlich's equations and maximum adsorption capacities were calculated.

1. Introduction

A number of health problems involving living species such as humans and animals have been attributed to the release of excess nitrogen-containing compounds into the environment. Therefore, controlling them is important in the protection of public health. Ammonia and ammonium ions are the more commonly encountered N-compounds in wastewater and groundwater. Physical, chemical and biological purification methods have been used in wastewater treatment for minimizing the concentration of ammonium ions [1–3]. Of these methods, adsorption using activated carbons has been widely considered [4–6]. A lot of raw materials could be used for the production of activated carbons. Both coal-based carbons and those obtained from agricultural waste proved to be equally important concerning their application. Thanks to their highly developed porous structure and large specific surface area they exhibit a considerable adsorption capacity towards various organic and inorganic pollutants. It is well known that the best activated carbons for removal of positively charged species are carbons with acidic functional groups. On the other hand, the removal efficiency of each different type of activated carbon depends on influence of the specific surface area values and of the type of porous textures of this materials, and that the influence is very specific for the different samples. That is why every specially activated carbon requires individual research.

The aim of the study is to compare the removal efficiency in regard to ammonium ions achieved with the two types of activated carbons based on charcoal, oxidized in advance under the same conditions, but differing in the texture parameters and to make an attempt to explain the effect of the these parameters on the adsorption of ammonium ions.

2. Experimental

Two kinds of activated carbons were used. Activated carbon (denoted as ACCh) was obtained by one-step steam pyrolysis-activation of Bulgarian lignite from Chukurovo deposit at 923 K [7]. A 0.70–1.25 mm fraction was used for the study. The second sample (denoted as ACN) was a commercial product Norit GAC 1240.

2.1. Oxidation of the activated carbons

The initial carbons were oxidized with concentrated nitric acid, 30% hydrogen peroxide and moist air. In the first two cases 10 g of carbon were stirred with 100 ml of an oxidized agent (HNO_3 and H_2O_2). The time of oxidation was 14 days and 3 h, respectively. The reactions took place at room temperature. The oxidized carbon was washed with distilled water until attaining a constant pH value of the washing water then dried at 383 K for 8 h. The samples treated with HNO_3 were indicated as ACCh_N and ACN_N and these oxidized with H_2O_2-ACCh_P and ACN_P, respectively. The oxidation of the initial carbons with moist air proceeded at 573–583 K for 18 h with an air flow rate of 100 cm^3 min^{-1}. The concentration of water in the moist air was 12 g l^{-1}. The samples obtained were denoted as ACCh_MA and ACN_MA.

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2.2. Characterization of the active carbons

Characterization of the surface and the porous texture of the samples was carried out by adsorption of nitrogen using a conventional volumetric apparatus. Adsorption isotherms at 77.4 K were measured for samples after outgassing at 453 K for 15 h to a residual pressure of 1.10^{-4} Torr or less. They were used for determining the following parameters: the specific surface area A_{BET}; the external surface area A_{EXT} (from the V_a–n plots [8]); the total pore volume V_t (calculated from the nitrogen uptake at the relative pressure of 0.95); the micropore volume V_{MI} and the specific surface area of the mesopores A_{MES} (according to the t/F method); the mesopore volume V_{MES} (determined by subtracting the total micropore volume (W_0) from the total pore volume); the mean pore radius r_{P} (as the ratio of the double total volume and A_{BET}, assuming a cylindrical pore model); the supermicropore volume V_{SMI} as the difference between the W_0 and V_{MI}; the total micropore volume W_0 and the half-width of the distribution curve maximum (x_0), according to the Simplified equation [9]. The surface amount of oxygen groups of increasing acidity was determined by Boehm's method [10] of titration with solutions of increasing basicity (0.1 N $NaHCO_3$, Na_2CO_3 and NaOH). The point of zero charge (pH_{PZC}) is termed as the pH value required give net surface charge, was estimated by the mass titration method [11]. XPS were registered using an ESCALAB MkII (VG Scientific). The portion of the oxygen on the surface was determined by using photoelectron intensities estimated by the corresponding Scofield's [12] cross section.

2.3. Adsorption studies

Batch experiments were performed in a stirred system at 295 K. The experiments were carried out in plugged 50 ml Erlenmeyer flasks containing 0.25 g activated carbon and 25 ml NH_4OH solution. On reaching equilibrium the adsorbents were eliminated by filtering through a Millipore filter (0.2 μm). Initial and equilibrium concentrations of ammonium ions were determined by spectrophotometrically with a Berthelot reactive using a Spekol 11 apparatus.

Analytical grade reagents were used for the experiments. The working solutions containing different concentrations of NH_4^+ in the range 35–280 mg l^{-1} were prepared by stepwise dilution of the stock solutions.

3. Results and discussion

3.1. Characterization of the activated carbons

The most important texture and surface parameters of initial activated carbons and the modified adsorbents prepared on its basis by oxidation with HNO_3, H_2O_2 and moist air are presented in Table 1.

From the data presented in Table 1 it may be concluded that both initial activated carbons belong to the same mixed micro–mesoporous type but they are essentially different in surface area values and porous texture parameters. For instance, the A_{BET} value for ACN is about 3.8 times higher than A_{BET} for ACCh. Similarly, V_t for ACN is about 1.9 times higher and W_0 is five times higher than is the case of ACCh. Only the mesopore volume (V_{ME}) has close values with the two carbons. It is obvious that the HNO_3 treatment affects the surface area and porosity of the carbons to a greater extent, as it is observed by some researchers [4,5], irrespective of the fact that in this case the effects with the two initial carbons are opposite to each other. Thus, with ACCh the treatment with HNO_3 leads to an about 1.1-fold increase of A_{BET} and W_0, while V_{ME} exhibits a two-fold decrease. On the contrary, treatment of ACN with HNO_3 results in an about 1.1-fold decrease in A_{BET} and an approximately 1.2-fold increase of V_{ME}. In an analogical way x_0 grows in the case of ACCh and drops for ACN while r_p decreases with ACCh and increases, although negligibly, with ACN. The effects of the oxidation with H_2O_2 and moist air on the texture parameters of ACCh and ACN are similar. Nevertheless, it may be concluded that the treatment with the above oxidizing agents exercises a stronger effect on ACCh, which is more pronounced with respect to the surface values: A_{BET}, A_{MES} and A_{EXT}.

The strongest effect on chemical nature of the surface of ACCh is proved by the pH_{PZC} value for the samples obtained from ACCh than those from ACN, after oxidation with the same oxidizing agent (Table 1). The results from acid/base neutralization according to Boehm's procedure explain the decrease in pH_{PZC} values with the formation of a larger amount of acid oxygen-containing surface groups during oxidation of carbons with HNO_3 and H_2O_2 [13,14]. According to XPS in the case of samples derived on ACCh base the oxygen on the surfaces is more in amount as compared to the same on the surface of samples derived on ACN base.

3.2. Adsorption properties

The optimum time to establish adsorption equilibrium between activated carbons and the ammonium ions of different concentrations were determined experimentally and was found to be 2 h. The adsorption studies were performed taking into account these preliminary experiments.

The removal efficiencies for the investigated adsorbents as a function of initial concentrations solutions are presented on Fig. 1. When the ammonium concentration in the solution increases the removal efficiency decreases due to the saturation of the adsorbent. From experimental data obtained, some theoretical

Table 1
Texture and surface properties of the initial and modified oxidized carbons

Parameters	ACCh	ACCh_N	ACCh_P	ACCh_MA	ACN	ACN_N	ACN_P	ACN_MA
A_{BET} ($m^2\ g^{-1}$)	271	293	194	171	1040	967	983	1010
A_{MES} ($m^2\ g^{-1}$)	247	264	163	161	475	884	852	711
A_{EXT} ($m^2\ g^{-1}$)	64	87	56	39	559	279	238	550
V_t ($cm^3\ g^{-1}$)	0.375	0.248	0.188	0.237	0.704	0.661	0.658	0.675
W_0 ($cm^3\ g^{-1}$)	0.094	0.102	0.073	0.064	0.425	0.346	0.354	0.351
V_{MI} ($cm^3\ g^{-1}$)	0.007	0.060	0.012	0.003	0.253	0.02	0.041	0.115
V_{SMI} ($cm^3\ g^{-1}$)	0.087	0.096	0.061	0.061	0.172	0.326	0.313	0.236
V_{MES} ($cm^3\ g^{-1}$)	0.281	0.146	0.115	0.173	0.278	0.314	0.304	0.323
x_0 (nm)	0.76	0.90	1.08	1.02	0.82	0.79	0.70	0.69
r_p (nm)	2.61	1.62	1.87	2.16	1.29	1.34	1.32	1.31
Carboxyl groups $* 10^3$ (meq m^{-2})	1.11	2.60	2.89	0.88	0.21	0.06	0.10	0.50
Phenolic groups $* 10^3$ (meq m^{-2})	2.80	5.22	6.39	1.34	0.46	1.26	0.26	0.36
Lactone groups $* 10^3$ (meq m^{-2})	5.54	11.09	13.4	5.09	0.97	2.17	0.63	1.13
pH_{PZC}	4.5	2.7	4.0	4.2	6.6	4.2	5.4	5.1
O% (XPS)	5.2	9.3	8.8	5.4	4.3	7.8	4.5	5.3