Polish J. of Environ. Stud. Vol. 19, No. 3 (2010), 659-662

Short Communication

The Effect of Carbonization and Activation on NO_2 Sorptive Capacity of Adsorbents Obtained from Sewage Sludge

Robert Pietrzak*

Laboratory of Coal Chemistry and Technology, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

Received: 22 June 2009
Accepted: 4 January 2010

Abstract

The effect of the processes of carbonization and activation on adsorbents obtained from sewage sludge and evaluation of the sorption properties of such adsorbents towards NO_2 was studied. Carbonaceous adsorbents were obtained by carbonization of sludge at 600ºC for four different times (30, 60, 90 and 120 min.) followed by activation of the carbonisates by CO_2 at 800ºC for 60 min. Adsorption of NO_2 was carried out in dry air. It has been shown that by appropriate thermal and chemical treatment of sludge, mesoporous adsorbents can be obtained that are capable of NO_2 removal. The activation of the carbonisates with CO_2 was found to substantially improve their sorption properties. The best NO_2 sorption capacity from among the samples obtained by carbonization at 600ºC or by carbonization at 600ºC followed by activation by CO_2 at 800ºC was obtained for the samples carbonised for 90 minutes.

Keywords: sewage sludge, carbonization, CO_2 activation, NO_2 adsorption

Introduction

Nitrogen oxides, among the most dangerous air pollutants, are known to contribute to the greenhouse effect, acid rains, photochemical smog, and enlargement of the ozone hole [1]. Growing pollution of the natural environment has stimulated the search for new raw products and new technologies for production of highly effective and cheap adsorbents for removal of pollutants from the gas phase. From the economical and ecological points of view, very promising is the use of waste products such as sawdust, fruit stones, fruit shells, straw or sludge [2-5]. The use of waste products for production of adsorbents can provide interesting and cheap alternatives to the hitherto used adsorbing materials and at the same time be an interesting method of waste product utilization.

*e-mail: pietrob@amu.edu.pl

One of the waste products that can be used as a precursor of adsorbents of specific sorption properties is sludge. It is the solid waste product obtained at wastewater and sewage treatment plants. Sludge has exceptional physico-chemical properties that result from its diverse chemical composition. This diversity determines its use, the character, and results of the processes of its treatment. Of particular importance is the content of metals. After treatment, sludge can be converted into mesoporous materials that can be effective adsorbents of metals, organic dyes, and phenol from the liquid phase [6-8], and sulphur compounds from the gas phase [9]. A relatively new application of sludge is that of a precursor of adsorbents of NO_2. So far the NO_2 sorption capacity of such adsorbents has been studied at the stage of carbonisates [5, 10].

The main aim of this study was to establish the effects of the processes of carbonization and activation on obtaining adsorbents from sewage sludge and evaluation of the sorption properties of such adsorbents toward NO_2.

Table 1. NO_2 breakthrough capacities and surface pH values for the initial and exhausted samples.

Sample	NO_2 breakthrough capacity		pH	
	mg/g of ads	mg/cm^3 of ads	initial	exhausted
SC-30-600-D	2.96	1.93	9.28	8.47
SC-60-600-D	2.73	1.67	9.52	8.83
SC-90-600-D	5.92	3.27	9.62	8.59
SC-120-600-D	3.41	1.55	9.47	8.90
SC-30-600-A-D	10.74	5.82	10.11	8.76
SC-60-600-A-D	7.74	4.04	9.54	8.47
SC-90-600-A-D	11.44	6.18	9.93	8.45
SC-120-600-A-D	10.85	6.00	9.77	8.61

Experimental Procedures

The initial material used in this work was sewage sludge (S) from the Central Wastewater Treatment Plant in Koziegłowy, near Poznań. Adsorbents were prepared via carbonization (C) of dry sludge (1-2 mm particle size) at 600ºC performed for 30, 60, 90 and 120 min., followed by activation (A) of the carbonisates by CO_2 at 800ºC for 60 min. The samples obtained are labelled as SC-X-Y and SC-X-Y-A, where X stands for the holding time of carbonization and Y is the temperature of carbonization.

The evaluation of NO_2 sorption capacity was carried out according to the procedures described in [11] with some modifications. The samples were packed into a glass column (length 300 mm, internal diameter 9 mm, bed volume between 3 cm^3). Dry air ("D") with 0.1% of NO_2 was passed through the column with the adsorbent at 450 ml/min for NO_2. The breakthrough of NO_2 was monitored using Q-RAE PLUS PGM-2000/2020 with an electrochemical sensor.

The pH of samples was measured using the following procedure: a portion of 0.4 g of the sample of dry sample powder was added to 20 ml of distilled water and the suspension was stirred overnight to reach equilibrium. Then pH of the suspension was measured.

Characterization of the pore structure of activated carbons was performed on the ground of low-temperature nitrogen adsorption-desorption isotherms measured on a sorptometer ASAP 2010 (Micrometrics Instrument Corp. USA), following BET and BJH techniques.

The surface oxide functional groups were determined by the Boehm method [12].

Results and Discussion

The NO_2 breakthrough capacity values determined for all carbonisates and activates obtained from them are collected in Table 1. According to these results, the highest NO_2 adsorption capacity was found for sample SC-90-600, which had the most basic character of the surface prior to adsorption. The other carbonisates are much poorer adsorbents. Although these samples do not have substantially different sorption properties, those carbonized for 30 or 60 min. have smaller NO_2 breakthrough capacity than the sample carbonized for 120 min. Analysis of the sorption capacity values of the carbonisates has shown that the carbonization time of 90 min. is optimum for the process and permits getting adsorbent of the highest sorption capacity. Activation of the carbonisates significantly improves their NO_2 sorption abilities. According to the results presented in Table 1, activation gives a significant increase in the sorption capacity, expressed either in mg/g or in mg/cm^3. The highest NO_2 breakthrough capacity was obtained for sample SC-90-600-A produced from the carbonisate of the best sorption abilities, while the lowest – for sample SC-60-600-A produced from the carbonisate of the poorest sorption abilities. The other two activates (SC-30-600-A, SC-120-600-A) have similar values of sorption capacity. Comparison of the surface pH values of the carbonisates and activates shows that adsorption for each of them leads to increased surface acidity. Most probably it is caused by the reactions of metal oxides or hydroxides formed on the surface of the adsorbents as a result of decomposition of salts, originally contained in the sludge, with NO_2 and NO formed by reduction of NO_2 on carbonaceous materials [5].

Structural parameters of all samples measured before and after NO_2 adsorption are given in Table 2. According to these data, carbonization of sludge at 600ºC permits getting mesoporous adsorbents of small surface area and very small total pore volume. Sample SC-90-600 has the greatest surface area and pore volume, while sample SC-60-600 has the smallest surface area and pore volume. These are the same samples that show the best and the poorest NO_2 sorption capacities (Table 1). This correlation means that the porous structure has significant effect on the NO_2 sorption capacity of the samples studied. Of particular significance for this process must have been micropores as, according to Table 2, their surface and volume have much decreased after NO_2 adsorption (a great decrease in

Table 2. Structural parameters and acid-base properties for initial and exhausted samples.

Sample	Surface area [m^2/g]		Total pore volume [cm^3/g]	V_{mic}/V_t	surface oxides groups [mmol/g]		
	Total (BET)	Micropore area			Acidic	Basic	Total
SC-30-600	44	29	0.054	0.24	0.70	3.78	4.48
SC-60-600	37	23	0.050	0.20	0.57	3.99	4.56
SC-90-600	48	31	0.061	0.23	0.80	4.47	5.27
SC-120-600	40	24	0.052	0.21	0.57	4.01	4.58
SC-30-600-D	15	4	0.031	0.06	1.04	4.44	5.48
SC-60-600-D	16	5	0.032	0.06	0.90	4.33	5.23
SC-90-600-D	15	6	0.037	0.05	2.24	5.27	7.51
SC-120-600-D	14	4	0.029	0.07	0.81	4.22	5.03
SC-30-600-A	116	83	0.108	0.44	0.32	4.85	5.17
SC-60-600-A	103	74	0.101	0.40	0.12	4.87	4.99
SC-90-600-A	184	134	0.174	0.42	0.17	4.82	4.99
SC-120-600-A	120	84	0.116	0.40	0.10	4.90	5.00
SC-30-600-A-D	36	12	0.059	0.10	0.72	3.86	4.58
SC-60-600-A-D	42	15	0.063	0.12	0.62	4.15	4.77
SC-90-600-A-D	35	12	0.080	0.11	0.72	3.89	4.61
SC-120-600-A-D	38	13	0.064	0.10	0.64	3.94	4.58

V_{mic}/V_t), which means that micropores were involved in the process of NO_2 sorption. After the process of adsorption the specific surface area also decreased, which indicates the presence of products of the chemical reactions taking place on the sorbent surface. Activation of the carbonisates by CO_2 significantly improves their structural properties. As follows from the data, similarly for the carbonisates and the activates, the best structural parameters and the greatest surface area were found for the sample of the best sorption abilities SC-90-600-A. After adsorption the structural parameters of the activates are significantly deteriorated.

For all samples studied, the content of the surface oxygen functional groups (acidic and basic) was estimated using the Boehm method [10] (Table 2). The carbonisates have basic surface character. The greatest content of the basic and acidic oxygen functional groups was determined for sample S-90-600. After NO_2 adsorption the content of the basic and acidic oxygen functional groups increases irrespective of the duration of carbonization. Activation of the carbonised samples leads to a decrease in the content of acidic oxygen functional groups and an increase in the content of basic ones. Analysis of the content of oxygen groups on the surface of the activates after NO_2 adsorption shows that the content of acidic groups increases, while that of basic groups decreases, which is consistent with the decrease in pH after adsorption (Table 1). The decrease in pH after adsorption is probably a consequence of the formation of relevant nitrates.

Conclusions

The above-discussed results have shown that by appropriate thermal and chemical treatment of sludge, mesoporous adsorbents can be obtained that are capable of NO_2 removal. From among the samples obtained by carbonization at 600ºC or by carbonization at 600ºC followed by activation by CO_2 at 800ºC, the best NO_2 sorption abilities had the adsorbents carbonized for 90 minutes. The activation of the carbonisates with CO_2 was found to substantially improve their sorption properties and lead to a decrease in the content of acidic oxygen functional groups and an increase in basic ones.

Acknowledgements

This work was supported by The Polish Ministry of Science and Higher Education project No. N N204 056235.

The work was presented at the Fuels-Energy-Environmental Protection Conference in 2009.

References

1. MANAHAN S.E. Environmental Chemistry. 7th ed. CRC Press LLC, pp. 405-430, **2000**.
2. IOANNIDOU O., ZABANIOTOU A. Agricultural residues as precursors for activated carbon production - A review. Renew. Sust. Energ. Rev. **11**, 1966, **2007**.

3. KAZEMIPOUR M., ANSARI M., TAJROBEHKAR S., MAJDZADEH M., KERMANI H.R. Removal of lead, cadmium, zinc, and copper from industrial wastewater by carbon developed from walnut, hazelnut, almond, pistachio shell, and apricot stone. J. Hazard. Mater. **150**, 322, **2008**.
4. INBARAJ B.S., SULOCHANA N. Mercury adsorption on a carbon sorbent derived from fruit shell of *Terminalia catappa*. J. Hazard. Mater. **133**, 283, **2006**.
5. PIETRZAK R., BANDOSZ T.J. Reactive adsorption of NO_2 at dry conditions on sewage sludge-derived materials. Environ. Sci. Technol. **41**, 7516, **2007**.
6. ROZADA F., OTERO M., MORAN A., GARCIA A.I. Adsorption of heavy metals onto sewage sludge-derived materials. Bioresource Techno. **99**, 6332, **2008**.
7. RIO S., FAUR-BRASQUET C., LE COQ L., LE CLOIREC P. Structure characterization and adsorption properties of pyrolyzed sewage sludge. Environ. Sci. Technol. **39**, 4249, **2005**.
8. OTERO M., ROZADA F., CALVO L.F., GARCIA A.I., MORAN A. Elimination of organic water pollutants using adsorbents obtained from sewage sludge. Dyes Pigments **57**, 55, **2003**.
9. BAGREEV A., BASHKOVAB S., LOCKE D.C., BANDOSZ T.J. Sewage sludge-derived materials as efficient adsorbents for removal of hydrogen sulfide. Environ. Sci. Technol. **35**, 1537, **2001**.
10. PIETRZAK R., BANDOSZ T.J. Interaction of NO_2 with sewage sludge based composite adsorbents. J. Hazard. Mater. **154**, 946, **2008**.
11. PIETRZAK R., BANDOSZ T.J. Activated carbons modified with sewage sludge derived phase and their application in the process of NO_2 removal. Carbon **45**, 2537, **2007**.
12. BOEHM H.P. Some aspects of the surface chemistry of carbon blacks and other carbons. Carbon **32**, 759, **1994**.