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Carbonaceous Materials Obtained from Sewage Sludge for NO_2 Removal under Wet Conditions at Room Temperature

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The effect of the processes of carbonisation and activation on adsorbents obtained from sewage sludge and their sorption properties towards NO_2 were studied. Carbonaceous adsorbents were obtained by carbonisation of sewage sludge at 600 °C for four different times 30, 60, 90 and 120 min followed by activation of the carbonisates by CO_2 at 800 °C for 60 min. Adsorption of NO_2 was carried out in wet air. It has been shown that by appropriate thermal and chemical treatment of sludge, mesoporous adsorbents capable of NO_2 removal can be obtained. The sorption abilities of the carbonised and activated samples to adsorb NO_2 have been shown to increase with increased time of carbonisation and reach maximum for the carbonisation maintained for 90 min. Further increase in this time causes a decrease in the adsorption abilities of the samples. The sorption properties of the carbonisates have been proved to be determined by the chemical character of the surface, while those of the activated samples — by the porous structure.

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1. Introduction

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, much promising is the use of waste products. One of such materials successfully applied in environmental applications is sewage sludge [1, 2], although its effective use requires some investigation because of its specific surface properties. It is a product obtained in the process of waste treatment at municipal or industrial wastewater treatment plants. Its specific physico-chemical properties follow from the diversity of its chemical composition determining the course of the treatment processes and the properties of the final products.

The search for possible utilisation of sewage sludge has shown that it can be used as a addition to construction materials. Lin and Weng [3] obtained bricks from a mixture of sewage sludge and clay. They have reported that a good quality product can be obtained as a result of addition of 20 to 40 wt% of the sludge to clay and burning of the mixture at 1000 °C. Khaja [4] found that replacement of 10% of cement with ashes in concrete improves its mechanical strength. Chen and Lin [5] proved that sewage sludge incinerated and cement mixed at the ratio of 4:1 can improve the flexibility of clay. This composite filler acts as a stabiliser improving the properties of construction materials. Merino et al. [6] applied the substance left after burning of sewage sludge for production of ceramic products. They have shown that the products obtained after thermal treatment of sewage sludge with addition of 25% of clayey minerals or powdered smooth glass have the best properties.

The products obtained as a result of pyrolysis of sewage sludge and subjected to thermal treatment have been proved to be effective adsorbents of metals, organic dyes and phenols from the liquid phase [7–9]. This ability is a consequence of chemical diversity of the carbonisate surface and the minerals it contains and which are engaged in ion exchange. Moreover, the mesoporous character of the materials is favourable for adsorption of large molecules. According to literature data [10, 11] pyrolysis of sewage sludge is also promising for getting materials for adsorption of H_2S and SO_2.

The sorption abilities of sewage sludge have been found to improve as a result of activation. The materials activated by steam were studied by Rio et al. [12] who reported that the adsorption properties of the activated sewage sludge towards Cu^{2+}, phenol and organic dyes from water solutions were better than those of the commercial adsorbates. Jindarom et al. [13] compared the adsorption abilities of carbonisates obtained in the nitrogen atmosphere and the products of direct activation of sewage sludge by carbon dioxide towards organic dyes to find that although all carbonisates and activates had mesoporous surface, the activates were more effective adsorbents of organic dyes because of the more basic character of their surface.

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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 [1, 2]. The study was undertaken to obtain carbonaceous adsorbents by carbonisation and activation of sewage sludge to check the effect of the contact duration and to characterise their sorption performance towards NO_2. Performance of the adsorbents obtained was evaluated in dynamic conditions at room temperature in wet conditions.

2. Experimental details

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 600 °C performed for 30, 60, 90 and 120 min, followed by activation (A) of the carbonisates by CO_2 at 800 °C 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 [14] with some modifications. The samples were packed into a glass column (length 300 mm, internal diameter 9 mm, bed volume between 3 cm^3). Wet (70% humidity) air ("W") 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 electrochemical sensor. The tests were stopped at the breakthrough concentration of 20 ppm. The interaction capacities of each sorbent in terms of milligram of toxic gases per gram of adsorbent were calculated by integration of the area above the breakthrough curves, and from the NO_2 concentration in the inlet gas, flow rate, breakthrough time, and mass of sorbent. To check the NO_2 reduction, the concentration of NO was also monitored till 240 ppm (electrochemical sensor limit).

The pH of samples was measured using the following procedure: a portion of 0.4 g 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 was performed on the basis of low-temperature (77 K) nitrogen adsorption-desorption isotherms measured on a sorptometer ASAP 2010 (Micrometrics Instrument Corp. USA). Before the isotherm measurements, samples were outgassed at 120 °C for 10 h. Surface area and pore size distribution were calculated by the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Harenda (BJH) methods, respectively. Total pore volume and average pore diameter were determined as well. Micropore volume and micropore area were calculated using *t*-plot method.

The surface oxide functional groups were determined by the Boehm method [15].

3. Results and discussion

Analysis of the chemical composition of sewage sludge performed at the Water Analysis Laboratory at the AQUANET in Poznań is presented in Table I. The initial sewage sludge besides carbon contains significant amounts of inorganic matter like e.g. chlorides, sulphates, fluorides, along with some oxides such as aluminium, potassium and sodium ones.

TABLE I

Chemical composition of sewage sludge (Water Analysis Laboratory at the AQUANET in Poznań).

Element	Content in dry matter
DOC*	5240 mg/kg
Zn	26 mg/kg
Ba	16 mg/kg
Cu	11 mg/kg
Pb	6 mg/kg
Cr	3.7 mg/kg
Ni	3.2 mg/kg
Se	0.6 mg/kg
Mo	0.5 mg/kg
Mn	0.44 mg/g
As, Cd, Co, Sb, Tl, V	minute quantities
$[Cl^-]$	740 mg/kg
$[SO_4^{2-}]$	330 mg/kg
$[F^-]$	15 mg/kg
Al (as Al_2O_3)	15 mg/g
K (as K_2O)	3.4 mg/g
Na (as Na_2O)	1.6 mg/g

*dissolved organic carbon

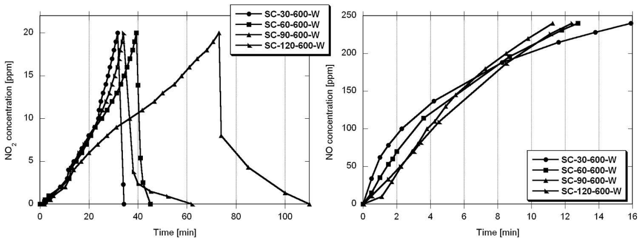

Fig. 1. NO_2 breakthrough curves and NO concentration curves for carbonisates obtained.

Table II presents the parameters and yields of products obtained in the processes of carbonisation and activation. The process of raw sewage sludge carbonisation at 600 °C gives the carbonisate with almost 50% yield, which is most probably related to decomposition of the salts originally contained in the sewage sludge upon pyrolysis (mainly sulphates of Zn, Cu, Ni, Al, Mn) leading

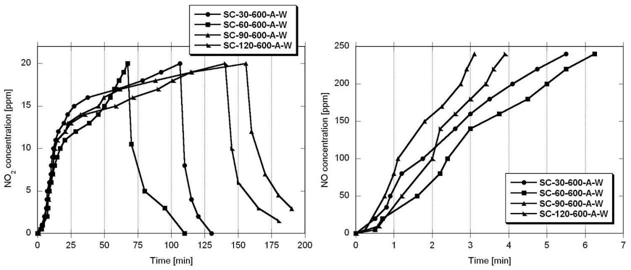

Fig. 2. NO_2 breakthrough curves and NO concentration curves for active carbons obtained.

to formation of oxides or hydroxides. Further activation of the carbonisates gives adsorbents with the yield up to 90%. This possibility is related to the high temperature of activation leading to further carbonisation of the material and further destruction of inorganic compounds that remained after carbonisation, as it is known that the majority of salts decompose above 600 ℃. Analysis of the results reveals a tendency of the yield of the carbonisation products to decrease (although slightly) with increasing time of the process, while the yield of the activation process increases with the time of this process. However, these changes are so small that it can be concluded that the time of the processes has insignificant effect on the yields of their products.

All the samples were tested for the NO_2 adsorption in wet conditions (70% humidity). The NO_2 breakthrough curves obtained for all samples are presented in Figs. 1 and 2, showing also the NO concentration curves, as nitrogen monoxide is known to be the product of surface reduction of NO_2, on carbonaceous adsorbents [16]. The shapes of the NO_2 breakthrough curves obtained for the carbonisates samples indicate that the samples maintained for 90 min (SC–90–600–W) show the best performance as NO_2 adsorbents. The shapes obtained for the other samples are very similar and show that these samples are worse adsorbents of NO_2. The NO emission is high for the all carbonisates obtained in this work, which indicates a high reduction potential of the surface or low adsorption capacity for NO.

TABLE II

Samples notation, parameters and yields of products obtained in the processes of carbonisation (C) and activation (A).

Sample	Time [min]		Temperature [℃]		Yield [%]	
	C	A	C	A	C	A
S–30–600–A	30	60	600	800	49.5	88.7
S–60–600–A	60	60	600	800	49.3	88.8
S–90–600–A	90	60	600	800	48.8	89.8
S–120–600–A	120	60	600	800	48.5	89.7

TABLE III

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–W	4.61	2.99	9.24	8.09
SC–60–600–W	5.13	3.48	9.47	8.07
SC–90–600–W	7.67	4.49	9.56	7.55
SC–120–600–W	4.93	3.15	9.40	8.09
SC–30–600–A–W	6.84	3.91	10.14	7.90
SC–60–600–A–W	7.90	4.29	9.58	7.75
SC–90–600–A–W	9.55	5.31	9.98	6.81
SC–120–600–A–W	8.57	4.79	9.83	7.34

The shape of the NO_2 breakthrough curves recorded for the activated carbonisates (Fig. 2) is completely different (Fig. 1). It is most probably related to the surface chemistry of the sample obtained by activation. These

TABLE IV

Structural parameters for initial and exhausted samples.

Sample	Surface area [m^2/g]		Total pore volume [cm^3/g]	V_{mic}/V_t
	Total (BET)	Micropore area		
SC–30–600	44	29	0.054	0.24
SC–60–600	37	23	0.050	0.20
SC–90–600	48	31	0.061	0.23
SC–120–600	40	24	0.052	0.21
SC–30–600–W	13	3	0.035	0.03
SC–60–600–W	13	4	0.036	0.06
SC–90–600–W	12	2	0.031	0.03
SC–120–600–W	12	3	0.035	0.03
SC–30–600–A	116	83	0.108	0.44
SC–60–600–A	103	74	0.101	0.40
SC–90–600–A	178	132	0.171	0.42
SC–120–600–A	120	84	0.116	0.40
SC–30–600–A–W	32	8	0.055	0.08
SC–60–600–A–W	38	11	0.059	0.10
SC–90–600–A–W	31	8	0.076	0.09
SC–120–600–A–W	34	9	0.060	0.08

chemical surface properties also influence the NO emission. The NO emission is very high for all samples, however in comparison with the NO emission of carbonisates (Fig. 1) for the activated samples the maximum concentration of NO in the outlet gas is reached over twice quicker even though the process of NO_2 adsorption proceeds considerably longer. On the basis of the all shapes of the NO_2 desorption curves (Figs. 1 and 2) it can be concluded that some NO_2 is weakly adsorbed and it is detected in the outlet gas when the source of NO_2 is disconnected.

The calculated breakthrough capacities and pH values for the all initial and exhausted samples are collected in Table III.

From among the carbonised samples, the largest breakthrough capacity expressed in mg/g as well as in mg/cm^3 has been found for those maintained for 90 min at 600 °C (SC–90–600). These samples were also characterised by the highest initial pH. The other samples obtained by carbonisation show similar breakthrough capacity. Analysis of the all NO_2 breakthrough capacities of the samples obtained by the activation of carbonisates shows that this process improves sorption properties. From among the activated samples the best breakthrough capacity was found in that carbonised for 90 min (SC–90–600–A).

Analysis of our results has shown that the sorption capacities of the carbonised and activated samples towards NO_2 adsorption increase with increasing time of carbonisation, reaching a maximum for the samples carbonised for 90 min (SC–90–600 and SC–90–600–A). Further increase in the time of carbonisation leads to a decrease in the sorption abilities of the adsorbents. On the surface of all samples obtained from carbonised sewage sludge, NO_2 is converted to NO and both compounds are adsorbed. These processes are related to the chemical properties of the material determined to a great degree by the presence of metal oxides. These metal oxides either come from the initial raw sewage sludge or are produced as a result of salts decomposition upon carbonisation. The presence of oxides was favourable for NO_2 removal as they can react with NO_2 leading to formation of nitrates(III) and (V) and NO. As follows from our data, the carbonisation time of 90 min seems to be optimal, that is ensures the greatest amounts of oxides formed from decomposition of the relevant salts. When this time is increased, the oxides are decomposed and the sorptive capacities decrease. In the wet conditions applied, the reaction of water molecules with NO_2 and the sample surfaces must have occurred. The reaction between H_2O and NO_2 led to formation of nitric(III) and (V) acids that would further react with the oxides or hydroxides present on the adsorbent surface. The liberation of acids in the process of adsorption is confirmed by the much reduced pH of the samples after adsorption. According to [17] the acids reacted also with the carbon phase of the adsorbents leading to the oxidation of their surface, which also affected the process of adsorption.

Structural parameters of all samples measured before and after NO_2 adsorption are given in Table IV. According to these data, carbonisation of sludge at 600 °C 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. Activation of the carbonisates by CO_2 significantly improves their structural properties. As follows from the data, similarly as for the carbonisates also for 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. This observation indicates that besides the chemical properties of the surface also the porous structure has substantial influence on the sorption abilities of the samples towards NO_2. After adsorption the structural parameters of the all samples are significantly deteriorated, which implies the presence of the products of chemical reactions on the surface of the sorbents. Besides the above-mentioned reactions, also those between the acids and carbonates could take place [18]. The outcome of all these reactions was the formation of a greater amount of nitrates that probably blocked the adsorbent pores. Analysis of the data collected in Table IV suggests also the influence of micropores. Their area and volume (in particular $V_{\mathrm{mic}}/V_{\mathrm{t}}$) significantly decreased after NO_2 adsorption, which means that micropores were engaged in NO_2 adsorption.

TABLE V

Acid-base properties for initial and exhausted samples.

Sample	Surface oxides groups [mmol/g]		
	Total	Acidic	Basic
SC–30–600	4.48	0.70	3.78
SC–60–600	4.56	0.57	3.99
SC–90–600	5.27	0.80	4.47
SC–120–600	4.58	0.57	4.01
SC–30–600–W	4.26	0.58	3.68
SC–60–600–W	4.09	0.50	3.59
SC–90–600–W	4.23	0.69	3.54
SC–120–600–W	4.12	0.51	3.61
SC–30–600–A	5.17	0.32	4.85
SC–60–600–A	4.91	0.18	4.85
SC–90–600–A	4.87	0.15	4.72
SC–120–600–A	5.00	0.10	4.90
SC–30–600–A–W	4.27	0.71	3.56
SC–60–600–A–W	4.21	0.52	3.69
SC–90–600–A–W	4.15	0.68	3.47
SC–120–600–A–W	3.98	0.64	3.34

For all samples studied, the content of the surface oxygen functional groups (acidic and basic) was estimated by the Boehm method [15], the values are collected in Table V. The results prove that both carbonisates and activates have surfaces of basic character. It should be mentioned that the process of activation leads to a decrease in the content of the acidic oxygen groups and increase in that of the basic oxygen groups relative to their levels in the initial carbonisates. From among the carbonisates the greatest content of basic and acidic oxygen groups was found in S–90–600, showing the best adsorption properties (Table III). From among the activates, the sample characterised by the best sorption performance (SC–90–600–A) had the lowest total content of oxygen groups and the lowest content of basic oxygen groups. These results indicate that the sorption capacity of carbonisates is determined by the chemical character of the surface, while that of activates — by the porous structure. After adsorption the content of the acidic and basic groups on the surface of the carbonisates decreases. The observation for the activates shows that after adsorption the content of basic oxygen groups decreases, while that of acidic groups significantly increases. This fact is reflected by a greater reduction of pH after adsorption of NO_2 by the activated samples, most probably caused by formation of respective nitrates.

4. Conclusions

The above-discussed results have shown that by appropriate thermal and chemical treatment of sewage sludge, it is possible to obtain mesoporous adsorbents capable of NO_2 removal under wet conditions. From among the samples obtained by carbonisation at 600 °C or by carbonisation at 600 °C followed by activation by CO_2 at 800 °C, the best NO_2 sorption abilities had the adsorbents carbonised for 90 min. Further increase in the time of carbonisation leads to a decrease in the sorption properties of the samples obtained towards NO_2. The activation of the carbonisates with CO_2 was found to substantially improve their sorption properties. The surfaces of all adsorbents obtained had definitely basic character. The process of activation caused a reduction in the content of the acidic oxygen groups and an increase in the content of the basic oxygen groups, relative to their contents in the initial carbonisates. After using the carbonisates for adsorption, the contents of both acidic and basic oxygen groups decrease. The sorption properties of carbonisates have been found to be determined by the chemical character of the surface, while those of the activates — by the porous structure of their surface.

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