Iodinated Carbon Material as a Chemisorbent for Mercury

B. M. SHAVINSKIY, L. M. LEVCHENKO, V. N. MITKIN, A. A. GALITSKIY and T. S. GOLOVIZINA

Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 3, Novosibirsk 630090 (Russia)

E-mail: luda@che.nsk.su

(Received June 5, 2008; revised June, 27, 2008)

Abstract

The features of application of porous materials impregnated with chemical reagents for obtaining high activity sorbents are considered. Processes of iodine absorption from its aqueous solution by a "Technosorb" carbon material as well as iodine desorption were studied. It has been demonstrated that the mentioned chemisorbent is efficient for mercury absorption from its aqueous solutions of high concentration.

Key words: iodinated carbon material, chemisorbents, mercury extraction, Raman spectroscopy

INTRODUCTION

It is well known that porous carbon materials are widely used as adsorbents. Various carbon containing waste products, peat, wood, shell of nuts, polymers, petrochemical and by-product coke pitches, *etc.* are commonly used as source components to obtain the materials. The variety of source materials determines various textural characteristics and sorption properties of the sorbents [1–3]. Among various carbon materials a Technosorb synthetic carbon material (further referred as CM) produced at the Institute of Hydrocarbons Processing, SB RAS (Omsk) is of particular interest [4–8].

A considerable contribution to the development of the modern technology for the CM obtaining and studying its properties has been made by the researchers of the Boreskov Institute of Catalysis, SB RAS (Novosibirsk). The Technosorb CM is obtained *via* depositing onto granulated soot the products of butane-propane mixture paralysis at 800–900 °C in a fluidized bed reactor with the subsequent activation by CO_2 or water vapour [7, 8]. The technology of CM synthesis allows one to control changing its textural characteristics, to vary the size and the total volume pores wherewith the CM could be considered as rather promising material in order to use it as a matrix for obtaining sorbents of various purposes.

One of the methods for the activation of carbon surface consists in introducing an appropriate chemical substance into the pores of a carrier, whereby the adsorbent is transformed into a chemisorbent becoming highly active. However, this method is efficient only in the event that the reagent introduced into the pores of the carrier is to an insignificant extent washed off by an eluent during the sorption.

The authors of [9-11] demonstrated that with the help of the chemical modifying of a carbon support one could obtain an efficient chemisorbent, in particular, for the extraction of mercury from technological lithium-containing solutions. For the first time the expediency of impregnated carbon application has been shown by the author of [12, 13] in accomplishing the task for the development of a respirator for the workers of mercury manufacture. He has investigated the saturation of coal with iodine and concluded that "... activated charcoal is absolutely unusable as an adsorbent of mercury vapour in airflow. The activated charcoal with iodine adsorbed is a good absorber. Iodine is extraordinarily strongly bound by coal". Later the conclusions about strong binding of iodine by coal and its high capacity of the latter with respect to iodine have found an experimental verification in the implementation of the technology for industrial scale iodine obtaining [14]. According to this technology, iodine is concentrated from dilute acidic aqueous solutions by means of the sorption on activated charcoal, then it is desorbed with a small amount of hot alkali solution, and then, with adding an acid, it is oxidized again to yield molecular iodine, *etc*.

The absorption of iodine by coal is often used as a characteristic for the sorption ability of the latter [15]. The authors of [16–19] demonstrated that iodine sorption on coal proceeds slowly being accompanied by the formation of a polymolecular adsorption layer. The sorption of iodine was studied using aqueous solutions containing KI. According to the opinion of the authors of [20], this process is described by Langmuir equation and proceeds almost without chemisorption.

At the same time the process of iodine sorption on coals from aqueous solutions of iodine itself (with no iodide added) remains almost unstudied as it was noted in [21]. To all appearance it is connected with a low and slow solubility of iodine in water as well as with a high absorption capacity of carbon materials with respect to iodine, which considerably complicates carrying out the studies.

The addition of iodide or (less often) alcohol "spoils" the experiment. The studies available from the literature are mainly devoted to the coal materials among those the Technosorb composite CM are favourably distinguished by better textural characteristics and an increased mechanical durability. In this connection the studies on the process of iodine absorption from its aqueous solutions with the subsequent mercury sorption on the CM obtained are of interest.

EXPERIMENTAL

For the experiments we have chosen a Technosorb-7 CM with the following characteristics: grain size ranging within 0.2-1.0 mm, the specific surface area amounting to (520 ± 80) m²/g, total volume of pores ranging within 0.7-1.1 cm³/g, the compression strength value being of 25-30 MPa, ash percentage being less

than 0.5 mass %. Due to the grain-size composition, the CM chosen can provide rather low hydraulic resistance of sorption columns.

The carbon material was washed out several times with distilled water via decantation until the visible pollution disappeared, then it was dried up under an infra-red lamp at the temperature of 140-150 °C and sifted through a corresponding mesh sieve. A 0.4-0.5 mm sized fraction was used in the experiments. A weighed sample of air-dry CM (6.5 g) was put into a column made from standard chemical titrating burette of 25 mL in volume capacity and 10 mm in internal diameter, being held with the help of a sieve made of glass-fibre fabric. The frame of the sieve was made of Teflon. A similar sieve was used for closing the CM from above. After loading the column the height of the CM layer prepared for operation amounted to 14.5 cm.

The process of CM saturation was carried out using the solution of iodine with the concentration of 254 mg/L. For the suppression of iodine hydrolysis the aqueous solution was acidified with sulfuric acid (1 mL of concentrated H_2SO_4 dissolved in 2 L of water) till obtaining the value of pH ~ 2. The solutions were passed through the column with the flow rate of 5–6 mL/min. After every 150 mL of the solution passed through the column, the solution absorption spectra was registered with the use of a Specord M40 spectrophotometer. The



Fig. 1. Iodine output curve from the column with the saturation of the carbon material. V is the volume of the solution passed through, C is output (final) concentration; initial iodine concentration being of 254 mg/L.



Fig. 2. Raman spectra for initial CM (1), for crystalline iodine powder (2) and for iodinated CM (3).

amount of iodide ion was calculated from the absorption band with the maximum at the wavelength of 226 nm, and that of molecular iodine was calculated basing on 204 and 400 nm absorption bands.

RESULTS AND DISCUSSION

It has been established that only iodide ion with almost constant concentration approximately equal to 1.6 mg/L is observed in eluates for 8.7 L of the iodine solution passed through the column. Further a spectral absorption band of iodine appeared, with iodine concentration rapidly increasing. The character of CM saturation with iodine is demonstrated in Fig. 1. The breakthrough of iodine into the eluate is observed after the content of iodine in CM reaching ~340 mg/g.

As the iodine concentration in eluate reached a value of 20 mg/L, the saturation of CM ceased and the process of its washing out of the column by pure solvent (acidified water)

TABLE 1

| Sorbent | Mass fraction, $\%$ | | | | |
|---------|---------------------|-----|-----|-----|--|
| | С | 0 | Ν | Н | |
| СМ | 93.9 | 5.0 | 0.6 | 0.5 | |
| OU-A | 92.5 | 4.8 | 0.2 | 2.5 | |
| OU-B | 92.2 | 5.5 | 0.3 | 2.0 | |

began. It has been established that the iodine washing out gradually increases grading into a stationary mode after the passing-through 0.9 L of the eluent. The concentration of iodine in the aliquots of the 2.7 L of eluent further sampled for every 150 mL of the eluent passed through the column is as high as 90 mg/L.

Figure 2 displays Raman spectra of the initial CM, iodinated CM and crystalline iodine. One can see that the peak of iodine in iodinated CM (160 cm^{-1}) is shifted by 18 cm^{-1} to the left from the peak of crystalline iodine. The insignificant shift and iodine washing-out indicate that there is a weak interaction between iodine and CM surface and, to all appearance, the formation of a clathrate-like compound occurring. In this connection one should note the fact that the peak of iodine at the wavenumber of 160 cm^{-1} is observes in the Raman spectrum of starch after its iodination, too. According to the elemental analysis data, CM contains up to 5%of oxygen (Table 1), which is in a good agreement with the known data for low-ash activated charcoal such as OU-A and OU-B [1].

Table 2 demonstrates the results of the determination of the content of COO^- groups in CM after the treatment by H_2O_2 solutions according to the method described in [22]. A weighed CM sample (1 g) was put in 100 mL of 0.1 M NaHCO₃ solution and held to age during 1 h, then the solution was filtered, an aliquot was taken and titrated with 0.1 M HCl solution. According to the titration results the content of carboxylic groups was calculated.

According to the authors of [23-28], the reaction of iodine hydrolysis

$$I_2 + H_2O \leftrightarrow H^+ + I^- + HIC$$

is characterized by the equilibrium constant value amounting to about 10^{-13} . At the same time, according to the results of [27], at 25 °C the equilibrium concentrations are $[H^+] = [I^-] =$

| TABLE 2 | | | | | |
|------------|------------------|--------|----|--------|----------|
| Content of | CO0 ⁻ | groups | in | carbon | material |

| Temperature, °C | Mass fraction, % | | |
|-----------------|------------------|------------------|--|
| | H_2O_2 | COO ⁻ | |
| 23 | 10 | 1.3 ± 0.1 | |
| 70 | 10 | 1.2 ± 0.1 | |
| 70 | 15 | 1.3 ± 0.1 | |

 $6.4 \cdot 10^{-6}$, $[I_2] = 0.0013$ mol/L. The concentration of the molecular iodine species is 200 times higher than the concentration of the ionic species. The acidifying of water causes the equilibrium to shift to the left so much that "in acidic solutions the hydrolysis of iodine cannot be detected using analytical methods" [29]. The concentration of hydrogen ions in the solutions under investigation preset in our experiments is almost an order of magnitude higher than the concentration of iodine, therefore iodide ion observed in eluates can be formed only due to the reduction of iodine by CM, the contribution of hydrolysis being negligibly small.

The authors of [30, 31] assumed that the process of iodine reduction by coal occurs, however at room temperature this reaction proceeds slowly, being activated with the increase in temperature up to 100 $^{\circ}$ C [29]. We have established that the reaction

 $C + I_2 + H_2O = 2HI + CO$

proceeds at room temperature, too, since the output of iodide ion from the column is registered in the absorption spectra at once.

The data of the eluate analysis indicate that the amount of iodide formed under CM saturation with iodine is much less as compared to the amount of the absorbed molecular iodine species. Hence, the amount of reduced iodine, *i.e.* the iodine washed out of the column could be neglected. In this case the calculated dynamic capacity of CM with respect to iodine (before the breakthrough) is equal to 340-350 mg/g.

As it was noted earlier, Raman spectra of iodinated starch and CM exhibit the peaks centred at the wavenumber of 160 cm^{-1} . The 18 cm^{-1} left shift of the spectral line with respect to the 178 cm⁻¹ centered peak inherent in crystalline iodine, is insignificant, which indicates the interaction between crystalline iodine and CM to be weak. To all appearance, in a similar manner as for starch, the compound of iodine with CM represents an inclusion complex, but rather weakly bound that. The data available allow one to assume only a certain clathrate-like form of the adsorption compound formed.

To all appearance, the retention of iodine in CM, as that in starch, is promoted by the presence of oxygen in the matrix, which oxygen plays the role of an electron donor. From the data presented in Table 1 it follows that 1 g of iodinated CM with 34 % content of iodine must contain about 80 mmol/L C, 1.4 mmol/L I_2 and 1.6 mmol/L O_2 . The comparable values for iodine and oxygen indicate that the scheme of iodine binding at the surface of CM through oxygen could be presented as it follows:

since it is rather unlikely that the considerable shift of iodine peak in the Raman spectrum can be caused only by the adsorption bond between iodine and carbon (see Fig. 2).

The value of iodine washout from CM (90 mg/L) determined in our experiments at the eluent flow rate amounting to 5-6 mL/min implies that about 30 mg of iodine would be washed out of CM during 1 h. It follows that when iodinated CM is used as an adsorbent the initial amount of iodine should be much more. It could be achieved with the use of columns high enough and of the CM with a high iodination level.

Owing to a high adsorption capacity of CM with respect to iodine, the bulk concentration of the latter within the sorbent layer is higher than 200 mg/cm³, which is 700 times higher than the concentration of the aqueous solution saturated with iodine. This fact allows one to use iodinated the CM for carrying out the sorption from the solutions with high concentration of the component under extraction, in particular mercury that exhibits a high chemical affinity with respect to iodine. When a consider-



Fig. 3. Hg(II) output curve for mercury nitrate solution (pH \sim 2) passing through the column with the iodinated CM. Initial mercury concentration being of 200 mg/L; for designations see Fig. 1.

| Sorbent | Mass fraction | Residual mercury content | Sorbent capacity, mg/g |
|---------|---------------|--------------------------|------------------------|
| | of iodine, % | in the solution, mg/L | |
| CM | 9.0 ± 0.5 | 18.0 ± 0.9 | 82.0±3.5 |
| PAN-HH | 8.8 ± 0.5 | 0.27 ± 0.02 | 99.7 ± 5.0 |
| PAN-HA | 9.0 ± 0.5 | 3.0 ± 0.2 | 97.0 ± 4.9 |
| PAN-CA | 8.2 ± 0.5 | 0.10 ± 0.01 | 99.9 ± 5.0 |
| | | | |

| TABLE 3 | | | |
|----------------|-------------|--------------------|--|
| Data on static | capacity of | iodinated sorbents | |

able height of the column is used, it is possible to reach high solution flow rate values, too. As opposed to the iodinated CM, the adsorption of mercury from aqueous solutions onto noniodinated CM does almost not occur.

Figure 3 shows the output curve for mercury resulting from passing the solution of mercury nitrate through the column packed with iodinated CM. The initial amount of iodine in CM amounts to 600 mg, the level of saturation with iodine is equal to 24 %, the flow rate of mercury solution (pH 2) through the column ranging within 4–5 mL/min. One can see that with the use of iodinated CM a very high level of mercury extraction of is attained: mercury concentration in 1 L of eluate determined by a "cold vapour" method using Yulia-2 device [32], is amounted to several thousandth fractions of a milligram per litre.

We have investigated the possibility of mercury absorption by other iodinated porous materials. The experiments were carried out under static conditions at a room temperature. The initial concentrations of $Hg(NO_3)_2$ solutions in all the experiments amounted to $(100\pm2) mg/L$, the value of pH ~ 2 due to HNO₃. The weighed samples of sorbents and the volumes of solutions amounted to (100 ± 2) mg and 100 mL, respectively. Are investigated iodinated polyacryl nitrile (PAN) fibers those were modified by hydrazine hydrate (PAN-HH), hydroxylamine (PAN-HA) and carbamide (PAN-CA) prior to the iodination.

The content of iodine in sorbents was calculated according to the amount of solution with known iodine concentration passed through a column with known amount of an air-dry sorbent. The sorbent taken from the column was used in the experiment. The content of iodine in the decolorized solution at the outlet from the column was registered using a Specord M 40 spectrophotometer. Solutions were agitated with the help of a magnetic stirrer, the contact time value for the phases amounted to 240 min. The residual content of mercury in the solution after the separation of the phases was determined according to the technique described in [32] (Table 3).

One can see that at the identical iodination level PAN exhibits a higher capacity with respect to mercury as compared to CM and a higher level of efficient iodine utilization.

TABLE 4

Results of determining the capacity of CM with various iodine content for Hg extraction from mercury nitrate solutions

| Initial mercury content, mg/L | Mass fraction of iodine, $\%$ | Residual mercury content in solution, mg/L | Capacity with respect to mercury, mg/g of sorbent |
|----------------------------------|-------------------------------|---|---|
| 200 | 2.0 ± 0.1 | 149.9 ± 1.5 | 25.3±1.3 |
| 200 | 5.0 ± 0.3 | 103.8 ± 3.8 | 52.0 ± 2.6 |
| 200 | 10.0 ± 0.6 | 51.8 ± 0.1 | 78.3 ± 3.5 |
| 200 | 15.0 ± 0.9 | 19.3 ± 0.02 | 92.9 ± 4.6 |
| 400 | 2.0 ± 0.1 | 346.8 ± 1.8 | 40.5 ± 2.0 |
| 400 | 5.0 ± 0.3 | 307.4 ± 0.9 | 57.8 ± 2.9 |
| 400 | 10.0 ± 0.6 | 253.6 ± 0.1 | 84.6 ± 4.2 |
| 400 | 15.0 ± 0.9 | 176.7 ± 0.5 | 118.9 ± 5.9 |

Table 4 demonstrates the data on the static capacity with respect to mercury. One can see that the CM capacity increases with the increase in the iodination level.

The absence of considerable mercury sorption by non-iodinated CM established in [9, 33] and the data presented in Table 4 indicate the chemisorption of mercury. The shape of adsorption isotherms for mercury [34] differs from the Langmuir type of isotherm being close to Freundlich adsorption isotherms. The authors of [35] reported on the development of a sorbent based on the activated coal for efficient Hg (II) extraction from water solutions, in this case the sorption process is described by the Freundlich adsorption isotherm. The chemical nature of mercury immobilization by the particles of ashes due to the formation of oxide compounds demonstrated basing on the isotherms of HgCl₂ sorption by ashes from the Karaganda coal combustion was mentioned also in [36].

The authors of [37] pay attention to the following important feature of mercury absorption by solid sorbents from smoke fumes with a high content of soot: X-ray spectra exhibit no evidence of the Hg-C chemical bond occurrence. It should be noted that the surface of a carbon matrix must be chemically modified for the absorption of mercury being efficient.

CONCLUSION

The CM impregnated with iodine exhibits a high level of absorption with respect to the molecular iodine species from an acidic aqueous solution of iodine. The iodine number amounts to 340–350 mg/g.

A weak binding between iodine and CM is observed with a hypothetical formation of a clathrate-like surface compound bound to the carbon matrix through C-O-J bonds.

The iodinated CM represents an efficient chemisorbent of mercury (II) from the solutions with high initial mercury concentrations.

REFERENCES

- 1 S. L. Glushankov, V. V. Konopleva, N. G. Lyubchenko, Ugli Aktivirovannye: Katalog, Cherkassy, 1983, p. 14.
- 2 T. G. Plachenov (Ed.), Uglerodnye Sorbenty i Ikh Primeneniye v Promyshlennosti, Nauka, Moscow, 1983.

- 3 V. V. Mukhin, A. V. Tarasov, V. N. Klushin, Aktivnye Ugli Rossii, in A. V. Tarasov (Ed.), Metallurgiya, Moscow, 2000.
- 4 V. Yu. Gavrilov, V. B. Fenelonov, G. V. Plaksin, Khim. Tv. Topliva, 2 (1990) 125.
- 5 N. S. Polyakov, V. F. Surovikin, *Izv. RAN. Ser. Khim.*, 8 (1993) 1377.
- 6 V. F. Surovikin, V. B. Fenelonov, G. V. Plaksin, Khim. Tv. Topliva, 3 (1995) 62.
- 7 V. B. Fenelonov, Poristy Uglerod, Izd-vo SO RAN, Novosibirsk, 2002.
- 8 V. B. Fenelonov, Vvedeniye v Fizicheskuyu Khimiyu Formirovaniya Supramolekulyarnoy Struktury Adsorbenta i Katalizatorov, Izd-vo SO RAN, Novosibirsk, 2002.
- 9 L. M. Levchenko, V. N. Mitkin, I. M. Oglezneva et al., Chem. Sust. Dev., 12, 6 (2004) 687.
- URL: <u>http://www.sibran.ru/English/csde.htm</u>
- 10 RU Pat. No. 2264856, 2005.
- 11 RU Pat No. 21726444, 2001.
- 12 V. A. Pyankov, Zh. Prikl. Khim., 8, 2 (1935) 238.
- 13 V. A. Pyankov, Ibid., 246.
- 14 V. I. Ksenzenko, D. S. Stasinevich, Khmiya i Tekhnologiya Broma, Yoda i Ikh Soyedineniy, Khimiya, Moscow, 1995.
- 15 C. M. Carson, L. B. Sebrell, Ind. Eng. Chem., 21 (1929) 911.
- 16 F. K. Shaenfield, Ibid., 27 (1935) 571.
- 17 W. R. Smith, F. S. Thornhill, R. R. Bray, Ibid., 33 (1941) 1303.
- 18 N. F. Ermolenko, Sbornik Trudov Instituta Khimii AN BSSR, Minsk, 1935, issue 1, p. 143.
- 19 N. F. Ermolenko, G. I. Taraykovskaya, I. M. Yakhnich, in G. L. Starobinets (Ed.), Sorbtsiya iz Rastvorov Vysokopolimerami i Uglyami (A Collection of Papers), Izd-vo BGU, Minsk, 1961, pp. 47–51.
- 20 J. W. Watson, D. Parkinson, Ind. Eng. Chem., 47 (1950) 108.
- 21 A. Sviontkovski, Adsorbtsiya i Adsorbenty (A Collection of Papers), Nauk. Dumka, Kiev, 1982, issue 10, pp. 20-24.
- 22 H. P. Boehm, Catalysis, Stereochemistry, and Mechanisms of Organic Reactions [Russian translation], Mir, Moscow, 1968, pp. 186-281.
- 23 V. G. Koloborodov, A. A. Sankov, A. V. Karnatsevich et al., Vopr. Atom. Nauki i Tekhn. Fiz. Rad. Povrezhd. i Rad. Materialoved., 6 (2003) 114.
- 24 F. Efraim, Neorganicheskaya Khimiya, in B. F. Berkengeim (Ed.), Goskhimtekhizdat, Leningrad, part 1, 1932, pp. 312-313.
- 25 H. Remy, Treatise on Inorganic Chemistry, Elsevier Publ. Co., Amsterdam, 1956.
- 26 B. V. Nekrasov, Osnovy Obshchey Khimii, Khimiya, Moscow, 1965, vol. 1, p. 280.
- 27 F. A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, John Wiley&Sons, Inc., NY etc., 1966, part 2, pp. 429-431.
- 28 V. I. Spitsyn, L. I. Martynenko, Neorganicheskaya Khimiya, Izd-vo MGU, Moscow, 1991, part 1, p. 63.
- 29 I. M. Kolthoff, V. A. Stenger, Ob'yemny Analiz, in Yu. Yu. Lurie (Ed.), Gos. Nauch.-Tekhn. Izd-vo Khim. Lit., Moscow-Leningrad, 1952, vol. 2, p. 339.
- 30 P. T. Danilchenko, M. I. Ravich, Zh. Rus. Fiz.-Khim. Ob-va, 1, 1 (1929) 123.
- 31 E.D. Zaverina, M.M. Dubinin, Zh. Fiz. Khim., 12, 4 (1938) 397.
- 32 Metodika Vypolneniya Izmereniy Massovoy Kontsentratsii Rtuti, v Prirodnykh i Ochishchennykh Stochnykh Vodakh Metodom Besplamennoy Atomno-Absorbtsionnoy Spektrometrii, PND F14.1.2.20-95. Min-vo

Okhrany Okr. Sredy i Prir. Resursov RF, Glavnoye Upravleniye Analiticheskogo Kontrolya i Metrologicheskogo Obespecheniya Prirodookhrannoy Deyatelnosti, PND F14.1.2.20-95, Moscow, 1995.

- 33 M. P. Tiunov, L. M. Levchenko, A. V. Ulanov et al., Mezhdunar. Konf. "Nanokhimiya. Novye Podkhody k Sozdaniyu Polimernykh Sistem s o Spetsificheskimi Svoystvami" (Proceedings), Tashkent, 2003, pp. 119–123.
- 34 B. M. Shavinskiy, L. M. Levchenko, V. N. Mitkin, *Khim. Ust. Razv.*, 14, 2 (2006) 181.
- 35 C. Namasivayam, K. Kadirvelu, Carbon, 37 (1999) 79.
- 36 M. A. Ilyushchenko, E. V. Lapshin, T. V. Tanton, A. Delebarre, Prom-st' Kazakhstana, 3 (2005) 60.
- 37 Ya. Yu. Yudovich, M. P. Ketris, Vestn. In-ta Geol. Komi NTs UrO RAN, 10 (2004) 6.