Chemistry for Sustainable Development **20** (2012) 497–501

UDC 67.014

Determining the Sorption Capacity of Modified Carbon Sorbents Using X-ray Fluorescence Analysis

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(Received February 20, 2012; revised May 28, 2012)

Abstract

Physicochemical properties inherent in chitosan-containing solutions as well as the sorption properties of carbon materials modified with chitosan were studied. It has been found that the composites obtained exhibit anion-exchange properties. The chitosan-containing materials have been shown to exhibit a sufficiently high sorption capacity, which makes them efficient as sorbents for the concentration and extraction of gold, and other heavy and radioactive metals in the future.

Key words: modified materials, chitosan, carbon material, sorption, gold, X-ray fluorescence analysis

INTRODUCTION

The world of ionites nowadays is large and manifold, whereas the ion exchange process quickly and comprehensively covers various fields of human activities. An increasing economic importance is obtained by ion exchange processes in connection with the introduction of closed technological schemes and comprehensive utilization of raw materials into industrial practice [1].

Earlier, the enterprises of the Rosatom State Nuclear Energy Corp. were provided by provide ion-exchange resins produced in Ukraine (Dniprodzerzhinsk) and in Russia (Omsk). For different reasons, almost all the manufacturers of ion exchange resins in Russia were closed, whereas Ukrainian companies appeared completely dependent on the external supply of raw materials, which immediately resulted in higher prices for the products. Within the last 15 years in Russia, two of the four companies producing ion-exchange resins have ceased their work. The remaining enterprises such as Tokem JSC (Kemerovo) and Ural-ChemPlast JSC (Nizhniy Tagil) are manufacturing outdated grades of resins, whereas the production volume is being steadily decreasing.

Thus, of importance is the development of scientific and technological base for the recreation of the Russian production of competitive sorbents demanded by nuclear power industry and gold mining industry [2].

One of the promising ways to create novel ion-exchange materials and technologies for the production thereof could be presented by a method of obtaining the ion exchangers from biological polymers, such as chitin and chitosan. These materials are of particular interest because of lower cost as to compare with ion-exchange resins. Another advantage of them consists in the fact that the manufacturing thereof uses reproducible naturally occurring raw materials, whereas the manufacturing technology does not require for complicated and expensive equipment [3].

To date, chitosan is considered one of the most understood biopolymers suitable for producing composite materials. The presence of a great number of amino groups in chitosan hydroxyl ring determines its physicochemical properties, in particular, polycationic, chelating and film-forming characteristics.

Aminosaccharide chitosan represents a derivative of a linear polysaccharide, whose macromolecules consist of randomly connected β-(1-4)-*D*-glucosamine units and *N*-acetyl-*D*-glucosamine. The main source of chitosan is presented by crustacean shells. This naturally occurring polymer exhibits unique properties: it is biocompatible, biodegradable, and non-toxic, it has antibacterial properties *etc*. Chitosan is capable of binding the ions of heavy and radioactive metals and thus it could be used as a sorbent for the removal thereof, including in the composition with different materials [4].

In this work we studied the sorption properties of carbon materials modified with chitosan. Carbon materials are widely known as adsorbents for the isolation of precious, heavy and rare metals from solutions, for the preparation of drinking water as well as for solving local problems concerning the processing of solutions in the nuclear industry.

The anodic deposition of chitosan onto the surface of a carbon material represents, in fact, a process of physical modifying the chitosan, which results in changing the crystallinity of the polymer with providing the availability of the polymer functional groups with respect to metal ions extracted from solutions.

The sorption capacity of the materials obtained was determined in the course of gold extraction.

EXPERIMENTAL

As a raw material for the production of modified ion exchange materials, we used chitosan with the deacetylation level equal to 85 %. The concentration of chitosan in solution did not exceed 1.5 %, because at higher concentration values of the polymer the solution tends to become gelatinous, which complicates the process of the coating formation.

As a basis for ion exchange materials we used a Busofit-T carbon material with the density equal to 1.8 g/cm^3 and the specific surface area amounting to 0.25 m^2/g. A scheme of experimental investigation is presented in Fig. 1.

RESULTS AND DISCUSSION

Choosing the solution for obtaining composite chitosan/carbon material

In order to obtain a carbon material modified with chitosan we prepared chitosan solutions with the concentration ranging within 0.1–1.5 %. To dissolve the polymer we used 10–70 % aqueous solution of lactic acid.

In order to choose an optimum solution for the formation of chitosan coatings, we determined viscosity and electrical conductivity for the solutions prepared. The viscosity of the solutions was measured using a VPZh-2 capillary glass viscometer. The electrical conductivity of the solutions was measured with the use of a Multitest KSL-101 conductivity meter. Table 1 demonstrates average data concerning these parameters.

The viscosity of chitosan solutions, like that inherent in the most of high-molecular substanc-

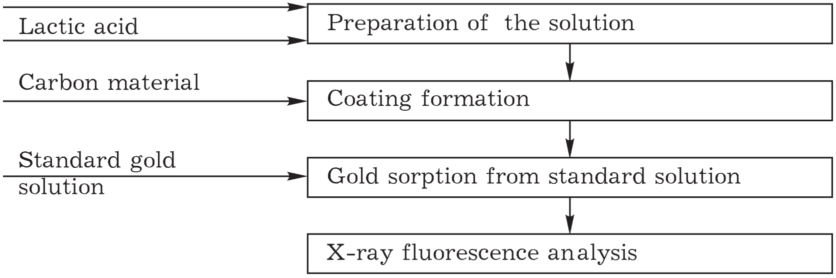

Fig. 1. Schematic diagram of the investigations.

TABLE 1

Electrical conductivity of solutions, mS/cm

Chitosan concentration, %	Acid concentration, %					
	1	5	10	20	40	70
0.1	1.449	3.450	4.257	4.192	2.307	0.327
0.3	1.249	3.141	3.944	3.954	2.189	0.3476
0.5	1.379	2.979	3.707	3.725	2.138	0.3369
1.0	1.1991	2.690	3.397	3.376	1.930	0.33686
1.5	2.758	2.960	3.333	3.284	1.928	0.3821

es exhibits an increase with increasing the polymer concentration. This is caused by the fact that at low concentration values the chitosan macromolecules move independently of each other. Upon reaching a certain concentration the mentioned molecules cannot be considered as independent kinetic units, and moving one of them results in changing the spatial position of other macromolecules, which causes an increase in the viscosity characteristics of the system [5].

The viscosity of the chitosan containing solutions also increases with increasing the concentration of an acid. This is caused by increasing the number of protonated amino groups, whereby the chitosan chains exhibit unwinding and a considerable elongation.

Figure 2 demonstrates the solution viscosity value depending on the concentration of chitosan and lactic acid. It can be seen that the viscosity of the solution increases uniformly with increasing the concentration of chitosan and lactic acid, wherein the acid concentration does not exceed 40 %. In the case of a 70 % lactic acid solution, the viscosity of the chitosan-containing solution exhibits an abrupt increase starting from the concentration of chitosan equal to 1 %.

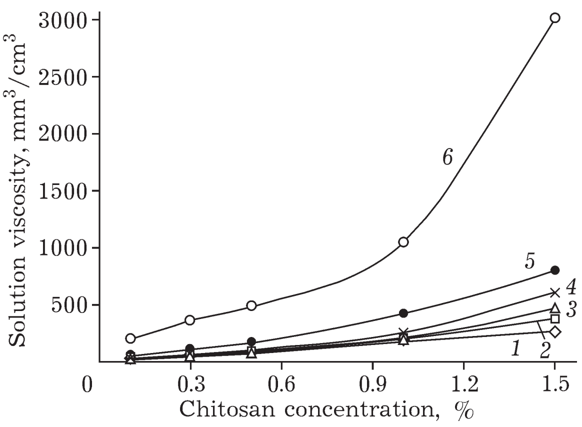

Fig. 2. Solution viscosity depending on on the concentration of chitosan and lactic acid. Lactic acid concentration (%): 1 (*1*), 5 (*2*), 10 (*3*), 20 (*4*), 40 (*5*), 70 (*6*).

The results of determining the electric conductivity of the solutions prepared are presented in Table 1. The lactic acid aqueous solutions with the concentration of 5, 10 and 20 % exhibit a relatively high electrical conductivity, whereas a 40 % solution of acid shows a medium value of the conductivity.

Solutions with a high viscosity and low electrical conductivity exhibit heating to a great extent, which is unacceptable since chitosan starts to decompose already at 60 °C. [6]. Therefore, the solutions with chitosan concentration ranging within 0.1–0.5 % in 40 % solution of lactic acid were considered optimal for the surface modification of the carbon material.

In order to choose an optimal concentration of dissolved chitosan we carried out the procedure of tetrachloroaurate sorption for standard solutions with the concentration of the mentioned substance equal to 20 and 50 mg/L, at pH 1. The qualitative X-ray fluorescence analysis (XFA) for the content of gold was performed using a Spectroscan X-ray fluorescence spectrometer (Spectron JSC). The main advantages of this analytical method consist in the rapidity of analysis as well as in non-destructive impact on the sample. In the course of studying the samples by means of XFA technique, the irradiation was carried out using a DRT-220 high pressure mercury lamp. The area of determining the concentration values for chemical elements ranges from a fraction of percent to one hundred percent [7]. The XFA results are presented in Table 2.

TABLE 2

Results of X-ray fluorescence analysis

Chitosan concentration, %	Intensity, pulses/s at the gold concentration, mg/L	
	20	50
0.1	339	2652
0.3	1392	5138
0.5	4407	13 451

From the XFA data one can see that at the same concentration values of gold, the greatest intensity of the analytical signal after the sorption is inherent in the samples with the highest concentration of the sorbent from the concentration interval under investigation equal to 0.5 %. After the sorption the solutions were tested for the residual gold content by means of stripping voltammetry. It has been found that at the chitosan concentration values equal to 0.1 %, and 0.3 %, a certain amount of gold remained in the solution after the sorption procedure, whereas with increasing the concentration of the chitosan up to 0.5 %, the gold was not detected in the solution. Thus, the gold present in the solution has been completely adsorbed by a chitosan-containing material.

A method of gold anodic deposition of onto a porous voluminous carbon sorbent is also described in the literature [8]. However, the electrochemical deposition from the solution of gold in trace amounts simultaneously with chitosan did not resulted in the XFA patterns corresponding to gold in the composition of the modified materials obtained. This could be caused, to all appearance by the formation of a chitosan layer that insulates the gold adsorbed by the carbon material. Furthermore, the process of electrochemical preparation of the material for the subsequent sorption requires for a less energy consumption than the direct gold electrowinning process, and allows one to perform also the activation of the ion-exchange groups of the polymer with a significant increase in the sorption capacity thereof.

Studying the sorption properties of carbon materials modified with chitosan

TABLE 3

Experimental and calculated values for the of isotherm of gold sorption on the carbon material modified with chitosan

C_{ini}, mol/dm^3	C_{eq}, 10^{-6} mol/dm^3	A_{exp}, 10^{-6} mol/g	C_{eq}/A_{exp}, g/dm^3
0.025381	0	0.662	0
0.050761	0.508	1.311	0.387205387
0.101523	29.442	1.682	17.5041617
0.253807	185.279	1.788	103.6236018
0.355330	290.863	1.810	160.6977901

Note. A_{exp} is the amount of sorbed substance (gold).

The studies performed earlier (the measurement of solution viscosity and electrical conductivity) allowed choosing the optimum concentration of acid and chitosan. For the carbon material surface modification we used chitosan solution with the concentration of 0.5 % in a 40 % aqueous solution of lactic acid.

The resulting samples were placed in the standard solution of gold with the concentration ranging within 5–500 mg/L for 48 h to determine the sorption properties. After 2 days the samples were taken from the solution. After drying, the sorbent was placed in a cuvette, compacted, closed with a 6 μm thick PEN-NE polyethylenterephthalate film (State Standard GOST 242347–80) to investigate using a Spectroscan spectrometer. The experimental data obtained are presented in Table 3.

Figure 3 demonstrates a sorption isotherm obtained in the experiment. It is seen that the sorption capacity of chitosan coating amounts to $1.68 \cdot 10^{-6}$ mol/g (29.01 mg/g) with respect to gold.

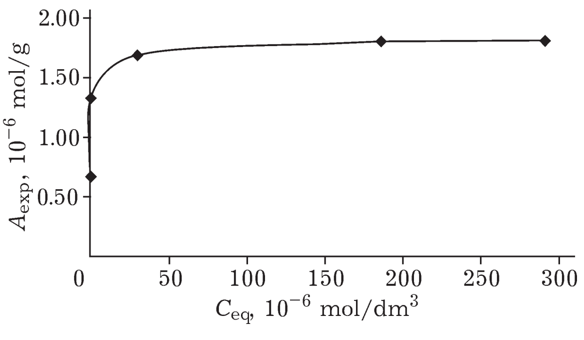

Fig. 3. Sorption isotherm for gold adsorbed on the carbon material modified with chitosan.

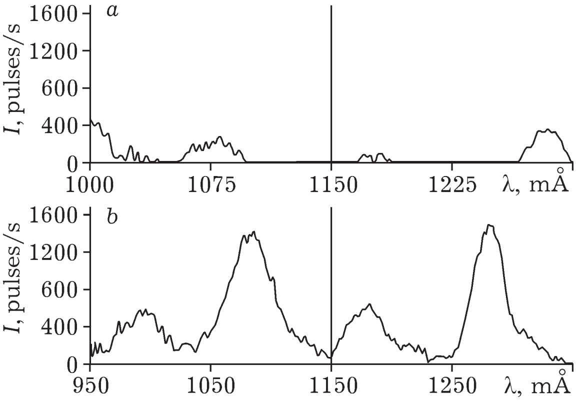

Fig. 4. XFA data after the sorption of gold under identical conditions: *a* – carbon material; *b* – carbon material modified with chitosan.

In the case of unmodified carbon material, this value is equal to $0.646 \cdot 10^{-6}$ mol/g (11.07 mg/g).

The high value of sorption capacity of the sorbent obtained could be caused also by the sorption properties of the carbon material, those are enhanced due to modifying by of chitosan [9]. The method proposed for the preparation of a chitosan-containing sorbent is economically advantageous being characterized by the availability of the materials used and environmental safety, as to compare with known methods for the treatment of carbon surface those have a limited application. Furthermore, all the known methods for producing carbon materials with a developed surface require for the use of special equipment, including those that provide heating the material up to high temperature values for the expansion thereof, which determines a high cost of the process as a whole [10].

Figure 4 demonstrates comparative XFA results after the sorption of gold under identical conditions by pure carbon material and by the carbon material modified with chitosan. It is seen that the adsorption capacity of the carbon material modified with chitosan is to a significant extent greater that the sorption capacity of pure carbon material (29.01 and 11.07 mg/g, respectively). Owing to this fact, the modified materials obtained could be considered as sorbents with further studying their selectivity with respect to the components under extraction.

CONCLUSION

1. Chitosan anodic deposition onto the surface of a carbon material represents a method for the chitosan physical modification method, whose result consists in changing the polymer crystallinity to provided the accessability of the polymer functional groups with respect to metal ions extracted from solutions.
2. The best sorption properties are exhibited by chitosan-modified carbon materials obtained from the solution with the polymer concentration equal to 0.5 %, in a 40 % aqueous solution of lactic acid.
3. The sorption capacity of the sorbent obtained amounts to 29.01 mg/g, at the sorption capacity of the carbon material equal to 11.07 mg/g.
4. The material obtained could be considered an adsorbent for the extraction of gold and other heavy and radioactive metals, as well as for improving the technique of gold determining by means of X-ray fluorescence analysis with a sufficiently low detection limit.

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