Jr. of Industrial Pollution Control 33(2)(2017) pp 1617-1621
www.icontrolpollution.com
Research Article

IMPACT OF CARBON DOPANTS ON SORPTION PROPERTIES OF CHITOSAN-BASED MATERIALS

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(Received 07 August, 2017; accepted 22 September, 2017)

Key words: Absorbents, Fullerene black, Water purification, Carbonized millet threshing waste, Chitosan

ABSTRACT

This paper presents several carbon materials (graphene, thermally expanded graphite, fullerenes, fullerene black), which are widely used in various areas of science and technology. Carbon materials are extensively used for water purification. Here we describe graphene-based nanocomposites which are used for sorption of heavy metals from water and for sorption of tetracycline from human body. We also describe composite materials based on thermally expanded graphite, which are highly effective for water purification from heavy metal ions and oil products. We provide examples of shungite with fullerenes usage for water purification and disinfection. We created sorption materials in the form of granules which consist of chitosan and carbon dopants. Carbonized millet threshing waste and fullerene black were used as carbon dopants. It was shown, that 10% additive of fullerene black increases mechanical integrity of the obtained granules and possesses almost the same properties as activated carbon of different grades. The following properties of the obtained sorption materials were determined experimentally: efficiency of model waste water purification from iron (III) cations; sorption capacity for iodine and methylene blue. It was shown, that carbon dopants (carbonized millet threshing waste and fullerene black) possess hydrophobic properties.

INTRODUCTION

The Pure water is a crucial point for people health. Although now there is a vast number of techniques for waste and natural waters purification, they are insufficient for rapidly increasing urbanization which leads to water and environment pollution. Various sorption materials are used for natural and waste waters purification and the most popular among them are those based on various modifications of carbon.

Nanocomposites based on chitosan with addition of graphene are now widely discussed in literature. Graphene addition improves mechanical, thermal and electrical properties. Graphene provides the necessary connection between nanocomposite components due to its large active surface, roughness and geometrical shape. Another positive effect arises due to the presence of additional functional groups. As (Terzopoulou, *et al.*, 2015) showed addition of just a few weight percents of graphene oxide significantly improves heavy metal ion removal from aqueous solutions. Aerogel of graphene oxide - chitosan was found to be a very effective absorbent for tetracycline (1.13×10^3 mg/g) (Zhao, 2014).

Absorbents based on thermally expanded graphite (TEG) are widely used for liquidation of oil spills at natural water and soil. For waste water purification (Sobgaida and Finaenov, 2005, Sobgaida, *et al.*, 2008) suggest to use not pure TEG, but that of the form of composites with fiber wastes (polyacrylonitriles and cotton). These composites allow one to resolve the technical difficulty of fiber TEG usage and thus to obtain highly effective absorbents for heavy metal ions and oil products removal from waste water.

Graphene and thermally expanded graphite are carbon foam two-dimensional structures. They

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possess hydrophobic properties, large specific surface and low bulk density and so they can be used for water purification.

Fullerene is an allotrope modification of carbon in the form of convex pentagons and hexagons. Fullerenes are widely used in a vast number of applications: from molecular electronics to medicine (Sidorov, *et al.*, 2000; Kovtun and Verevkin 2010). Spherical fullerenes (C60) possess some properties similar to those of TEG and graphene and can remove pollutants from water.

(Chae, *et al.*, 2009) from Duke University discovered that fullerenes do not allow bacterias and other microorganisms to accumulate on filter membranes at waste treatment facilities. Covering of pipes and membranes with such nanoparticles was found to be an effective strategy to solve one of the most vital problems and can decrease expenses for water purification.

Shungite mineral is a natural source for fullerenes. In Russia it is mined at Karelian mine field. This natural shungite with fullerenes was examined as a water filter by (Reznikov and Polekhovskii, 2000). The results have shown that various bacterias, heavy metals, nitrates, pesticides, clorine, etc. can be removed from water by shungite fullerene filters.

MATERIALS AND METHODS

To perform our investigation, we obtained granulated composite absorbents (granules) of the following compositions:

• No.1: Chitosan

• No.2: Chitosan + Fullerene black

• No.3: Chitosan + carbonized millet threshing waste

• No.4: Chitosan+ fullerene black + Carbonized millet threshing waste

Sample 1

Special mix is prepared for obtaining granules: 40 g of chitosan is added to 960 g of 3% acetic acid. It is stirred for about 4-5 hours until chitosan is completely dissolved. Then the obtained jellous mixture is dropwise added through a syringe in a 5% NaOH solution. The resulting granules are kept in alkali solution (NaOH) for 24-hour period and after that they are rinsed in water to get pH 7.0-7.5.

Sample 2

Is prepared by addition of FB (10% of total mass) to the mix of chitosan and acetic acid, described above for sample 1. Then the mixture is thoroughly stirred and dropwise added through a syringe in a 5% NaOH solution.

Sample 3

Is prepared by addition of CMTW (20% of total mass) to the mix of chitosan and acetic acid, described above for sample 1. Then the mixture is thoroughly stirred and dropwise poured in a 5% solution of NaOH.

Sample 4

Is prepared by addition of FB (10% of total mass) and CMTW (20% of total mass) to the mix of chitosan and acetic acid, described above for sample 1. Then the mixture is thoroughly stirred and dropwise poured in a 5% solution of NaOH.

The obtained granules for samples 1-4 are kept in alkali solution (NaOH) for 24-hour period until the total saponification and granulation. After that they are rinsed in water to get pH 7.0-7.5 and dried at room temperature until complete dry-out.

In order to investigate the sorption properties of the obtained materials, the granules of 20 g/l amount (Politaeva, *et al.*, 2017) were added to the model solutions containing iron (III) ions. The initial concentration was 30 mg/l and the sorption process was held in static conditions for 60 min. Further, the model solutions were filtered and the residual content of iron ions was analyzed using photocolorimetric technique according to technique PND F 14.1:2.4.50-96 using UNICO 1208 spectrophotometer.

Iodine absorption of the samples was investigated by titrimetric analysis. Iodine adsorption activity was determined according to Russian State Standard GOST 6217-74 "Activated crushed charcoal". For this purpose 1g of the material was diluted by 100 ml of iodine in potassium iodide solution. Then it was stirred using mixing machine for 15 min, and the obtained solution was settled. After this 10 ml of the obtained solution was titrated in the presence of 1 ml starch.

Methylene blue adsorption was determined according to GOST 4453-74 "Activated clarifying powdered charcoal". For this purpose 0.1 g of sorbent was diluted by 25 cm^3 of methylene blue solution of 1500 mg/l concentration. Then it was shaken at shaker for 20 min, and centrifuged for 15 min. After this 1 ml of the obtained solution was transported into the 100 ml flask and was diluted by distilled water. Optical density of the obtained solution was determined using UNICO 1208 spectrophotometer.

Attrition of the obtained samples was investigated according to (Russian State Standard GOST 51641-

2000, 2000) “Porous filtering materials. General specifications”. Samples (100 g) were sifted through sieves № 0.2 и № 5.0 and then put into glass flasks with 150 ml of distilled water. The samples were shaken at shaker for 24 hours, evaporated in porcelain cups and dried. After this the samples were sifted through sieves № 0.5 и № 0.25. The attrition is determined as a difference in masses for samples passed through sieve № 0.5 and remained at sieve № 0.25.

RESULT AND DISCUSSION

The aim of this work was to study the influence of carbon dopants (carbonized millet threshing waste and fullerene black) on sorption properties of chitosan-based materials and efficiency of model waste water purification from iron (III) ions.

(Taranovskaya, *et al*., 2016; Taranovskaya, *et al*., 2016; Politaeva, *et al*., 2017) showed that it is reasonable to use carbon-containing additives in order to improve sorption properties and decrease the bare cost. They suggested using carbonized millet threshing waste (CMTW). 20% of CMTW additives allow one to increase zinc cations sorption capacity (A Zn^{2+}, mg/g) from 36 to 50. Also it helps to decrease the bare cost of chitosan by more than 30 times (Politaeva and Shaihiev, 2016). Unfortunately, CMTW additive makes the granules more porous and, consequently, more breakable. At CMTW additive of more than 20% (30% and 40%), the granules become not sharply shaped and fall to decay during water purification process (Politaeva, *et al*., 2017). Basing on negligible amount of various investigations and having the knowledge of fullerene properties, we supposed that fullerenes might be effectively used for water purification. It is known from literature that fullerenes improve mechanical strength of composites, but pure fullerenes cost too much. Fullerene black (FB), the co-product of fullerene manufacturing, costs about 50 times less. So we decided to use fullerene black dopants (produced in China) with fullerene content of less than 10%.

The initial and final concentrations were used to calculate the efficiency of model solution purification. The results are presented in Table 1.

It is seen, that CMTW addition to granules (sample 2) allows one to get high purification efficiency up to 98%. Iron (III) ions removal efficiency for granules with FB dopant is lower: from 83.0% for sample 2% to 86.7% for sample 4. This is due to the fact that fullerene black addition doesn't allow one to get sufficiently porous sample structure as it can be achieved using CMTW dopant. This can be proved by microstructure analysis data from electron microscope TESCAN Mira-03M (Fig. 1)

(Fig. 1) shows that sample 2 (only with CMTW dopant) has porous structure. Sample with fullerene black doesn't have pores. The sample with both CMTW and FB dopants has more loose surface, and it doesn't have tube pores as sample with CMTW dopant has.

Physical-mechanical properties (attrition,%) of the obtained samples 1-4 were investigated using the technique, described in Russian State Standard GOST 51641-2000 (Table 1). It is seen from Table 1 that addition of fullerene black significantly increases mechanical properties and results in attrition less than 0.5%. So we recommend to use sample 4 for high efficiency of wastewater purification from iron (III) ions.

Hydrophobic properties of carbon dopants were estimated by contact angle of wetting. During the first minute at the surfaces of CMTW and FB liquid drops are formed with wetting angle $\alpha > 90°$, which indicates their hydrophobic properties. After 5 minutes the angle α remains the same for fullerene black surface, but for CMTW surface we see the drop spreading. Consequently, fullerene black possesses more hydrophobic properties than CMTW. This fact is also proved by granules production technique. When chitosan+FB mix is dropwise added to alkali solution, granules of a round shape are formed exactly on alkali surface.

Methylene blue adsorption (which is characterized by presence of 1.5 nm diameter pores) and iodine absorption (which is characterized by presence of 1.0 nm diameter pores) were determined for all 4 samples. In order to compare the obtained data on sorption properties we used the known data for the standard sorbent “Activated crushed charcoal” (GOST 4453-74; 6217-74). The results are presented in Table 2.

Table 1. The relationship between sorption, mechanical properties and granula composition

Granula composition	C Initial, mg/L	C Final, mg/L	E,%	Attrition, %
Sample 1	30	6.34	78.0	0.2
Sample 2	30	4.87	83.0	0.2
Sample 3	30	0.41	98.6	0.3
Sample 4	30	4.20	86.7	0.2

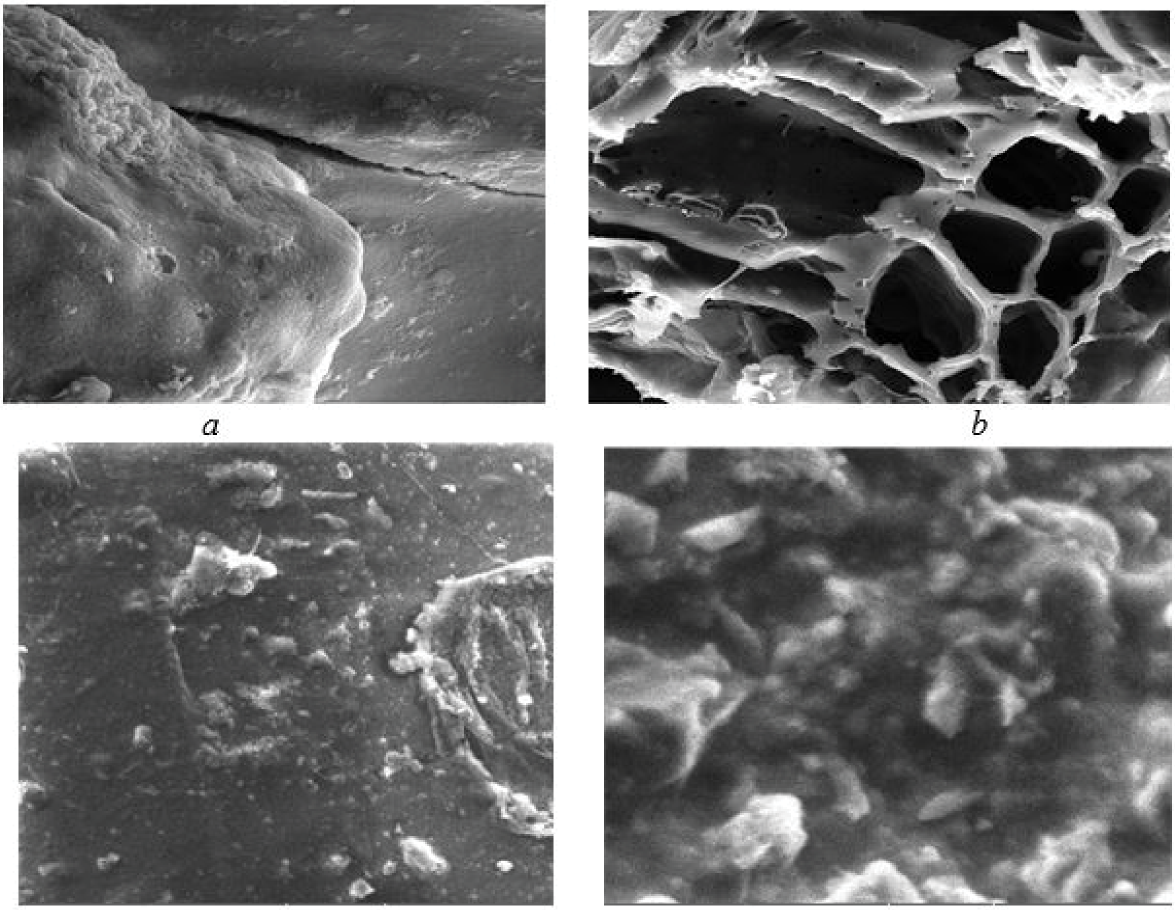

Fig. 1 Surface morphology of granulated samples x200; a - Sample 1; b - Sample 2; c - Sample 3; d - Sample 4.

Table 2. Characteristics of granulated samples

Absorbent type	Methylene blue adsorption, mg/g	Iodine absorption, %	Bulk density, g/dm^3
Sample 1	349.8	21.6	692 ± 3
Sample 2	348.4	18.4	585 ± 3
Sample 3	348.2	22.2	331 ± 3
Sample 4	350.3	31.7	239 ± 2
Activated crushed charcoal (GOST 4453-74; 6217-74)	225.0	30.0	240 ± 2

It is seen from Table 2, that sample 4 sorption properties are highly competitive with that ones for activated crushed charcoal: its iodine absorption is 1.7% more, methylene blue adsorption is 125 mg/g more, bulk density is almost the same. Sample 4 is characterized by the highest amount of pores of less than 1 nm in diameter and the lowest apparent density. Most probably this phenomenon can be explained by the maximum presented amount of carbon dopant (20% of CMTW + 10% of FB). Pores of 1.5 nm diameter are presented almost in all samples practically in equal amount.

Iron (III) ion radius varies from 0.063 to 0.092 nm, which is significantly less than pore diameters of the obtained samples. So it is likely that processes of physical sorption of iron cations into the obtained absorbent pores take place.

The utilized granules after the water treatment can be used according to the method, described by (Politaeva and Shaihiev, 2016).

CONCLUSION

Carbon dopants (CMTW and fullerene black) were used to obtain granulated sorption materials based on chitosan in this study. It was shown that these carbon dopants increase the efficiency of model wastewater purification from iron (III) ions from 78% to 98.6% for CMTW and up to 83% for FB. The mechanical strength of materials is decreased when adding CMTW dopant and increased with fullerene black dopant. The special composition (chitosan+ CMTW+FB) is discussed to have acceptable sorption and mechanical properties which are not worse than that for standard sorbent "Activated crushed charcoal".

(GOST 4453-74; 6217-74).

Microstructure analysis has shown that tube pores are formed when CMTW is added to chitosan, and this leads to water purification efficiency improvement. FB dopant doesn't form pores, but makes the structures stronger.

It was established that these carbon dopants are hydrophobic.

ACKNOWLEDGEMENTS

This work was performed within the implementation of Federal Targeted Programme for Research and Development in Priority Areas of Development of the Russian Scientific and Technological Complex for 2014-2020, the project "Development and implementation of innovative biotechnologies for treatment of microalgae *Chlorella sorokiniana* and duckweed *Lemna minor*" (Agreement No. 14.587.21.0038)

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