Study of the Impact of –NH$_2$ Modification on Adsorptive Properties of Graphene Oxide

KWAK Anna[1,a], DYLONG Agnieszka[1,b*] and MALISZEWSKI Waldemar[1,c]

[1]Military Institute of Engineer Technology, Obornicka 136 Str., 50-961 Wroclaw, Poland

[a]kwak@witi.wroc.pl, [b]dylong@witi.wroc.pl*, [c]maliszewski@witi.wroc.pl

In memoriam of Kazimierz Szyszka

Abstract. Graphene oxide is a nanomaterial of very high adsorption capabilities due to its vast surface area. Moreover, numerous oxygen functional groups present on the surface of graphene oxide enable its modifications to be performed. The authors aimed to create adsorbents based on activated carbon impregnated with amine-modified graphene oxide. The study showed that the amino group functionalisation, both with the use of ethylenediamine (GO-EDA) and using polyaniline (GO-PANI), causes the adsorbent to remove lead, mercury, copper, and iron ions from aqueous solutions very efficiently. Both adsorbents also reduce the cadmium, nickel, zinc, and arsenic ion content, however to a lesser extent but nevertheless still significantly. The two sorbents can be applied in field water treatment to remove specific contaminants.

Introduction

Graphene oxide (GO) indicated increased adsorption, as far as the removal of heavy metal compounds dissolved in water is concerned, when compared to active carbons, widely used in water purification processes. The addition of graphene oxide to active carbon increases the adsorption capacity of the adsorbent obtained in this manner relative to selected heavy metals. The surface of graphene oxide contains hydroxyl-, carboxyl-, ketone- and epoxy functional groups, as well as others which enable the formation of hydrogen or polarized bonds not only with organic compounds but also with inorganic compounds of heavy metals [1]. It was also proven [2÷9] that a further increase in adsorption properties can be achieved via modification of graphene oxide with –NH2 and –SH groups or with some metal oxides (including iron-, titanium-, manganese- and tin oxides). The authors developed detailed technologies for the fabrication of carbon adsorbents containing GO modified with compounds with –NH$_2$ groups. The obtained adsorbents were evaluated for aqueous solution heavy metal adsorption, and this allowed for the assessment of their possible suitability for use in field water treatment processes to be performed.

Experimental Procedure

Synthesis of Graphene Oxide Flakes. Graphene oxide was obtained via the modified Hummers method [10, 11]. 20 g of flake graphite was added to a 1-litre beaker and the acid mixture (432 cm^3 of H$_2$SO$_4$ and 42 cm^3 of H$_3$PO$_4$) was slowly poured into the same beaker. After the mixture was stirred for 30 minutes, the graphite oxidation process was initiated using KMnO$_4$ (~60 g), which was being added to the beaker for 2 hours and stirred continuously, keeping the temperature of the mixture at below 60°C. After the oxidant was dosed into the mixture, the contents of the beaker were stirred for another 2 hours and then set aside sealed for 24 hours. While stirring

continuously, the oxidized mixture was slowly added to the beaker containing water. It was topped up with water up to 5 dm^3 and stirred for 6 hours. The brown liquid obtained after stirring was first set aside for 24 hours and then centrifuged, while the sediment was topped up with water up to 5 dm^3 and mixed. Following another centrifugation, the liquid was sonicated for 6 hours. A thick, brown, greasy substance containing graphene oxide was obtained, and derivative thermogravimetry was used for its analysis.

Compounds Used to Modify Graphene Oxide with Amino Groups. To modify graphene oxide with amino groups, the following compounds containing such groups were selected: ethylenediamine (EDA) and polyaniline (PANI). In its molecule, ethylenediamine contains two -NH2 amine groups, which makes it easy for it to bond the metal and form heterocyclic structures. Moreover, EDA coupled with graphene oxide (GO) in the presence of N,N'-dicyclohexylcarbodiimide (N-DHC) [6] which is an organic chemical compound mainly used as a condensing agent in organic synthesis, e.g. for the coupling of amino acids in peptide synthesis.

Polyaniline (PANI) is an aniline polymer synthesized directly on the surface of graphene oxide. Aniline polymerization is conducted in a hydrochloric acid environment. Ammonium persulfate [9] is used as the oxidant. Depending on the degree of oxidation, some segments of the polyaniline molecule can transform into a quinone form, which allows polyaniline to exist in various forms that differ in colour and their properties.

Active Carbon Impregnation with Graphene Oxide with Ethylenediamine. The initial stage in the preparation of a new adsorbent was functionalizing graphene oxide with ethylenediamine. A concentrated aqueous slurry of graphene oxide containing 2 g of GO was mixed with 80 g of ethylenediamine and 7 g of N,N'-dicyclohexylcarbodiimide. The mixture was stirred for 48 hours under reflux at 60°C, then filtered through a funnel with sintered disc G4 and washed first with water, and then with ethanol. The obtained greasy substance was dried for 8 hours in a dryer at 80ºC. Graphene oxide functionalised with ethylenediamine (GO-EDA) was synthesised.

100 g of active carbon was weighed out and dried in a drier for 2 hours at a temperature of 120°C, then cooled to room temperature. Distilled water, in the amount equal to the mass of prepared active carbon, was poured onto 2 g of the weighted out GO-EDA and stirred for 1 hour using a magnetic stirrer, followed by sonication for 3 hours in an ultrasonic cleaner.

The dried active carbon was mixed with the entirety of the obtained composition of graphene oxide and ethylenediamine. It was stirred for 30 minutes and set aside for 2 hours at room temperature. The impregnated carbon was dried for 12 hours at a temperature of 120°C.

The cooled GO-EDA modified sorbent containing 2% of the impregnant was ready to be used in the water purification process for the removal of heavy metal compounds.

Active Carbon Impregnation with Graphene Oxide with Polyaniline. To obtain graphene oxide with polyaniline, 2 g of GO were mixed with 200 cm^3 of distilled water. 10 g of aniline was added to the homogeneous suspension while stirring, and then 30 cm^3 of concentrated hydrochloric acid was poured into the suspension. A magnetic stirrer was used to stir the obtained suspension for 1 hour. Then 20 g of ammonium persulfate dissolved in 1 molar hydrochloric acid was added to the mixture. The mixture was first stirred for another 2 hours in a cooling bath with ice and sodium chloride, maintaining the temperature at 5 ÷ 7°C, and then transferred to a refrigerator and set aside for 16 hours. The cooled reactor was transferred to the bath with a cooling mixture, and it was kept at a temperature of 5 ÷ 7ºC for another 3 hours while stirring.

The resulting greasy, homogeneous suspension was diluted with 4 litres of distilled water and precipitated through a funnel with sintered disc G4. The precipitate was washed using 1 litre

of distilled water on the filter, and 62 g of wet sorbent containing 15% GO-PANI was obtained. 100 g of active carbon was prepared for impregnation as described above. 13.3 g of wet GO-PANI was mixed with 90 cm^3 of distilled water for 1 hour using a magnetic stirrer and then sonicated for 3 hours in an ultrasonic cleaner. The obtained product was added to a dried active carbon sample, seasoned for 2 hours at room temperature, and then dried for another 2 hours at 120°C and cooled.

The adsorbent obtained in this manner contained containing 2% of the impregnant and was ready to be used in the water purification process for removal of heavy metal compounds

Method for verifying the effectiveness of modified adsorbents. The following cations were selected for the study of the adsorption of metals from water: Hg^{2+}, Pb^{2+}, Cd^{2+}, As^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}. Selected metals salt solutions with cation concentrations equal to 1mg/dm3 and 5mg/dm3 were prepared. The study utilized the static method, which consisted in pouring 100 cm3 of individual solutions onto 1 g weights of the adsorbent (containing GO-EDA or GO-PANI) and stirring the mixture for 30 minutes using a magnetic stirrer. The contents of the flask were then filtered, and the metal content in the filtrate was determined by means of inductively coupled plasma optical emission spectrometry (ICP-OES), and then the adsorption efficiency of the studied element was calculated according to the formula:

$$A\% = [(c_i - c_f)/c_i] \cdot 100 \qquad (1)$$

where:
A – adsorption efficiency, in percent;
c_i – initial metal ion concentration in the solution, in milligrams per cubic decimetre;
c_f – final metal ion concentration in the solution, in milligrams per cubic decimetre.

Table 1. *Heavy metal adsorption efficiency for GO-PANI- and GO-EDA-modified activated carbon.*

p	C_i	$C_{fGO\text{-}PANI}$	$A_{GO\text{-}PANI}$	$C_{fGO\text{-}EDA}$	$A_{GO\text{-}EDA}$
	[mg/dm^3]	[mg/dm^3]	[%]	[mg/dm^3]	[%]
Pb^{2+}	1	0.000	100	0.000	100
Cd^{2+}	1	0.079	92.1	0.061	94.0
Ni^{2+}	1	0.225	77.5	0.156	84.4
Hg^{2+}	1	0.000	100	0.000	100
Zn^{2+}	1	0.222	77.8	0.072	92.8
Cu^{2+}	1	0.022	97.8	0.010	99.0
Fe^{2+}	1	0.023	97.7	0.024	97.6
As^{3+}	1	0.251	74.9	0.242	75.8
Pb^{2+}	5	0.007	99.9	0.000	100
Cd^{2+}	5	1.720	64.8	1.322	73.6

Ni^{2+}	5	2.108	57.8	2.019	59.6
Hg^{2+}	5	0.041	99.2	0.062	98.8
Zn^{2+}	5	2.806	43.9	2.340	53.2
Cu^{2+}	5	0.481	90.4	0.048	99.0
Fe^{2+}	5	0.556	88.9	0.265	94.7
As^{3+}	5	2.325	53.5	2.068	58.64

As shown in Table 1, both the GO-PANI and GO-EDA adsorbents are characterized by high adsorption efficiency with relation to the lead and mercury ions. Both at the concentration of 1 mg/dm3 and 5 mg/dm3, water contaminated with these metal compounds was completely purified. The Pb and Hg adsorption efficiency approximated 100%.

As far as water containing copper ions is concerned, the absorption efficiency in case of both concentrations (1 mg/dm3 and 5 mg/dm3) equalled 99% for the GO-EDA adsorbent, whereas for the GO-PANI adsorbent it is lower and amounts to 97.8% at the Cu^{2+} concentration of 1mg/dm3 and 90.4% for 5 mg/dm3 copper concentration in the initial solution. Such a high adsorption efficiency for copper ions from water solutions proves that the filter beds prepared from these adsorbents will significantly reduce the copper content in water.

The adsorption of iron ions from solutions with a metal content of 1 mg/dm3 was at the level of 97.6%, whilst from solutions when the metal amounts to 5 mg/dm3, it was lower and equalled 88.9% for GO-PANI and 94.7% for GO-EDA. Both adsorbents are characterised by the capability to significantly reduce iron content in the water.

GO-PANI and GO-EDA are weak adsorbents with regard to cadmium, zinc, nickel, and arsenic salts in particular. When examining the cadmium sorption, the adsorption efficiency recorded was above 90% for the initial solution of 1 mg/ dm3 Cd, but in the case of 5 mg/ dm3 Cd, the value was under 74%. Adsorbents of such kind do not ensure sufficient removal of cadmium, zinc, nickel, and arsenic cations from the water to be purified. If the content of one of these metal cations is at 5 mg/dm3, more than half of its mass remains unadsorbed.

Summary
The GO-EDA adsorbent is characterized by a very high (i.e. close to 100%) absorption efficiency towards lead and mercury ions, as well as for copper (99%) and iron (approx. 95%). The GO-EDA adsorbent sorbs cadmium to a lesser degree (about 74%). The same could be seen for nickel (ca. 60%), zinc (about 53%) and arsenic (about 58%). The disadvantage of this adsorbent is the long preparation process, lasting even several days which includes 48-hour heating under a reflux condenser.

The GO-PANI sorbent is characteristic in that it exhibits a remarkably high (close to 100%) lead and mercury ion adsorption efficiency, while the same for copper and iron was approx. 90%. The remaining investigated metals are adsorbed much less efficiently: cadmium at about 65%, nickel at 58%, zinc at about 44% and arsenic (ca. 53%). GO-PANI is therefore an adsorbent with a narrowed metal ion absorption spectrum, capable of removing selected ions from contaminated water to a high degree. The preparation process requires a number of hours of stirring at a low temperature (approx. 5°C).

Both sorbents seem to be useful in removing specific contaminants, such as metal ions or arsenic from water.

References

[1] P. Janik, K. Komorowska, E. Turek, B. Zawisza, R. Sitko. Graphene oxide as a new adsorbent in analytical chemistry, 6th Scientific Seminar: Current Issues in Analytical Chemistry, Katowice, May 18th, 2012.

[2] B. Zawisza, A. Baranik, E. Malicka, E. Talik, R. Sitko. Preconcentration of Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Pb(II) with ethylenediamine-modified graphene oxide. Microchimica Acta 183 (2016) 231-240. https://doi.org/10.1007/s00604-015-1629-y

[3] R. Sitko, P. Janik, B. Zawisza, E. Talik, E. Margui, I. Queralt. Green approach for ultratrace determination of divalent metal ions and arsenic species using total-reflection X-ray fluorescence spectrometry and mercapto-functionalised graphene oxide nanosheets as a novel adsorbent, Analytical Chemistry 87 (2015) 3535-3542. https://doi.org/10.1021/acs.analchem.5b00283

[4] P. Janik, B. Zawisza, E. Talik, E. Margui, I. Queralt, R. Sitko. Application of graphene oxide functionalised with thiol groups in the determination of heavy metals and arsenic speciation using the total reflection x-ray fluorescence (TXRF) technique, 9th Scientific Seminar: Current Issues in Analytical Chemistry, Katowice, May 15th, 2015.

[5] P. Janik, B. Feist, E. Talik, A. Gagor, R. Sitko. Graphene oxide functionalised with aminosilanes as a selective adsorbent in the determination of Pb^{2+} ions using electrothermal atomic absorption spectrometry (ET-AAS), Winter Congress of SSPTChem, Wroclaw, December 13th, 2014.

[6] P. Janik, A. Baranik, U. Porada. Testing the adsorption capacity of graphene oxide and carbon nanotubes modified with amine groups relative to lead ions, 8th Scientific Seminar: Current Issues in Analytical Chemistry, Katowice, May 16th, 2014.

[7] P. Janik, U. Porada, A. Baranik, R. Sitko. Sorption properties of graphene oxide functionalised with sulfonic groups relative to Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) metal ions, 23rd Poznan Analytical Seminar: Modern Methods of Sample Preparation and Determination of Trace Quantities of Elements, Poznan, May 8th-9th, 2014.

[8] X. Luo, C. Wang, S. Luo, R. Dong, X. Tu, G. Zeng. Adsorption of As(III) and As(V) from water using magnetite Fe3O4-reduced graphite oxide-MnO2 nanocomposites, Chemical Engineering Journal 187 (2012) 45-52. https://doi.org/10.1016/j.cej.2012.01.073

[9] R. Li, L. Liu, F. Yang. Preparation of polyaniline/reduced graphene oxide nanocomposite and its application in adsorption of aqueous Hg(II), Chemical Engineering Journal 229 (2013) 460-468. https://doi.org/10.1016/j.cej.2013.05.089

[10] W. S. Hummers, Jr., R.E. Offeman. Preparation of Graphitic Oxide, J. Am. Chem. Soc. 80 (1958) 1339-1339. https://doi.org/10.1021/ja01539a017

[11] D.C. Marcano, D.V. Kosynkin, J.M. Berlin, A. Sinitskii, Z. Zun, A. Slesarev, L.B.A. Lemany, W. Lu, J.M. Tou. Improved synthesis of graphene oxide, ACS Nano 4 (2010) 4806-4814. https://doi.org/10.1021/nn1006368