Advanced Materials and Technologies for Environmental Applications - AdvMatTechEnv
Open Acces Journal
powered by SciEdTech

GRAPHENE BASED MATERIALS FOR ENVIRONMENTAL APPLICATIONS

Anton FICAI[1], Maria SONMEZ[2], Denisa FICAI[1,*], Ecaterina ANDRONESCU[1]

[1.] *Department of Science and Engineering of Oxide Materials and Nanomaterials, Faculty of Applied Chemistry and Material Science, University POLITEHNICA of Bucharest, 1–7 Polizu Street, 011061 Bucharest, Romania (denisaficai@yahoo.ro)*

[2.] National Research & Development Institute for Textiles and Leather– Division: Leather and Footwear Research Institute, 93 Ion Minulescu St., Bucharest, Romania

Abstract

Graphene and its derivatives are extensively used in many applications from medical to environmental or electronic applications, as well. The high interest for this kind of materials is due to the extraordinary electrical and mechanical properties, the good biocompatibility and a remarkable specific surface area. From the point of view of environmental applications, two properties are essential: very high specific surface area (can reach 2600m^2/g, twice comparing to Single Wall Carbon Nanotube) and the ability of graphene to be oxidized and thus, the hydrophobic backbone and the hydrophilic moieties can selectively bind the desired hazardous compounds from different media, regardless their hydrophobic or hydrophilic nature. Among the many preparation routes presented in the literature only a few are suitable for obtaining graphene and graphene oxide at reasonable price at large scale. Along with the ability of selectively remove different species, graphene and its derivatives can be used as sensor.

Keywords: Graphene, Graphene Oxide, Environmental Applications, Graphene Synthesis,

1. Introduction

A wide variety of carbon based materials are increasingly studied during the last decades, including fullerenes, single and multiwalled carbon nanotubes, carbon onions, graphene and graphene oxide. These materials are especially studied for medical applications (including tissue engineering, biosensors, drug targeting and delivery, etc.), energy sector (carbon nanotubes and graphene are known due to their remarkable electric conductivity, cathode in battery application, etc.), environmental applications (as sorbent for many organic and inorganic species, catalyst for the degradation of many species, etc.), photocatalyst, etc. [1-9].

Graphene is a special class of 2D material which, theoretically can be obtained by detaching the layers of graphite as presented in Figure 1. As presented in Figure 1, the cleavage on the “c-axis” is responsible with the formation of the graphene sheets with atomic thickness of these sheets [10]. Most chemical techniques allowing the detaching of the sheets of graphite lead to the oxidation of these sheets leading to graphene oxides – GO which can be used accordingly of can be reduced to obtain the so-called reduced Graphene Oxide – rGO. If graphene is a remarkable electrical conductor, graphene oxide is rather an insulator because during the oxidation, some of the double groups (π bonds) are destroyed and the conjugation is altered. The increasing oxygen content leads to lower electric conduction.

From environmental point of view, both graphene and graphene oxides exhibit good potential in hazardous compound removal from aqueous solutions. The specific surface area of graphene is similar to that of graphene oxide being twice comparing to the Single Wall Carbon Nanotube (SWCNT) and many times higher than Carbon Black and other Activated Carbon. This high surface area is especially important from the point of view catalytic activity, adsorption capacity, interaction with different species.

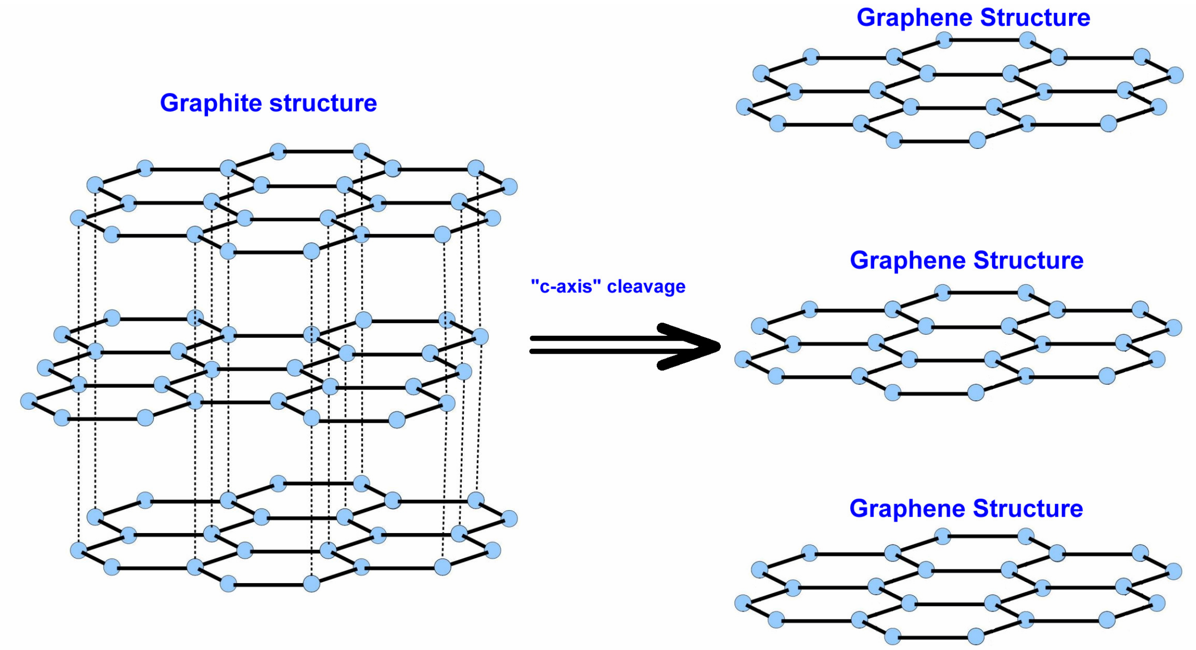


Figure 1. Structure of graphite and graphene and the schematic transformation of graphite into graphene

2. Preparation of Graphene Like Materials

Several preparation methods of graphene structures are known and used in the literature [10-13] and are synthesized in Figure 2. Various physical and chemical routes of detaching of the bonds on the "c-axis" are known but only a few are suitable for large scale preparation of graphene/graphene oxide. Most probably, the Hummer's method is one of the most suitable method of preparation of graphene oxide but need high amount of sulfuric acid and potassium permanganate. By short, the initial Hummer's method was adapted and currently, to the original method a pre-oxidation step was added. In this case, the preparation starts from graphite powder which is pre-oxidized by using concentrated sulfuric acid and followed by the oxidation step which involve the immersion of the pre-oxidized graphite in concentrated H_2SO_4 followed by slowly addition, in ice bath, of the $KMnO_4$. This step, according to different authors, can be done at 4-5^{o}C followed by maintaining the mixture at room temperature (for even 5 days). The oxidation step is then conducted at 90^{o}C for additional 2-3h. Finally the reaction was interrupted by the addition of H_2O_2 and the graphene oxide was purified by centrifugation and washing with proper solvents [13]. Mechanical cleavage was firstly applied in order to obtain graphene but this method do not allow large scale preparation of graphene. Nowadays, instead of the mechanical cleavage, sonication is used to induce the exfoliation process while surfactants are used to stabilize the as obtained graphene sheets [10].

Preparation methods of Graphene and Graphene Oxide

Physical routes [10-12]	**Chemical routes [12, 13]**
• Mechanical cleavage	• Chemical Vapour Deposition
• Sonication assisted liquid phase exfoliation	• Chemical Synthesis starting from Aromatic Precursors
• Epitaxial Growth	• Chemical Reduction of Graphene Oxide
• Thermal deposition	• Graphene oxide preparation via Hummer method followed by reduction
• Plasma discharge etching of graphite	

Figure 2. Preparation routes of Graphene and Graphene Oxide

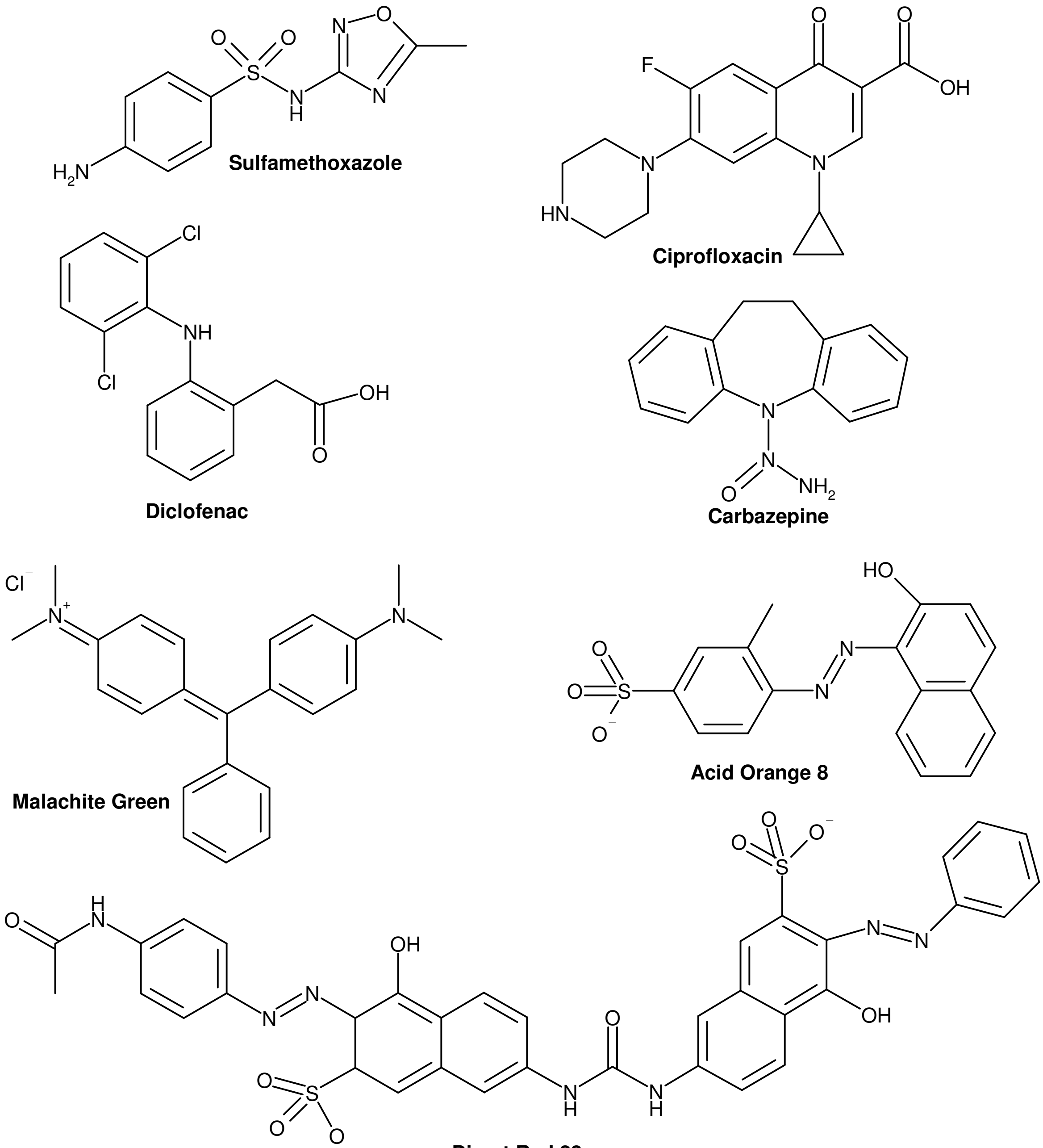
3. Applications of graphene-like materials for environmental applications

Graphene and Graphene Oxide based materials are extensively used in environmental applications both as active agent or as support for the active agents. These carbon-based materials are especially used as sorbent but also can act as sensor of various pollutants. Some of the most important classes of the environmental applications are presented in Table 1. The sorbent capacity of graphene is mainly exhibited due to the electrons of the π bonds and the vacant orbitals of many heavy metals (or other cations) while, in the case of graphene oxide, along with these interactions, new interactions/bonds (coordinative bonds, especially) can occur between the carboxylic or hydroxyl groups and the cations of interest. The more complex molecules can interact via several ways including hydrophobic interactions of the alkyl or aryl groups and the carbonaceous backbone and various interactions between the functional groups and the carbonaceous backbone or the various groups decorating the carbonaceous backbone.

Table 1. Some of the most important applications of graphene and graphene oxide based materials in environmental applications

Materials	**Applications**		**References**
Graphene and graphene based materials	**Sorbent for:**	F^-, anionic dyes, Pb^{2+}, methylene blue, antibiotics, lysozyme; 1-pyrenebutyric acid, 2,4-dichlorophenoxyacetic acid, diquat dibromide, etc.	[7, 14-16]
	Sensors for:	Bisphenol A, nitrophenol, antibiotics, hydrochinone, etc.	[17-20]
Graphene Oxide and Graphene Oxide related materials	**Sorbent for:**	Cd^{2+}, Pb^{2+}, U^{6+} antibiotics, clofibric acid, humic acid, lysozyme, microcystin, methylene blue, etc.	[15, 16, 21-28]
	Sensors for:	H_2O_2, Cd^{2+}, Pb^{2+}, phenol, pesticide, microcystin, etc.	[29-32]

Thousands of papers related to materials based on graphene are recently published in the literature related to the field of environmental application. Both graphene and graphene oxide are used as sorbents and even sensors of cations, especially heavy metals and radionuclides but also for organic matters. It is important to mention that in all these cases graphenic materials are acting as sorbent of as support for the active agents.



Direct Red 23

Figure 3.Chemical structure of the biological active agents from drugs or dyes suitable for removing from aqueous solution by using graphene based materials

3.1. Graphene-based materials as sorbent

Graphene-based materials are attractive for removal heavy metals from water and wastewater especially because they are stable, have limited reactivity, highlight high specific surface area and remarkable antioxidant activity [33]. Lead removal can be done on bare graphene [33], on modified graphene structures, for instance tetraethylenepentamine modified graphene foam [34] or nitrogen doped graphene aerogels [35]. Certainly, graphene functionalization or doping will increase the adsorption capacity, Han *et al*. [34] reporting a 304.9mg/g adsorption capacity for the tetraethylenepentamine modified graphene foam compared to the bare graphene aerogels which is about 80mg/g.

Another heavy metal with high toxicity which can be removed by using graphene oxide is cadmium being potential cancerogenic agent. The adsorption capacity can reach 23.9 mg/g (pH=6-7) as reported by Bian *et al.* [36].

Even uranium can be removed by using graphene oxide nano-sheets especially after surface modification by cyclodextrin. Based on the results published by Song *et al.* [24] the cyclodextrin is chemically grafted onto the graphene oxide sheets and the presence of humic acid enrich the sorption of U(IV) at low pH but reduce it at high pH. Regardless the pH, the presence of U(IV) enhance the adsorption of the humic acid.

Removal of various active agents of drugs: sulfamethoxazole, ciprofloxacin, diclofenac, carbamazepine, etc. or dyes: malachite green, direct red 23, acid orange 8 (**Figure 3**) etc. from aqueous solutions by using graphene oxide was proved [22, 37-42]. It can see that many aromatic agents can be easily removed from aqueous solution because by using graphene oxide, the adsorption being most probably due to the interactions between the electronic clouds of the graphemic backbone and the aromatic moieties of those agents as also highlighted by Radulescu *et al.* [43]. If some agents can be removed only by adsorption, sulfamethoxazole, for instance, can be also degraded by using graphene and Ag in Ag_3PO_4-based photocatalyst [41]. Clofibric acid (*2-(p-chlorophenoxy)-2-methylpropionic acid*) is a herbicide but also can be a degradation product of the cholesterol-lowering pharmaceutical drug called clofibrate. The removal of this agent is recommended because of the potential environmental persistence. The tests realized on zebrafish was highlighted that growth and triglyceride content of the muscle reduction appears but also a significant decrease of the fecundity was observed and so, its removal from aqueous media is recommended [23, 44].

Protein removal from wastewater is important because of the risks of formation of toxic by-products especially during the chlorination process. Among the Carbon-based materials, graphene oxide seems to be superior from the removal capacity and this can be explained based on the presence of the carboxy and hydroxy groups which can form strong hydrogen bonds and electrostatic interactions with the proteins – the adsorption capacity is up to 500mg protein/g of graphene oxide. In the case of graphene and CNT the adsorption mainly involves van der Walls forces and do not exceed 100mg protein / g of sorbent [16].

3.2. Graphene-based materials as sensor for environmental applications

Heavy metals level in environment and especially in drinking water is well defined by the international agencies (EPA - U.S. Environmental Protection Agency and WHO - World Health Organization. It is worth to mention that sensors for rapid detection of different heavy metals were developed, which are just turning its colour in the presence of various heavy metals [45] or more complex sensors able to quantify the level of the heavy metals, even mixtures of heavy metals, as published by Wei *et al.* [46]. SnO_2/Reduced Graphene Oxide Nanocomposite was developed and tested for the simultaneous electrochemical detection of Cadmium(II), Lead(II), Copper(II), and Mercury(II) from water. The detection limit was as low as 1.015×10^{-10}M, 1.839×10^{-10} mM, 2.269×10^{-10}M, and 2.789×10^{-10} M for Pb(II), Cu(II) and Hg(II), respectively, being low enough to be used in environmental applications (comparing with the WHO regulations for drinking water).

Phenol detection is many times problematic (especially in the case of using non-enzymatic detection) because of the oxidation products which are inducing surface fouling and inactivation. Sha *et al.* [31] developed a stable, non-enzymatic phenol sensor based on reduced graphene oxide-zinc oxide composite modified glassy carbon electrode. The main advantage comparing with other detection system is related to the possibility of working at lower potential (even 0.35V) because it is not necessary to renewal the surface because of the surface fouling.

Trace level of organophosphoric pesticide can be done also by using graphene-based nanocomposites as sensing agent. The sensing agent / graphene-based nanocomposite was synthesized by starting from graphene oxide (obtained according to Hummer's method) followed by reduction in the presence of ascorbic acid and polymers (polypyrrole and poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate), under reflux (24h). Finally, the addition of $HAuCl_4$ and sodium citrate will allow the formation of the nanocomposite system. Based on the work of Facure *et al.* [32], the as obtained enzyme-free electronic sensor can allow detection of organophosphorus pesticides at trace levels, even if mixtures of two such pesticides are present.

4. Conclusions

Carbonaceous materials are good candidates for environmental applications, along or in association with various other materials. They can be active agent or support. Graphene and graphene oxides were discovered and isolated less than 2 decades, has already demonstrated remarkable properties, some of them being exploitable in environmental applications, for removal (adsorption or degradation) or as sensing element of certain hazardous species. At this moment, studies were carried out on removing or sensing heavy metals, dyes, drugs (their active agents), pesticides, but also, many other applications are expected to be developed in the close future.

Acknowledgements:

The present work was possible due to the EU-funding grant POSCCE-A2O2.2.1-2013-1, Project No. 638/12.03.2014, code *SMIS-CSNR 48652*. The financial contribution received from the national project No: 18 (PN-III-P2-2.1-PTE-2016-0146) is also highly acknowledged.

References:

[1] Li F, Jiang X, Zhao JJ, Zhang SB. Graphene oxide: A promising nanomaterial for energy and environmental applications. Nano Energy. 2015;16: 488-515.

[2] Yu JG, Yu LY, Yang H, Liu Q, Chen XH, *et al.* Graphene nanosheets as novel adsorbents in adsorption, preconcentration and removal of gases, organic compounds and metal ions. Science of the Total Environment. 2015;502: 70-9.

[3] Huang CC, Li C, Shi GQ. Graphene based catalysts. Energy & Environmental Science. 2012;5 (10): 8848-68.

[4] Bao CL, Bi SG, Zhang H, Zhao JL, Wang PF, *et al.* Graphene oxide beads for fast clean-up of hazardous chemicals. J Mater Chem A. 2016;4 (24): 9437-46.

[5] Zhang X, Zhang HT, Li C, Wang K, Sun XZ, *et al.* Recent advances in porous graphene materials for supercapacitor applications. Rsc Advances. 2014;4 (86): 45862-84.

[6] Worsley MA, Pauzauskie PJ, Olson TY, Biener J, Satcher JH, *et al.* Synthesis of Graphene Aerogel with High Electrical Conductivity. Journal of the American Chemical Society. 2010;132 (40): 14067-9.

[7] Peng BQ, Chen L, Que CJ, Yang K, Deng F, *et al.* Adsorption of Antibiotics on Graphene and Biochar in Aqueous Solutions Induced by pi-pi Interactions. Sci Rep-Uk. 2016;6.

[8] Li X, Yu JG, Wageh S, Al-Ghamdi AA, Xie J. Graphene in Photocatalysis: A Review. Small. 2016;12 (48): 6640-96.

[9] Al-Khateeb LA, Almotiry S, Salam MA. Adsorption of pharmaceutical pollutants onto graphene nanoplatelets. Chemical Engineering Journal. 2014;248: 191-9.

[10] Buzaglo M, Shtein M, Kober S, Lovrincic R, Vilan A, *et al.* Critical parameters in exfoliating graphite into graphene. Physical Chemistry Chemical Physics. 2013;15 (12): 4428-35.

[11] Ciesielski A, Samori P. Graphene via sonication assisted liquid-phase exfoliation. Chemical Society Reviews. 2014;43 (1): 381-98.

[12] Li AH, Liu JQ, Feng SY. Applications of Graphene Based Materials in Energy and Environmental Science. Science of Advanced Materials. 2014;6 (2): 209-34.

[13] Hsu HC, Shown I, Wei HY, Chang YC, Du HY, *et al.* Graphene oxide as a promising photocatalyst for CO2 to methanol conversion. Nanoscale. 2013;5 (1): 262-8.

[14] Wu JR, Zhao HY, Chen R, Chuong PH, Hui XH, *et al.* Adsorptive removal of trace sulfonamide antibiotics by water-dispersible magnetic reduced graphene oxide-ferrite hybrids from wastewater. Journal of Chromatography B-Analytical Technologies in the Biomedical and Life Sciences. 2016;1029: 106-12.

[15] Yu F, Li Y, Han S, Ma J. Adsorptive removal of antibiotics from aqueous solution using carbon materials. Chemosphere. 2016;153: 365-85.

[16] Smith SC, Ahmed F, Gutierrez KM, Rodrigues DF. A comparative study of lysozyme adsorption with graphene, graphene oxide, and single-Walled carbon nanotubes: Potential environmental applications. Chemical Engineering Journal. 2014;240: 147-54.

[17] Jiao SF, Jin J, Wang L. Tannic acid functionalized N-doped graphene modified glassy carbon electrode for the determination of bisphenol A in food package. Talanta. 2014;122: 140-4.

[18] Wang YC, Cokeliler D, Gunasekaran S. Reduced Graphene Oxide/Carbon Nanotube/Gold Nanoparticles Nanocomposite Functionalized Screen-Printed Electrode for Sensitive Electrochemical Detection of Endocrine Disruptor Bisphenol A. Electroanalysis. 2015;27 (11): 2527-36.

[19] Madhu R, Karuppiah C, Chen SM, Veerakumar P, Liu SB. Electrochemical detection of 4-nitrophenol based on biomass derived activated carbons. Analytical Methods. 2014;6 (14): 5274-80.

[20] Arduini F, Cinti S, Scognamiglio V, Moscone D, Palleschi G. How cutting-edge technologies impact the design of electrochemical (bio)sensors for environmental analysis. A review. Analytica Chimica Acta. 2017;959: 15-42.

[21] Hazell G, Hinojosa-Navarro M, McCoy TM, Tabor RF, Eastoe J. Responsive materials based on magnetic polyelectrolytes and graphene oxide for water clean-up. Journal of Colloid and Interface Science. 2016;464: 285-90.

[22] Chen H, Gao B, Li H. Removal of sulfamethoxazole and ciprofloxacin from aqueous solutions by graphene oxide. Journal of Hazardous Materials. 2015;282: 201-7.

[23] Zhang YL, Liu YJ, Dai CM, Zhou XF, Liu SG. Adsorption of Clofibric Acid from Aqueous Solution by Graphene Oxide and the Effect of Environmental Factors. Water Air and Soil Pollution. 2014;225 (8).

[24] Song WC, Shao DD, Lu SS, Wang XK. Simultaneous removal of uranium and humic acid by cyclodextrin modified graphene oxide nanosheets. Science China-Chemistry. 2014;57 (9): 1291-9.

[25] Jia WB, Lu SS. Few-layered graphene oxides as superior adsorbents for the removal of Pb(II) ions from aqueous solutions. Korean Journal of Chemical Engineering. 2014;31 (7): 1265-70.

[26] Dichiara AB, Sherwood TJ, Benton-Smith J, Wilson JC, Weinstein SJ, *et al.* Free-standing carbon nanotube/graphene hybrid papers as next generation adsorbents. Nanoscale. 2014;6 (12): 6322-7.

[27] Pavagadhi S, Tang ALL, Sathishkumar M, Loh KP, Balasubramanian R. Removal of microcystin-LR and microcystin-RR by graphene oxide: Adsorption and kinetic experiments. Water Research. 2013;47 (13): 4621-9.

[28] Yang ST, Chen S, Chang YL, Cao AN, Liu YF, *et al.* Removal of methylene blue from aqueous solution by graphene oxide. Journal of Colloid and Interface Science. 2011;359 (1): 24-9.

[29] Kumar GG, Babu KJ, Nahm KS, Hwang YJ. A facile one-pot green synthesis of reduced graphene oxide and its composites for non-enzymatic hydrogen peroxide sensor applications. Rsc Advances. 2014;4 (16): 7944-51.

[30] Lv MJ, Wang XB, Li J, Yang XY, Zhang CA, *et al.* Cyclodextrin-reduced graphene oxide hybrid nanosheets for the simultaneous determination of lead(II) and cadmium(II) using square wave anodic stripping voltammetry. Electrochimica Acta. 2013;108: 412-20.

[31] Sha R, Puttapati SK, Srikanth VVSS, Badhulika S. Ultra-sensitive phenol sensor based on overcoming surface fouling of reduced graphene oxide-zinc oxide composite electrode. Journal of Electroanalytical Chemistry. 2017;785: 26-32.

[32] Facure MHM, Mercante LA, Mattoso LHC, Correa DS. Detection of trace levels of organophosphate pesticides using an electronic tongue based on graphene hybrid nanocomposites. Talanta. 2017;167: 59-66.

[33] Chawla J, Kumar R, Kaur I. Carbon nanotubes and graphenes as adsorbents for adsorption of lead ions from water: a review. Journal of Water Supply Research and Technology-Aqua. 2015;64 (6): 641-59.

[34] Han Z, Tang ZH, Sun YH, Yang JH, Zhi LJ. Controllable Synthesis of Tetraethylenepentamine Modified Graphene Foam (TEPA-GF) for the Removal of Lead ions. Sci Rep-Uk. 2015;5.

[35] Wei Y, Xu L, Tao YX, Yao C, Xue HG, *et al.* Electrosorption of Lead Ions by Nitrogen-Doped Graphene Aerogels via One-Pot Hydrothermal Route. Industrial & Engineering Chemistry Research. 2016;55 (7): 1912-20.

[36] Bian Y, Bian ZY, Zhang JX, Ding AZ, Liu SL, *et al.* Effect of the oxygen-containing functional group of graphene oxide on the aqueous cadmium ions removal. Applied Surface Science. 2015;329: 269-75.

[37] Nam SW, Jung C, Li H, Yu M, Flora JRV, *et al.* Adsorption characteristics of diclofenac and sulfamethoxazole to graphene oxide in aqueous solution. Chemosphere. 2015;136: 20-6.

[38] Qiu HM, Fan LL, Li XJ, Li LL, Min S, *et al.* Determination sulfamethoxazole based chemiluminescence and chitosan/graphene oxide-molecularly imprinted polymers. Carbohydrate Polymers. 2013;92 (1): 394-9.

[39] Rostamian R, Behnejad H. A comparative adsorption study of sulfamethoxazole onto graphene and graphene oxide nanosheets through equilibrium, kinetic and thermodynamic modeling. Process Safety and Environmental Protection. 2016;102: 20-9.

[40] Wang C, Li H, Liao SH, Zheng H, Wang ZY, *et al.* Coadsorption, desorption hysteresis and sorption thermodynamics of sulfamethoxazole and carbamazepine on graphene oxide and graphite. Carbon. 2013;65: 243-51.

[41] Zhou L, Alvarez OG, Mazon CS, Chen L, Deng HP, *et al.* The roles of conjugations of graphene and Ag in Ag3PO4-based photocatalysts for degradation of sulfamethoxazole. Catal Sci Technol. 2016;6 (15): 5972-81.

[42] Konicki W, Aleksandrzak M, Moszynski D, Mijowska E. Adsorption of anionic azo-dyes from aqueous solutions onto graphene oxide: Equilibrium, kinetic and thermodynamic studies. Journal of Colloid and Interface Science. 2017;496: 188-200.

[43] Radulescu M, Popescu S, Ficai D, Sonmez M, Oprea O, *et al.* Advances in Drug Delivery Systems, from 0 to 3D Superstructures. Current Drug Targets. 2016;17.

[44] Dai CM, Liu YJ, Zhou XF. Molecularly imprinted polymer assembled on Fe3O4/graphene oxide for clofibric acid (CA) removal from aqueous solution. Abstracts of Papers of the American Chemical Society. 2014;248.

[45] Fu XL, Lou TT, Chen ZP, Lin M, Feng WW, *et al.* "Turn-on" Fluorescence Detection of Lead Ions Based on Accelerated Leaching of Gold Nanoparticles on the Surface of Graphene. Acs Applied Materials & Interfaces. 2012;4 (2): 1080-6.

[46] Wei Y, Gao C, Meng FL, Li HH, Wang L, *et al.* SnO2/Reduced Graphene Oxide Nanocomposite for the Simultaneous Electrochemical Detection of Cadmium(II), Lead(II), Copper(II), and Mercury(II): An Interesting Favorable Mutual Interference. Journal of Physical Chemistry C. 2012;116 (1): 1034-41.