SORPTION OF ZIRCONIUM AND IRON WITH GRAPHENE OXIDE AND PREPARATION OF GRAPHENE SHELLS FOR ELECTROSORPTION

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Abstract

The graphene shells were prepared to apply as the electrosorbent for the electrosorption. Firstly, graphene oxide was collected to determine sorption activities of zirconium and iron. The solubility (dispersion in water) of graphene oxide was studied. And then, the interaction of zirconyl chloride solution with the graphene oxide was also determined. Moreover, the sorption of iron with graphene oxide gave the magnetic sorbent. The hollow nanosphere graphene shells with the thickness of 6 – 8 nm were obtained by the methane pyrolysis on spherical SiO_2 particles. The electrosorption of Na^+ ions (NaCl aqueous solution) was carried out on the nanosphere carbon shells electrodes. The electrosorption of Zr ions ($ZrOCl_2$ aqueous solution 1.8 – 5.0 mg/g) on the graphene electrodes was also determined. From the experimental results the maximum sorption capacity was Zr (50.56 mg/g) on graphene electrode.

Keywords: graphene, graphene oxide, electrosorbent, solubility, nanosphere.

Introduction

Graphene and graphene oxide are relatively new carbon materials, in which recent years had attracted much attention of researchers, because of their unusual properties and wide possibilities of practical application in various branch of engineering. Graphite oxide is related to graphene oxide (GO) material, which is often considered an analogue of graphene oxide, and has been obtained for the first time more than 150 years ago (Brodie, 1859; Brodie, 1860), and the first report of it was done twenty years earlier (Schafhaeutl, 1840). The synthesis was based on the oxidation of graphite; oxidation afterwards became the basis of all chemical (covalent) methods of obtaining colloidal dispersions of graphite. The ratio of C:O in the graphite oxide is 1.62 – 2.57 (Buchsteiner *et al.*, 2006). For graphene oxide with a few

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different values: 2 – 4, which correspond to the formula is $C_8O_4H_5 - C_8O_2H_3$ (Pei and Cheng, 2011).These materials are closely related to each other but in some properties they are quite different. Graphene is bad wettability on liquid, insoluble in water and organic solvents and is capable of forming very dilute solutions at the expense of the weak interactions with solvents. The study of comparative experimental and molecular dynamics model behavior on changing the pH showed that the GO is protonated at low pH and forms aggregates (Shih *et al*., 2012). Graphene is well electrically conductive and can participate in the electrosorption process (capacitive deionization) – nonchemical form of ion sorption on polarized electrodes in the absence of electrolysis (Hou *et al*., 2006). By reducing and removing of potential, as well as change in sign of the charge and the simultaneous change of the flow direction of fluid, capacitive deionization allows concentrate of salt without cost of reagents (Porada *et al*., 2012). Graphene oxide (GO), in contrast to graphene is capable of forming stable dispersions in water and organic solvents (Nakajima and Matsuo, *1994)*, so far as on the surface contains different functional groups (carboxyl, hydroxyl, phenolic, epoxy, and others) (Lee *et al.,*2010).These groups are easily formed by oxidation of graphene in strongly acidic medium and in aqueous solutions it can participate in the ion exchange process. Since the concentration of ion exchange groups on the surface of the graphene oxide may be very high, on the sorption capacity of graphene oxide is significantly superior to conventional ion exchange resin based on a polymer.

The main aim of this research was to study graphene oxide as an ion-exchange sorbent and graphene as electro-sorbent. In this work several problems were solved:

- Preparation of aqueous dispersions of graphene oxide and study the effect of pH on the solubility of graphene oxide;
- To study the interaction of zirconyl chloride with graphene oxide;
- To synthesise the magnetic sorbents based on graphene oxide and magnetite nanoparticles to facilitate phase separation with ion-exchange sorption;
- To develop the methods for grapheneproducing by pyrolysis of the most accessible of hydrocarbons from methane (town gas) on metal oxides with a large surface area;

- To obtain hollow carbon nanospheres and test created from these electrodes for electrosorption of sodium chloride;
- To study an electrosorption of zirconyl chloride solutions on the graphene electrodes.

Materials and Methods

Materials

Graphene samples were obtained from the plants of Global Co. Ltd. (Davydov *et al*., 2012). Graphene samples have been a specific surface area 1003 m^2/g; 1406 m^2/g 1660 m^2/g and 1906 m^2/g. Additionally, graphene shells were used, which were produced by pyrolysis of CH_4 on SiO_2 at 600˚C for 30 min. Purification of catalyst was performed by hydrofluoric acid (48 wt. %).

Preparation of graphene oxide

Several graphene samples were used for the preparation of graphene oxide. Graphene sample was mixed with a solution of H_2SO_4 and HNO_3 (volume ratio acid 3:1) followed by ultrasonication with the help of dispersant rod for 2 min and then oxidized in a domestic microwave oven (100 – 200 watts) at different times. After cooling, the mixture was centrifuged, the precipitate was diluted with distilled water and again centrifuged 3-4 times until the dispersion was ceased. Thereafter 200 mL of distilled water and 5mL of 38% HCl were added, subjected to ultrasonic treatment and centrifuged. These operations were also repeated several times to obtain colorless overflow. The precipitate was dried at 60˚C.

Ion-exchange sorption method

A weighed amount of the GO is dispersed with a certain volume of water and a solution $Zr(OH)_2Cl_2$, $FeSO_4$, $Fe(NO_3)_3$ and $FeSO_4 + FeCl_3$(1:2) was added. After mixing for 1-2 h, the precipitate was filtered on paper and dried at atmosphere. And then it was calcined at 800˚C for 3 h, cooled in the desiccator and weighed the remaining ZrO_2 or Fe_2O_3. The value of pH was measured by pH meter, Martini pH-56.

Carbon coating of metal oxides

Carbon coating of metal oxides was performed by pyrolysis. Pyrolysis was carried out in a tubular quartz reactor using municipal (domestic) gas containing 99% CH_4. Quartz boat with the portion of the precursor SiO_2 particles (250 mg) was added rapidly via the rod in the hot zone heated to a predetermined temperature while feeding it into methane (50–660 mL/min) and maintained within necessary time (20–60 min) and then so-quickly moved into the cold zone. The mass obtained was determined by weighing the sediment product before and after aging for 3 h in air at 750 – 800 ˚C.

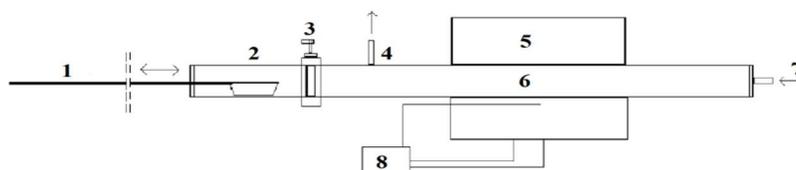Pyrolysis was carried out in a quartz tubular reactor as shown in Figure 1.

Figure1: Scheme of pyrolytic setting: 1 – boat rod for introducing into the reaction zone; 2 – boat with a substance; 3 – gas seal; 4 – output connection for the reaction gases; 5 – electric furnace; 6 – quartz tube; 7 – inlet for introducing gas; 8 – a device for measuring and regulating the temperature.

Apparatus and equipment

Measurement of specific surface area was carried out by using the apparatus AUTOSORB-1C/MS/TPR (Quantachrom) and SORBI-MS by volume adsorption of N_2.

Electron micrographs (photomicrographs) were obtained by using the scanning microscope (Chem JEOL, JSM-6510LV, Oxford instruments X-Max 20 mm^2,batch switching center, MUCTR) and transparent microscope (FEI Tecnai G^2 30 ST, Institute of Crystallography, Russian Academic Science).

The pH-meter (MARTINI pH-56) was used for measuring pH of sample solution.

The preparation of GO dispersion was carried by using ultrasonic sonicator (dispersant). After centrifugation, the remaining GO particles were dried and weighed. TDS-3 meter was used for the measurement of total dissolved solid(TDS) of solution.

Results and Discussion

Study of the solubility of graphene oxide

Oxidation of graphene was carried out with a mixture of concentrated H_2SO_4 and HNO_3, with a volume ratio is 3:1.

Table 1 shows the GO samples with different solubilities as a function of pH. The solubility of GO samples was found to increase at pH neutral condition.

Table 1: Dependence of Solubility of GO samples on pH.

Sample	pH	Solubility of GO, mg/mL	pH	Solubility of GO, mg/mL
GO -1	2.69	3.27	7.13	10.6
GO -2	2.90	4.06	7.01	11.6
GO -3	2.77	6.10	7.05	14.3
GO -4	3.60	0.30	7.01	1.90
GO -5	2.82	0.57	7.05	2.10
GO -6	2.48	1.70	7.08	6.40
GO -7	3.74	5.40	7.02	7.50
GO -8	2.82	6.82	7.10	14.8
GO -9	3.62	7.30	7.06	7.70

The series of experiment was attained with a more high solubility and were studied the influence of pH value on the solubility. These results are shown in Figure 2.
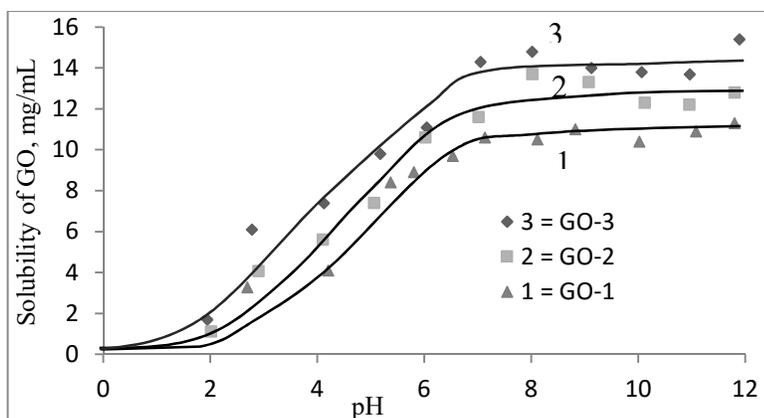
Figure 2: The dependence solubility of three GO samples with different oxidation state on pH value.

The solubility of GO in lower pH value (in strong acid condition) is near to zero. By increasing the pH value from 2–3 to 6–8 which is gradually increased, reached to 11 and even 15 g/L, but after pH value of 8–9 rather fall and then rise.

The most characteristic curves of dependence composition from concentration of zirconyl chloride was obtained with the samples of GO - 4, GO -7, GO -9in Figure 3.
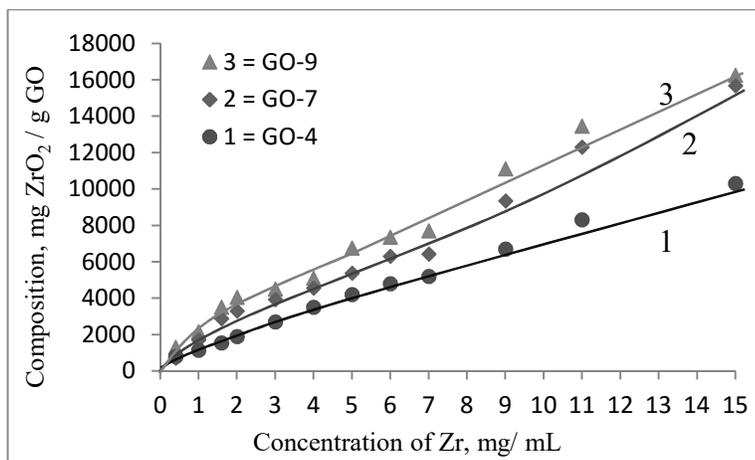
Figure 3: The dependence of composition product, the interaction of GO with the concentration of Zr, at the correlation of mass of GO and volume of Zr solution is 1:10, and the contact time is τ_c = 120 min.

Ion-exchange sorption of Fe^{2+} and Fe^{3+} with graphene oxide

In this research the GO samples with different solubilities in water (concentration in stable colloidal solution) were used. For the determination of metal sorption amount, the dry precipitate was calcined in atmosphere at 750–800°C for 3 h, and cooled in the desiccator and weighed as an oxide form (Fe_2O_3). The capacity of sorbent in all process conditionally expressed in Fe_2O_3 wt. per 1 g of sorbent.

Figure 4 indicates that as the solid liquid ratio decreases the sorption capacity of GO gradually increases.
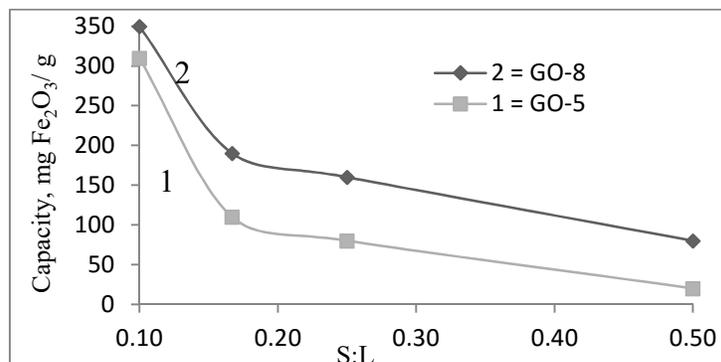

Figure 4: The dependence of capacity of GO-5 (1) and GO-8 (2) on S:L ratio with a concentration of $FeSO_4$ 0.108 g Fe/L, the initial pH value is 4.31 (pH precipitation of solution is 4.36)

The experiments were carried out with the solution of $Fe(NO_3)_3$. Figure 5 shows the equivalence values was settled at 20–30 min and, this means the different sorption capacity of sample GO with a different solubility.
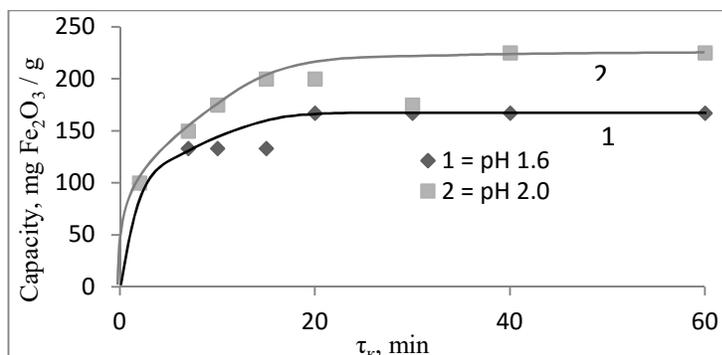

Figure 5: Influence of contact time on the capacity of GO-6 with concentration of $Fe(NO_3)_3$ 0.167 g Fe/L, S:L = 0.58, pH = 1.6 (1) and pH = 2.0 (2).

Preparation of magnetic sorbent from graphene oxide

The mixture solution of $FeCl_3$ (1 g) and $FeSO_4$ (0.5 g) was prepared in 1 L of distilled water, at pH = 3.45 and S:L = 0.1.

The GO dispersion sample was mixed with a given concentration and volume of $FeCl_3$ and $FeSO_4$ (1.5 g/L), after then the contact time was 2 h without any shaking, and obtained then filtered the residue. The obtained residue was dried at 50°C. Thereafter to get through on 1 h at 350°C in the flow rate of CH_4 is 588 mL/min.
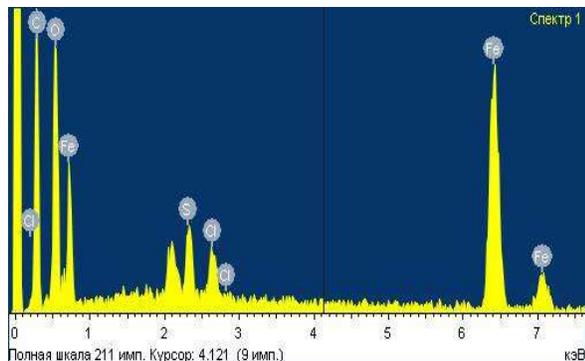

Figure 6: EDX spectrum of magnetic sorbent particles and its composition

The composition of elements in the magnetic sorbent in Table 2 shows the atomic ratio of O:Fe was composed of 1.36 and near to the calculated value for the Fe_3O_4 (1.33). Other impurities of sulfur and chlorine were detected in the precursors.

Table 2: Composition of magnetic sorbent

Element	Mass %	Atom %
C	32.87	57.23
O	17.79	23.25
S	2.42	1.58
Cl	1.73	1.02
Fe	45.18	16.92
Total	**99.99**	**100.00**

Preparation of hollow carbon nanosphere

The SiO_2 initial particles were regular sphere with high scattered diameter as shown in Figure 7.
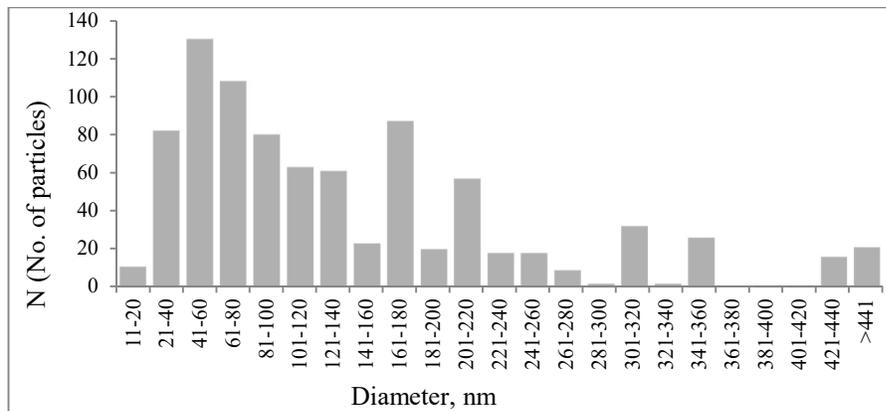

Figure 7: The distribution diameter of spherical SiO_2 particles

The value of N was characterized by the number of particles with defined diameter on photomicrograph.

The CH_4 pyrolysis of SiO_2 was carried out at 500 – 800 $°$C. The typical dependence of mass increment with time at the two different temperatures is shown in Figure 8 and the influence of gas flow rate is shown in Figure 9.
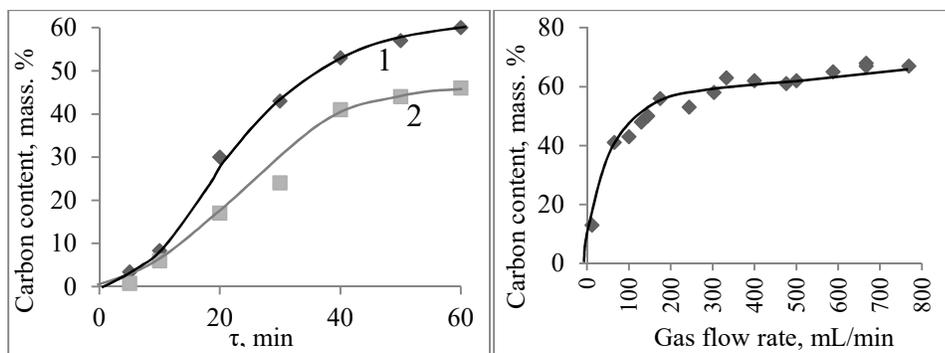

Figure 8: The mass increment on the pyrolysis at temperature 800 $°$C (1) and 700$°$C (2)

Figure 9: The influence of gas flow rate no mass increment at the pyrolysis temperature of 850 $°$C for 120 min

The deposition of carbon on SiO_2 becomes steady in the flow rate ranging from 400 to 800 mL/min at pyrolysis temperature 850 ˚C for 60 min. The increment of gas flow rate more than 200–250 mL/min shows the weakly deposit amount of carbon (and, consequently the rate of pyrolysis). The mass increment of maximum amount has reached to 72 mass % at the temperature range of 850 – 900 ˚C. This behavior was attested the catalytic effect of SiO_2 particles, which is weaken the increment of carbon deposit layer thickness on the particles shown in Figure 10.

On the submitted photomicrograph it can be seen in Figure 11 that the spherical form of particles were maintained. This also confirmed the photomicrograph of hollow carbon spheres, obtained by dissolution of SiO_2 in dilute hydrofluoric acid.
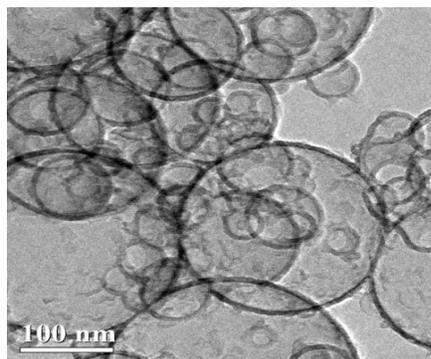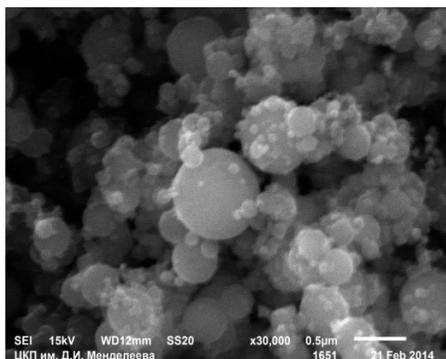

Figure 10: SEM photomicrograph of carbon shells coating on SiO_2 particles

Figure11: TEM photomicrograph of hollow sphere carbon shells

Table 3 shows the calculated values of the carbon shells thickness, obtained by pyrolysis at different temperatures and assumption, that the medium diameter of SiO_2 particles were composed of 60 nm.

Table 3: The Composition of Carbon on SiO_2 Particles at Different Temperatures and Calculated Thickness of Carbon Shells

Temperature, °C	Contact time, min	Carbon content, mass. %	Thickness of shells, (nm) at diameter of SiO_2 particles, (nm)			
			50	60	70	80
550	60	5.0	0.5	0.6	0.7	0.8
600	30*	7.5*	0.6	0.9	1.0	1.2
600	60	10	0.8	1.2	1.4	1.6
650	60	34	3.0	3.6	4.2	4.8
700	60	47	3.5	4.2	4.9	5.6
750	60	65	5.5	6.6	7.7	8.8
800	60	72	5.6	6.7	7.8	8.9

*Gas flow rates 466 mL/min, in other cases 333 mL/min.

The specific surface area (S_{sa}) of carbon nanospheres are 175 m^2/g at 600°C with a specific density of 0.029 g/mLobtained at 850-900°C and with the specific surface area of 12–13 m^2/g (that is near the $S_{sa}$of SiO_2). However, the nanospheres were found to make easier for molecules of solvent permeable.

Study of NaCl electrosorption on carbon nanospheres

For the study of electrosorption one sample was chosen from the obtained carbon microspheres with the specific surface area 175 m^2/g. The total mass of carbon nanospheres in each electrode was composed of280 mg, the intermediate electrical voltage in sorption was 2.0 V, the distance between the two electrodes was 2 cm. For the measurement of concentration of solution were used the analyzer TDS-3 meter (ppm, mg/L). The results of NaCl sorption experiments are shown in Figure 12.

The result were shown for the first time, that the sorption capacity of graphene shells on NaCl sorption proved in this stage that an electro-sorption is likely to take place on another carbon materials. From the results, an electrosorption of the electrode construction occurred relatively slowly, and desorption became faster.
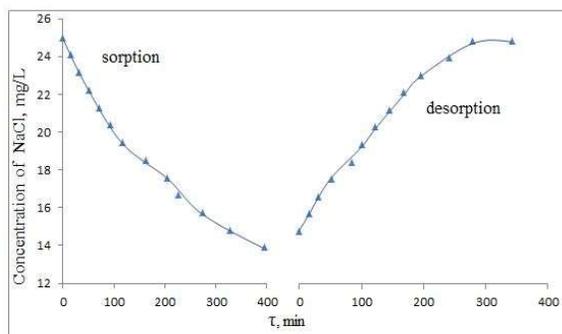
Figure 12: The measurement of NaCl concentration versus time in the aqueous solution at the electrosorption and desorption with mechanical stirring

Study of electrosorption of zirconyl chloride with graphene

For the determination of zirconium content in the solution the gravimetric method, amperometric titration and the pH meter were used. The zirconyl chloride were precipitated with ammonia and dried in vacuum, sintered with the crucible and weighed the remaining oxides.

For carrying on the electrosorption process, the zirconyl chloride solution was prepared with the concentration in the range of 1.8–5.0 mg Zr/mL. The aliquot was then taken out and were analyzed; its concentration was determined by the gravimetric analysis. Experimental results are shown in Figure 13, the initial voltage 1.47 V, the distance between the two electrodes are 2 cm and the initial concentration of zirconyl chloride 2.0 g/L.
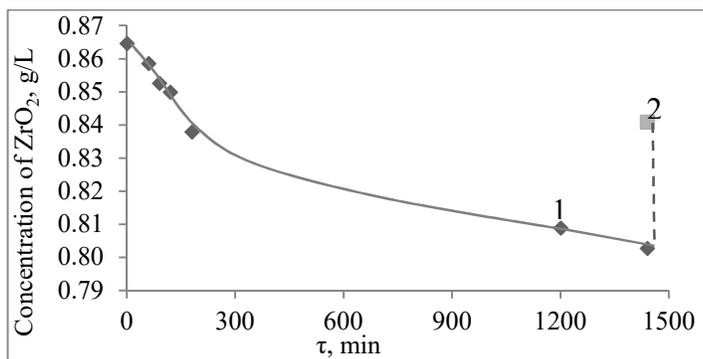

Figure 13: Sorption on one pair of electrode and two parallel connecting batteries, sorption (1) and desorption (2)

The summary of experiment results are shown in table 4.

Table 4: Sorption Capacity of Graphene

Amount of parallel connecting battery on the calculated electrodes	Sorption capacity, mg ZrO_2/ g graphene	Sorption capacity, mg Zr/g graphene
2	47.56	35.20
2	48.86	36.16
3	60.53	44.80
3	68.31	50.56

The most complex and sensitive to the different properties of initial aqueous solution proved an electrosorption process of zirconyl chloride. Therefore the application of graphene have been the definite perspective and for the purification of electrosorption and concentration of technological solution from the different composition.

Conclusion

The study of the solubility (dispersion in water) of GO has shown that it is dependent on the degree of oxidation and gradually rises from nearly pH ~ 1 to pH 8–9the solubility increased 11–15 mg/mL. The interaction of zirconyl chloride solution with the GO at the contact time 120 min were studied; that the product compositions were separated in acidic condition, which depends on the Zr concentration, the solubility of GO, and the ratio of reagents. The highest composition value of ZrO_2 were found to consist of 10 – 16 g/g GO.

When the ion-exchange sorption of Fe^{2+} and Fe^{3+} individually by the GO was investigated, it was found that the sorption capacity of 2.5 g/g was obtained. When the two salts of Fe were used to form Fe_3O_4, using the GO sample, the sorption capacity is found to be 63 mass percent was obtained. At the temperature 500 – 900 ˚C, the pyrolysis of SiO_2 particles in the low density of graphene shells with thickness of 6 – 8 nm was obtained.

The test experiment of Na^+ ions electrosorption was carried out from the aqueous solution of NaCl on the nanosphere carbon shells electrodes, it was shown that the sorption capacity was achieved to 10 – 11 mg/g of C shells. From the aqueous zirconyl chloride solution studied on electrosorption

of Zr ions with the concentration of 1.8–5.0 mg Zr/mL on the graphene electrodes, it showed that the maximum sorption capacity were composed of 50.56 mg Zr/g of C.

Acknowledgements

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