

Article

Use of Reduced Graphene Oxide to Modify Melamine and Polyurethane for the Removal of Organic and Oil Wastes

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Abstract: Methods for obtaining efficient sorption materials based on highly porous melamine and polyurethane matrices modified with reduced graphene oxide were developed. These materials are promising for solving environmental problems such as water pollution with organic products by sorption treatment. Reduced graphene oxides (rGOs) were synthesized from graphene oxide suspensions using potassium hydroxide, ascorbic acid or hydrazine hydrate. Composites with obtained rGO and melamine and polyurethane foam were produced for further characterization. The composites demonstrate high sorption of organic pollutants (oil, diesel fuel and gasoline) and low sorption of water. The composites were comprehensively analyzed by physicochemical techniques (SEM, XPS, Raman spectroscopy, UV–Vis) to elucidate the mechanism of sorption.

Keywords: reduced graphene oxide; sorption; melamine; polyurethane; oil; diesel; XPS



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1. Introduction

Technological disasters associated with oil spills on water occur quite often in the modern world and require a quick and effective solution. In recent years, porous polymer sorbents, such as polyurethane foam [1–3], polystyrene [4] and melamine [5–9], have often been used to mitigate the consequences of such disasters. These sorbents are efficient materials due to their low density, ease of use, accessibility and low operating costs, but they have the disadvantage of poor sorption selectivity for organic pollutants. This disadvantage can be solved by modifying these sorbents with carbon nanomaterials [10–12], which can also be used as separate sorbents for the removal of oil and petroleum products from a water surface [13–17].

In an enterprise's operation of the nuclear fuel cycle, it continuously generates liquid radioactive waste (LRW), which has organic and inorganic origins. Organic radioactive wastes are the main extractants, and their solvents are used in the spent nuclear fuel reprocessing cycle. Due to their high toxicity and explosiveness, such wastes require special handling [18]. With liquid extraction at various stages of nuclear fuel processing, the release of various radionuclides leads to a partial entry of organic substances into the LRW solution, significantly complicating their further handling. Therefore, an urgent problem is the purification of aqueous solutions of LRW from traces of organic substances. In this regard, selective sorbents that would only sorb organic substances are also needed. Hydrophobic materials can be used for the sorption of organic polar compounds.

Various types of sorbents have already been studied for pollutant removal from aqueous solutions, such as clay [19], activated carbon [20] and biosorbents [21,22]. In the past decade, graphene has attracted attention due to its unique physicochemical properties, such as a large specific surface area, high thermal conductivity, hydrophobicity and excellent mechanical properties [23–25]. Because of these properties, graphene has demonstrated

outstanding performance in various applications [26–28]. Moreover, it also showed promising results for oil or organic pollutant removal from aqueous solutions [29,30]. Graphene oxide (GO) with various hydrophilic functional groups is an effective material for the sorption of heavy metals and organic dyes [31,32]. Reduced graphene oxide (rGO) also shows efficient sorption of oil and heavy metals [33,34]. Many studies have already been devoted to the sorption characteristics of GO and rGO powders [35,36]. Carbon nanotubes also have adequate sorption characteristics [37]. However, since GO, rGO and carbon nanotubes are nanomaterials by themselves, the practical application of these powders and their collection after the sorption process are challenging. These materials lead to additional complications during the elimination of man-made environmental pollution. Because of these difficulties in collecting and processing powders, graphene-containing highly porous monolithic materials may be more effective. Porous materials have excellent sorption characteristics [30,38]. For example, the sorption capacity of graphene aerogel to organic solvents reaches 86 g/g [30], which is much higher than commonly used sorbents. Most studies are devoted to the sorption of oils and organic solvents by graphene aerogels [39,40]. An increase in material porosity leads to an increase in sorption values [30,38].

Given this context, we developed a new, effective method for obtaining effective sorbents based on highly porous, commercially available matrices using the example of polyurethane foam and melamine with surface modification by hydrophobic carbon materials. Colloidal solution of GO was used as the starting material for processing matrices. Due to its stability, it is possible to place GO sheets evenly on the polymer sponge surface for further reduction in order to obtain a hydrophobic material.

To obtain hydrophobic materials for the sorption of organic pollutants, it is necessary to synthesize rGO. There are various reduction techniques; one of them is using ascorbic acid as a reducing agent [41,42]. This technique is a “green” recovery method without the use of toxic reagents. Moreover, the synthesis does not require the use of expensive equipment, high temperatures and other energy-consuming resources, and also occurs in a fairly short period of time. Another “green” method for obtaining reduced graphene oxide is based on concentrated alkali solution as a main reagent [43]. The most common and effective method is reduction using hydrazine [44,45].

This work is devoted to the surface modification of melamine and polyurethane sponges. These modified composite materials are promising for purifying aqueous solutions from oil and gasoline product pollutants with minimal water sorption. rGO was chosen as the reagent for surface modification. In this work, three different methods of graphene oxide reduction were utilized to assess the degree of reduction using various reagents and to select the most suitable reagent to modify highly porous matrices of polyurethane foam and melamine. Commercial polyurethane foam sponge and melamine polymer sponge were used for following rGO treatment. Melamine polymer sponge was chosen due to its high porosity, excellent elasticity and high adsorption of both oil and water [5,46–48]. Polyurethane sponge material was selected due to its high porosity and excellent elasticity; however, polar functional groups, such as carboxyl groups, which are present in the composition of polyurethane frameworks, lead to adequate water wettability of the surface, thereby reducing the selectivity and overall efficiency of the material in terms of sorption of organic pollutants [3]. The samples were characterized by physical and chemical methods including Raman spectroscopy, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and ultraviolet–visible spectroscopy (UV–Vis). Sorption experiments were also carried out using oil, diesel fuel, gasoline and water.

2. Materials and Methods

2.1. Chemicals and Materials

Raw materials: Melamine foam (GORDANA, Russia), polyurethane foam (Russia), graphene oxide (Zonko LLC, Houston, TX, USA). Precursors were characterized by X-ray photoelectron spectroscopy (Figure S1, Table S1). Reagents used: Ethanol (C_2H_5OH , 96%), ascorbic acid (purissimum), ammonia (25%), hydrazine hydrate ($N_2H_4 \times H_2O$, 99%),

potassium hydroxide (purissimum), deionized water (with a specific resistance of at least 1 MΩ·cm).

Oil from the Tsarichanskoye deposit was used (density at 20 °C equal to 848 kg/m³). We also used gasoline BR-2 with a density of 700 kg/m³ at 20 °C and DT-3-K5 brand diesel fuel, type I, with a density of 818 kg/m³ at 15 °C.

All chemicals were used as received without further purification.

2.2. Preparation of Melamine-rGO and Polyurethane-rGO Foam Composites

2.2.1. Synthesis of rGO Precursors

GO powder was used to obtain a colloidal solution. First, 1 g of GO was dispersed in 1 L of deionized water, and 5 mL of ammonia (25%) was added to obtain a stable GO solution (pH ≈ 10). The colloidal solution was under ultrasonic treatment for 2 h.

Three methods were used to obtain rGO suspensions. The first method of GO reduction was performed by using ascorbic acid as a reducing agent. For this, 0.5 g of ascorbic acid was placed in the prepared 500 mL dispersion of GO with a concentration of 1 g/L. The prepared mixture was heated to 60 °C and kept for three hours. The second method of GO reduction was performed using hydrazine hydrate as a reducing agent. For this, 10 mL of hydrazine hydrate was placed in the prepared 500 mL dispersion of GO with a concentration of 1 g/L. The prepared mixture was heated to 90 °C and kept for 1 h. The last method of GO reduction was performed using potassium hydroxide as a reducing agent, where 10 mL of 8 M potassium hydroxide solution was added to the prepared 500 mL dispersion of GO with a concentration of 1 g/L. The prepared mixture was heated to 90 °C and kept for 1 h. A general scheme of the reduction of graphene oxide is given in the Supplementary Materials (Figure S2).

2.2.2. Preparation of Composites

The general scheme for obtaining sponge composites is shown in Figure 1. First, 2 × 2 × 2 cm³ pieces of melamine or polyurethane were cut using a special thin blade. These pieces were placed into the prepared colloidal solution of rGO. After three hours of treatment in the colloidal solution, the samples were placed in an oven for 12 h (T = 60 °C).

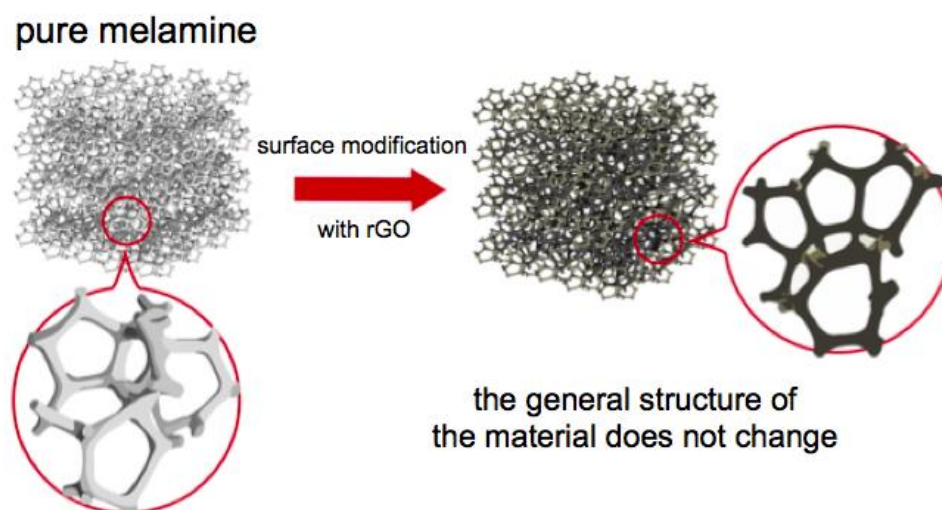


Figure 1. General scheme for obtaining sponge composites.

Dried samples were treated with ethanol to wash out an excessive amount of reduced graphene oxide. After the cleaning, samples were processed again in the oven for 12 h (T = 60 °C).

2.3. Characterization of Composites

Raman spectra were obtained with a Renishaw inVia Reflex Microscope system (Renishaw, New Mills Wotton-under-Edge, UK) with a 633 nm He–Ne laser as the excitation source. The 50× magnification was used for laser focusing and the laser power was kept at about 0.2 mW.

The surface morphology of the samples was studied using scanning electron microscopy (SEM). SEM images were obtained using a Carl Zeiss NVision 40 microscope (3000–300,000×).

X-ray photoelectron spectroscopy was used to characterize the surface of highly porous matrices before and after modification. Spectra were acquired on an Axis Ultra DLD spectrometer (Kratos Analytical, Manchester, UK) using the monochromatic AlK α radiation source. The pass energies of the analyzer were 160 eV for survey spectra and 40 eV for high-resolution scans.

2.4. Sorption Experiment Procedure

A series of sorption experiments of composites in water, gasoline, oil and diesel fuel were conducted to characterize their sorption properties. In the first step, the mass of the samples was fixed before the experiment (m_0). After measurement, samples were kept in a beaker with an excess amount of sorbing liquid for 2 min, which was the time needed to saturate the sample with organic matter. At the end of the sorption process, highly porous matrices were carefully collected using special sieves to drain excess liquid. The mass of the samples after the sorption process (m_1) was measured. The gravimetric sorption capacity (Q_m) was calculated using the obtained data according to the formula:

$$Q_m = \frac{m_1 - m_0}{m_0} \quad (1)$$

where m_1 is the mass of the sample after the sorption process and m_0 is the initial mass of the sample [8,49,50].

3. Results and Discussion

3.1. Synthesis of the rGO

rGO samples were synthesized using three different reducing agents: ascorbic acid (rGO–ascorb), hydrazine hydrate (rGO–HH) and potassium hydroxide (rGO–KOH). Graphene oxide reduction mechanisms are given in the Supplementary Materials. Figure 2 shows UV–Vis spectra and photos of rGO colloidal solutions obtained using various reducing agents. (The full spectrum of rGO–ascorb is given in Figure S4.) The color of suspensions changed from yellow-brown (initial GO) to black (rGO), which is evident in the GO reduction implementation process [42]. The aggregation of rGO sheets also confirms the removal of hydrophilic functional groups due to π – π stacking interaction [51]. The rate of aggregation increases from rGO–KOH to rGO–HH, which is clearly seen from the synthesized colloidal solutions, in which black rGO aggregates are formed. This indicates a more effective removal of oxygen-containing functional groups. The initial colloidal solution of GO has two distinctive features: the main absorption peak at 227 nm, which is characterized by π – π^* transitions in the C=C bond, and a broad absorption peak at 303 nm. The last peak is associated with n – π^* C=O transitions in carboxyl and carbonyl groups [52]. This peak can also appear due to optical transitions between the π and π^* states in nanosized sp^2 -domains that remained in GO after oxidation [53]. During the reduction process, the absorption peak corresponding to 227 nm in GO is gradually red-shifted, up to 268 nm for rGO–HH. The peak of the rGO–HH spectrum is similar to the peak of the π – π^* transition, which is in the 265–268 nm region. This is a distinct sign of a high degree of GO reduction [54]. Meanwhile, absorption peaks at 228 nm and 243 nm for rGO–ascorb and rGO–KOH, respectively, indicate that oxygen functional groups are not completely eliminated when ascorbic acid and potassium hydroxide are used as reducing agents. In the case of reduction with ascorbic acid, the UV–Vis spectrum has an absorption peak at 284 nm,

which refers to the residues of unreacted ascorbic acid. Due to the incomplete reduction of GO using KOH, the resulting colloidal solution is stable. It can have a satisfactory effect on the surface modification processes of highly porous polyurethane foam and melamine matrices, particularly on the uniformity of the coating with a graphene-containing material due to the stability of the colloid for processing.

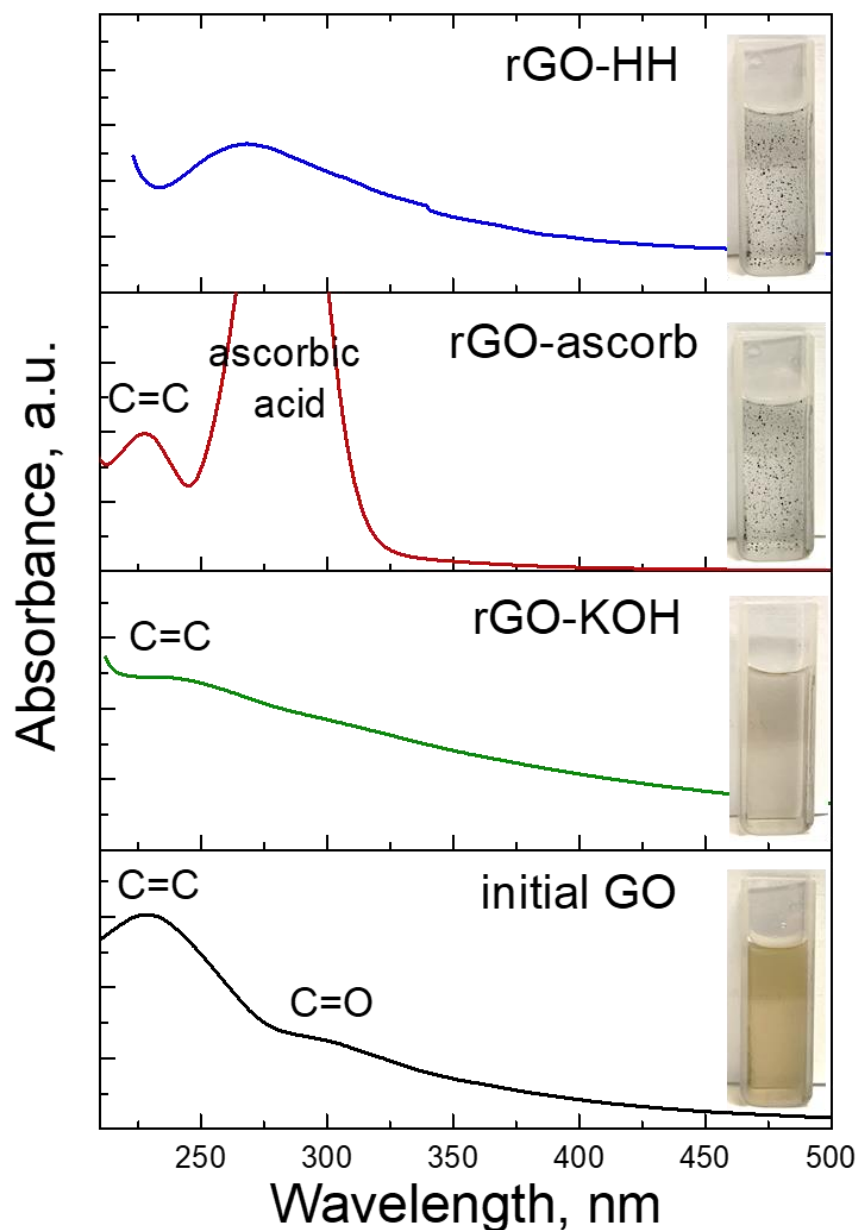


Figure 2. Absorption spectra of rGO-HH, rGO-ascorb, rGO-KOH and initial GO suspensions. The inset shows photographs of the obtained colloidal solutions. The full-scale data for rGO-ascorb are presented in Figure S3.

3.2. Comparison of Obtained rGO-Foam Composites

Figure 3 shows a photo of the melamine-rGO composite. The resulting composite is visually evenly filled with rGO. At the same time, the sample is extremely light, as can be seen in the photo.

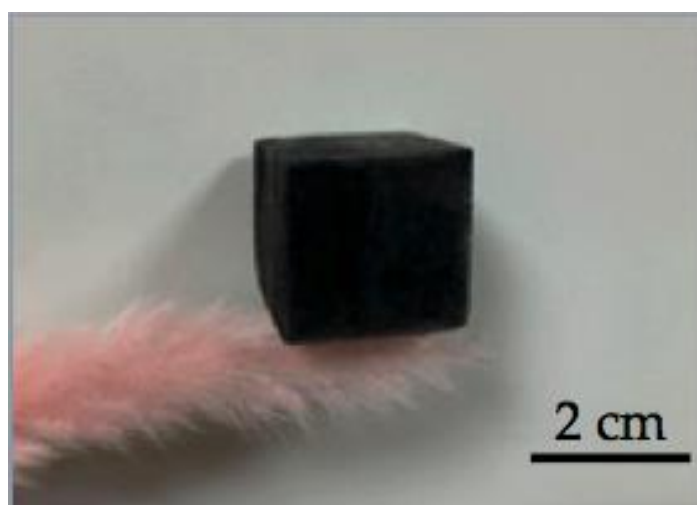


Figure 3. The photo of the M-rGO-ascorb composite placed on a tinted feather.

The obtained materials represent a series of eight sorption experiments: melamine (without pretreatment); melamine treated with different rGOs, with GO reduction reagents ascorbic acid (M-rGO-ascorb), hydrazine hydrate (M-rGO-HH) and potassium hydroxide (M-rGO-KOH); polyurethane foam (without pretreatment); and polyurethane foam treated with rGO, with GO reduction reagents ascorbic acid (PF-rGO-ascorb), hydrazine hydrate (PF-rGO-HH) and KOH (PF-rGO-KOH).

All obtained composites demonstrated high hydrophobic properties. The pure melamine sponge instantly sinks in water, while the M-rGO-ascorb composite remains on the surface of water (Figure 4).



Figure 4. Pure melamine sponge and M-rGO-ascorb in contact with water.

Sorption experiments with water, diesel fuel, oil and gasoline were carried out for all obtained samples. The process of organic substance sorption by highly porous materials is spontaneous and represents physical sorption [55]. The pores of materials modified with rGO are filled with air at the initial moment of time; therefore, in order to implement physical sorption, the oil needs to displace air [56,57], which occurs in the described experiments.

Figure 5 shows the experiments' main step. The final step shows that the composite effectively sorbs organic liquid while practically not sorbing water.

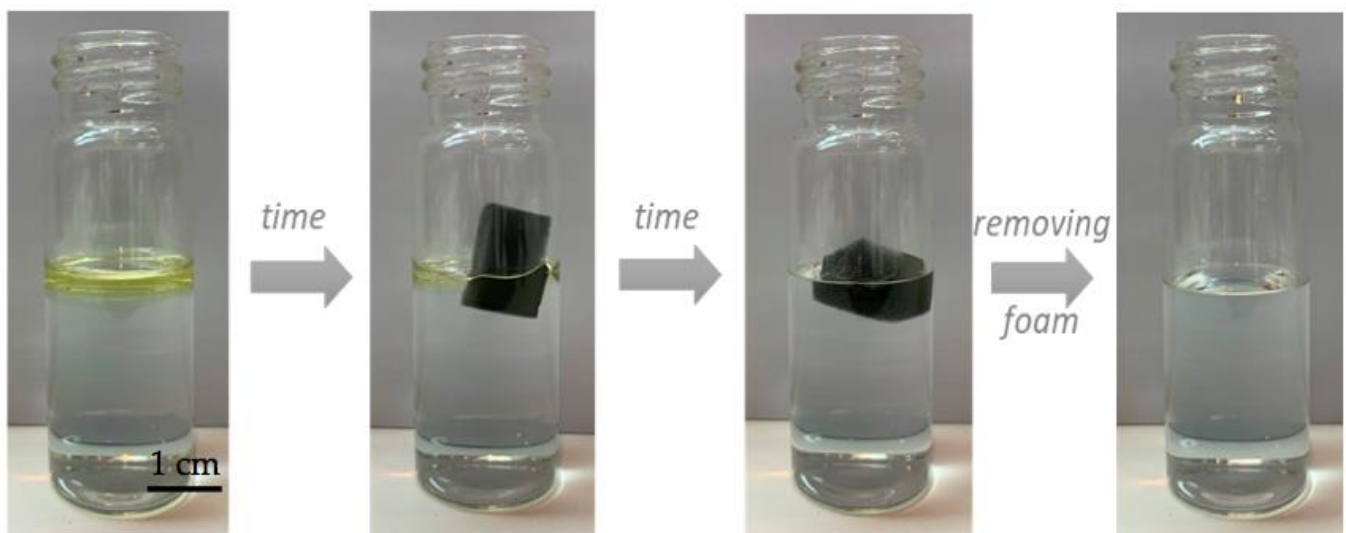


Figure 5. The photo of sorption of diesel fuel from water by M-rGO-ascorb.

Table 1 shows the results of sorption experiments obtained for melamine and polyurethane sponge composites. Melamine modification with carbon nanomaterials leads to the selective sorption of diesel fuel and oil in relation to water (Figure 6). Water sorption is significantly decreased due to material modification, while organic liquids are still well sorbed. In this case, the best sorption properties are achieved for the M-rGO-HH sample and the worst for M-rGO-KOH.

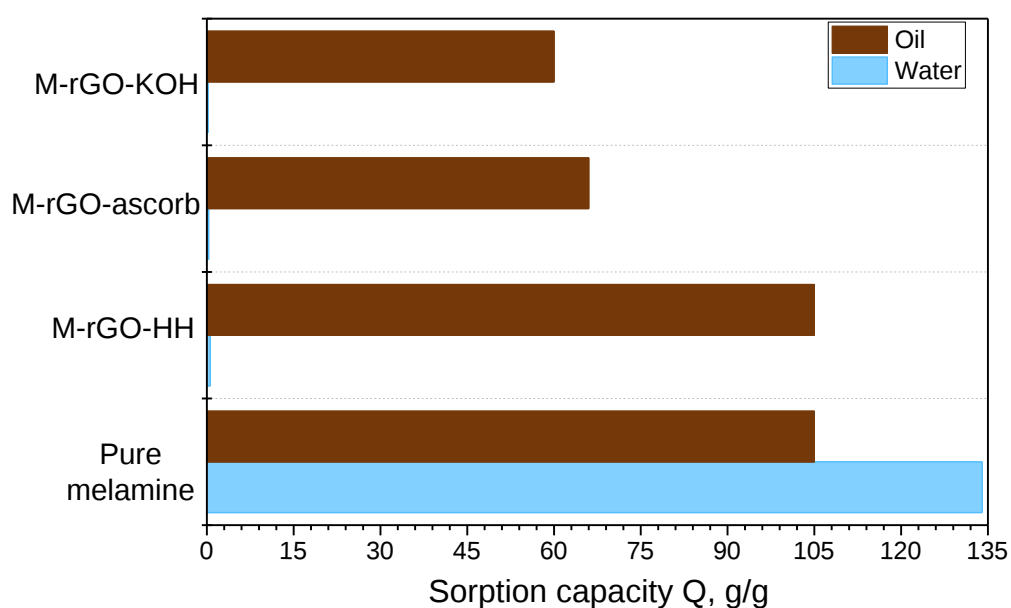


Figure 6. Sorption of water and oil by melamine-rGO composites compared to an untreated melamine matrix.

Table 1. The results of sorption experiments of studied samples.

Sample	Gravimetric Sorption Capacity, Q_m , g/g				Selectivity Q_{oil}/Q_{water}
	Oil	Diesel Fuel	Gasoline	Water	
Pure Melamine	105	98	80	134	0.8
M-rGO-KOH	60	69	55	0.2	300
M-rGO-ascorb	66	87	60	0.3	220
M-rGO-HH	105	98	80	0.6	175
Pure Polyurethane	2	47	28	4	0.5
PF-rGO-KOH	40	38	22	0.6	66.7
PF-rGO-ascorb	49	45	26	0.7	70
PF-rGO-HH	51	46	30	2	25.5

Modifying the surface of polyurethane foam sponges with graphene-containing materials also decreases water sorption, even though this material sorbed water poorly without treatment. Oil sorption by modified matrices increases by an order of magnitude compared to untreated material. The diesel fuel and gasoline gravimetric sorption capacities of PF-KOH, PF-ascorb and PF-HH are comparable to or greater than the gravimetric sorption capacity of non-modified polyurethane foam.

At the first stage of obtaining composite materials, highly porous matrices were exhaustively wetted with a colloidal solution of rGO (for this, the sponges were repeatedly squeezed to improve wetting). As a result, during the reduction process, rGO was already on the surface of highly porous matrices and was subjected to self-assembly under the given conditions. As a result of the reaction, the reduction of graphene oxide occurred, shown by a decreased number of carbonyl and carboxyl groups (Figure 2). Moreover the interaction between graphene sheets had the character of π - π stacking [58,59], which leads to self-assembly of graphene sheets on surfaces of the frame of highly porous matrices [60]. Finally, under the action of the van der Waals force between the graphene sheets and the sponge framework, the rGO is fixed on the surface of the sponges.

The surface morphology of the obtained samples and melamine before processing was studied using scanning electron microscopy and is shown in Figure 7A,B.

As expected, samples after treatment with carbon nanomaterials had the same porous structure as the melamine sponge. The porous structure was not destroyed during modification, and there was no pore overlap. The pore sizes before and after modification are the same, since the graphene-containing material is observed on the surface of the pore walls. Therefore, according to microscopy data, it can be concluded that the surface roughness increased (Figure 7C,D).

As shown in Figure 7, the surface of the synthesized M-rGO-ascorb samples (Figure 7C,D) is characterized by the presence on the surface of the modifying material, rGO, which leads to an increase in the roughness of the material compared to the untreated highly porous matrix (Figure 7A,B).

Based on the scanning electron microscopy data, it can be concluded that the coating based on carbon nanomaterials is unevenly deposited onto the surface of highly porous matrices.

Raman spectroscopy was used to characterize the synthesized samples. A laser with a given wavelength (633 nm) was used, as it provided a more intense spectral signal. The results are shown in Figure 8. In addition, the rGO and GO itself do not change during the measurement.

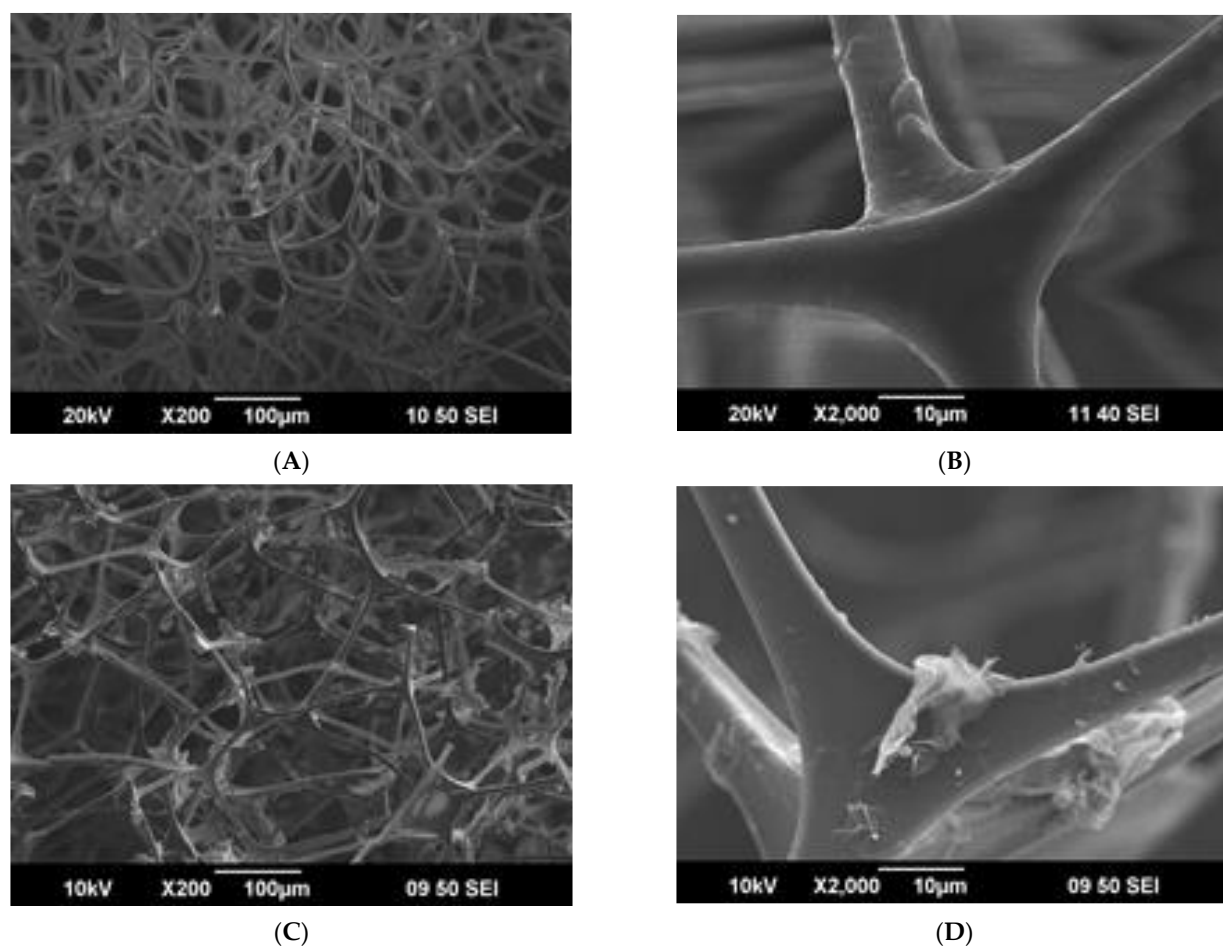


Figure 7. Scanning electron microscopy images of (A,B) pure melamine; (C,D) M-rGO-ascorb.

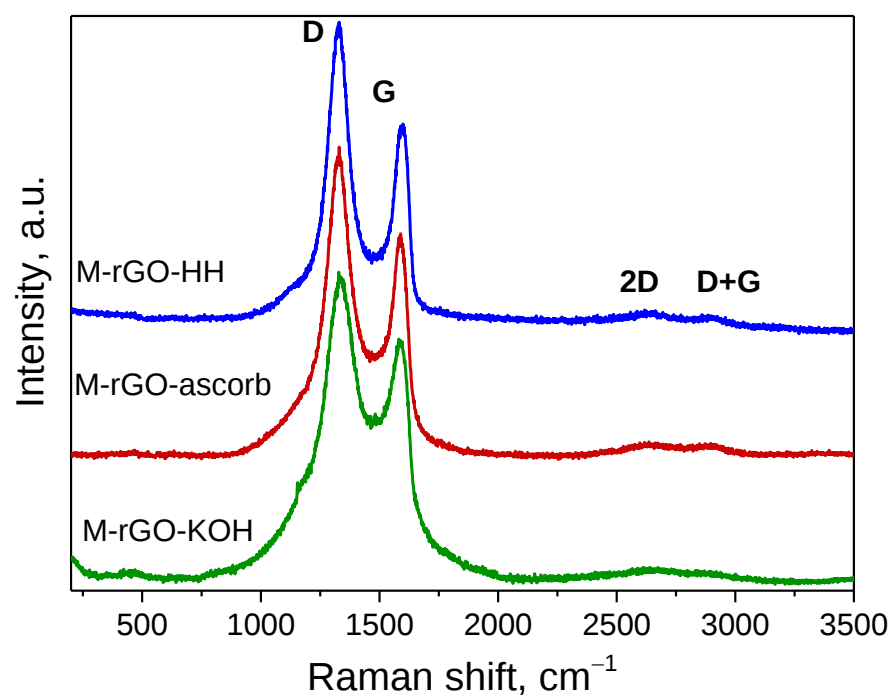


Figure 8. Raman spectra of samples of melamine-rGO composites: M-rGO-KOH, M-rGO-ascorb and M-rGO-HH.

During the characterization of carbon materials, for Raman spectra of defect-free graphene, only one mode at $\approx 1570\text{--}1595\text{ cm}^{-1}$ can be observed. This mode is called G-mode and is characterized by the vibration of sp^2 -hybridized carbon atoms directly in the layer [61].

When studying graphene materials, it is also possible to observe an additional D-mode at $\approx 1310\text{--}1430\text{ cm}^{-1}$. The mode arises from the presence of sp^3 -hybridized carbon atoms in the graphene plane and at the edges [61].

Carbon nanomaterials have superpositions of G- and D-modes in the 2D Raman spectra and D + G-modes at $\approx 2500\text{--}2800\text{ cm}^{-1}$ and $\approx 3000\text{ cm}^{-1}$, respectively [61,62].

The oxygen-containing functional groups of graphene oxide are removed in the reduction stages, and the flat carbon network is partially restored, but additional defects may appear due to the reduction stages.

The intensity ratio of the D- and G-mode peaks, I_D/I_G , changes in the following sequence for melamine-modified matrices from 1.48 to 1.17 for the series M-rGO-HH > M-rGO-ascorb > M-rGO-KOH. Raman spectroscopy data for composite samples based on a polyurethane foam matrix are given in the Supplementary Materials (Figure S4, Table S4). The intensity ratio for the second series changes in the same sequence as the composites based on the melamine sponge.

All data from Raman spectra calculations are given in Table 2.

Table 2. Data obtained from Raman spectra calculations.

Sample	Position, cm^{-1}				I_D/I_G	L_a , nm
	D-Mode	G-Mode	2D-Mode	D+G-Mode		
M-rGO-KOH	1329	1582	2617	2908	1.17	32.9
M-rGO-ascorb	1331	1587	2604	2882	1.34	28.8
M-rGO-HH	1330	1591	2642	2890	1.48	26.0

The intensity ratio of the D- and G-modes (I_D/I_G) can serve as a measure of disorder in the carbon lattice. The I_D/I_G can also be used to estimate the size of L_a domains of sp^2 as follows [63]:

$$L_a = \frac{(2.4 \times 10^{-10}) \lambda_L^4}{\frac{I_D}{I_G}} \quad (2)$$

where λ_L is the wavelength (in nm) of the excitation laser. The domain size L_a estimated from Equation (2) is equal to changes in the following sequence from 26 to 32.9 nm for a number of samples: M-rGO-HH, M-rGO-ascorb and M-rGO-KOH. All data obtained are shown in Table 2. The size of the domains can affect the sorption capacity of materials in relation to organic substances and water.

X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical composition of the samples and the degree of carbon oxidation. The C1s spectrum of pure melamine (Figure 9) can be fitted with four main components attributed to C–C (sp^3) (284.9–285.5 eV); C–O (286.7–287.0 eV); and N=C(–N)–N, O=C–O, O=C–N (288.2–288.3 eV) species and a minor component of presumably adsorbed carbonates (289.5–290.2 eV) (Table 3). The additional component of sp^2 -carbon species at 284.5–284.9 eV dominates in the spectra of all melamine-rGO composites. The content of sp^2 -carbon species is similar on the surface of these composites and close to 50 at %. These species are evidently responsible for the hydrophobicity of the composites. The C1s spectra of polyurethane-rGO composites (Figure S5, Table S3) also showed high contribution of sp^2 -carbon species compared to the precursor, but their content was lower than in the melamine-based composites.

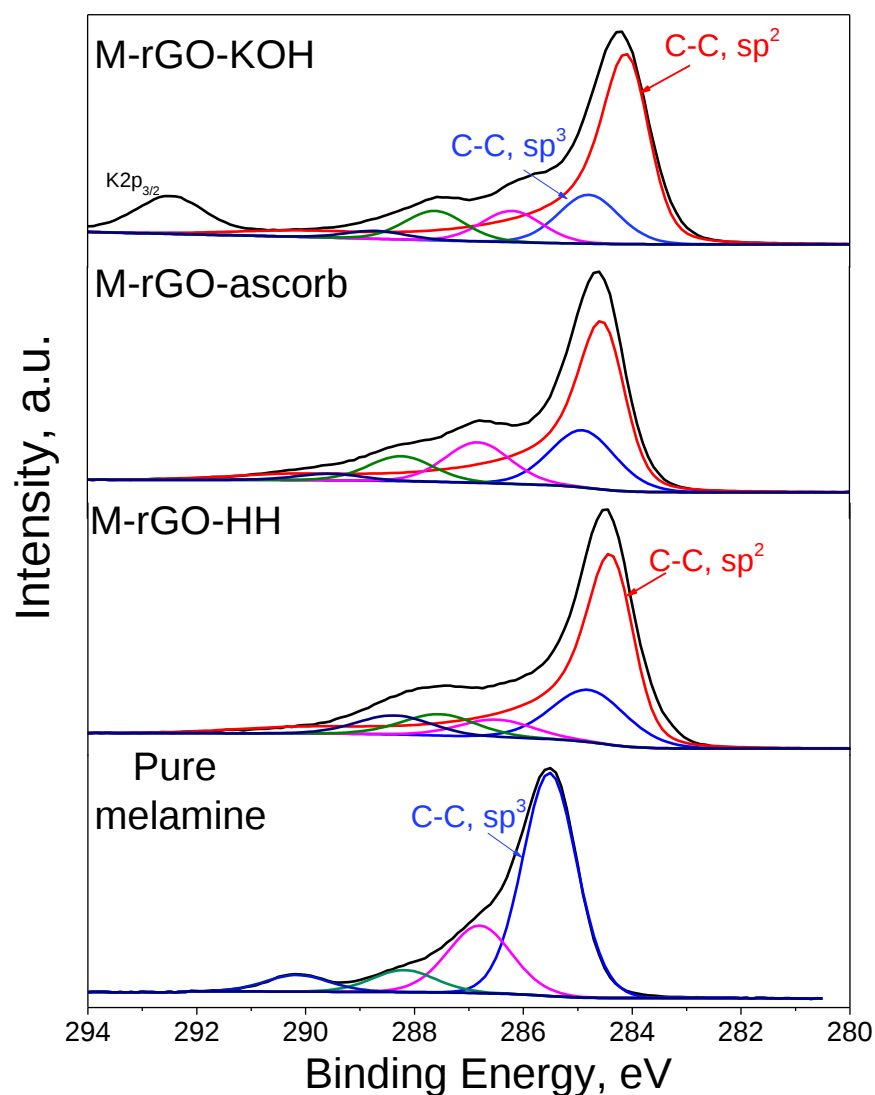


Figure 9. C1s XPS spectra of melamine-rGO composites.

Table 3. Contents of different carbon species on the surface of melamine and melamine-based composites determined by XPS.

Sample	Fraction, at %				
	C-C (sp ²)	C-C (sp ³)	C-O	N=C(-N)-N, O=C-O, O=C-N	Carbonate (CO ₃ ²⁻)
Pure Melamine	–	46	16	5.3	4.0
M-rGO-KOH	50	11	6.9	8.3	0.2
M-rGO-ascorb	46	14	10	6.3	1.6
M-rGO-HH	46	13	4.4	10	–

4. Conclusions

The creation of effective sorbents for repeated use in emergency oil and petroleum product spills is a promising direction for the use of highly porous composites obtained by the proposed method, i.e., the modification of porous materials (polyurethane, melamine) by rGO suspensions. This method is easily scalable and environmentally friendly. Moreover, the dimensions of the sorbing material are limited only by the dimensions and parameters of highly porous matrices, which are pre-prepared for further modification.

Sorption tests were performed for obtained composites in this work, along with characterization by SEM, Raman spectroscopy and XPS. Depending on the material of the initial sponge, the modification has different results. For example, the modification of the melamine surface leads to significantly reduced water sorption, increasing the selectivity of the material. On the other hand, polyurethane foam modification leads to increased organic liquid sorption.

The maximum values of organic sorption capacities demonstrated in this work were 80 g/g for gasoline, 98 g/g for diesel fuel and 105 g/g for oil.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/en15197371/s1>, Table S1: Element concentrations on the surface of initial substances obtained by XPS spectra, at. %. Figure S1: C1s XPS spectrum of (A) Graphene oxide, (B) Melamine and (C) Polyurethane sample. Figure S2: General scheme reduction of graphene oxide by using: (1) ascorbic acid; (2) hydrazine hydrate; (3) potassium hydroxide [64,65]. Figure S3: Absorption spectra of rGO-ascorb. Figure S4: Raman spectra of polyurethane-rGO composites. Table S2: Data obtained from Raman Spectra calculations. Figure S5: C1s XPS spectra of polyurethane-rGO composites. Table S3: Contents of different carbon species on the surface of polyurethane and polyurethane-based composites determined by XPS.

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Conflicts of Interest: The authors declare no conflict of interest.

References

- Wang, P.; Zou, C.; Zhong, H. The study of highly oil absorption polyurethane foam material and its application in the emergency disposal of hazardous chemicals. *Adv. Mater. Res.* **2012**, *518–523*, 847–853. [\[CrossRef\]](#)
- Barroso-Solares, S.; Pinto, J.; Fragouli, D.; Athanassiou, A. Facile oil removal from water-in-oil stable emulsions using PU foams. *Materials* **2018**, *11*, 2382. [\[CrossRef\]](#) [\[PubMed\]](#)
- Anju, M.; Renuka, N.K. Magnetically actuated graphene coated polyurethane foam as potential sorbent for oils and organics. *Arab. J. Chem.* **2020**, *13*, 1752–1762. [\[CrossRef\]](#)
- Lin, J.; Shang, Y.; Ding, B.; Yang, J.; Yu, J.; Al-Deyab, S.S. Nanoporous polystyrene fibers for oil spill cleanup. *Mar. Pollut. Bull.* **2012**, *64*, 347–352. [\[CrossRef\]](#) [\[PubMed\]](#)
- Huang, S.; Li, X.; Jiao, Y.; Shi, J. Fabrication of a superhydrophobic, fire-resistant, and mechanical robust sponge upon polyphenol chemistry for efficiently absorbing oils/organic solvents. *Ind. Eng. Chem. Res.* **2015**, *54*, 1842–1848. [\[CrossRef\]](#)
- Chen, X.; Weibel, J.A.; Garimella, S.V. Continuous Oil-Water Separation Using Polydimethylsiloxane-Functionalized Melamine Sponge. *Ind. Eng. Chem. Res.* **2016**, *55*, 3596–3602. [\[CrossRef\]](#)
- Zhu, H.; Chen, D.; An, W.; Li, N.; Xu, Q.; Li, H.; He, J.; Lu, J. A Robust and Cost-Effective Superhydrophobic Graphene Foam for Efficient Oil and Organic Solvent Recovery. *Small* **2015**, *11*, 5222–5229. [\[CrossRef\]](#)
- Si, H.; Liu, Q.; Fan, Z.; Wang, B.; Tong, Q.; Lin, M. A Durable Magnetic Superhydrophobic Melamine Sponge: For Solving Complex Marine Oil Spills. *Nanomaterials* **2022**, *12*, 2488. [\[CrossRef\]](#)
- Shui, Y.; Xian, Y.; Chen, L.; Li, M.; Yao, Y.; Zhang, Q. High oil absorbable superhydrophobic melamine sponges and evaluation in oil spill clean-ups. *J. Appl. Polym. Sci.* **2020**, *137*, 49306. [\[CrossRef\]](#)
- Nguyen, D.D.; Tai, N.H.; Lee, S.B.; Kuo, W.S. Superhydrophobic and superoleophilic properties of graphene-based sponges fabricated using a facile dip coating method. *Energy Environ. Sci.* **2012**, *5*, 7908–7912. [\[CrossRef\]](#)
- Gupta, S.; He, W.-D.; Tai, N.H. A comparative study on superhydrophobic sponges and their application as fluid channel for continuous separation of oils and organic solvents from water. *Compos. Part B Eng.* **2016**, *101*, 99–106. [\[CrossRef\]](#)
- Dashairya, L.; Sahu, A.; Saha, P. Stearic acid treated polypyrrole-encapsulated melamine formaldehyde superhydrophobic sponge for oil recovery. *Adv. Compos. Hybrid Mater.* **2019**, *2*, 70–82. [\[CrossRef\]](#)
- Tan, I.A.W.; Ahmad, A.L.; Hameed, B.H. Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: Equilibrium, kinetic and thermodynamic studies. *J. Hazard. Mater.* **2008**, *154*, 337–346. [\[CrossRef\]](#)
- Toyoda, M.; Inagaki, M. Sorption and recovery of heavy oils by using exfoliated graphite. *Spill Sci. Technol. Bull.* **2003**, *8*, 467–474. [\[CrossRef\]](#)

15. Zhang, S.; Shao, T.; Kose, H.S.; Karanfil, T. Adsorption of Aromatic Compounds by Carbonaceous Adsorbents: A Comparative Study on Granular Activated Carbon, Activated Carbon Fiber and Carbon Nanotubes. *Environ. Sci. Technol.* **2010**, *12*, 6377–6383. [[CrossRef](#)] [[PubMed](#)]
16. Liang, H.W.; Guan, Q.F.; Chen, L.F.; Zhu, Z.; Zhang, W.J.; Yu, S.H. Macroscopic-scale template synthesis of robust carbonaceous nanofiber hydrogels and aerogels and their applications. *Angew. Chemie Int. Ed.* **2012**, *51*, 5101–5105. [[CrossRef](#)]
17. Gui, X.; Wei, J.; Wang, K.; Cao, A.; Zhu, H.; Jia, Y.; Shu, Q.; Wu, D. Carbon nanotube sponges. *Adv. Mater.* **2010**, *22*, 617–621. [[CrossRef](#)]
18. Rahman, R.O.A.; El Kamash, A.M.; Ali, H.F.; Hung, Y.-T. Overview on Recent Trends and Developments in Radioactive Liquid Waste Treatment Part 1: Sorption/Ion Exchange Technique. *Int. J. Environ. Eng. Sci.* **2011**, *2*, 1–16.
19. Almeida, C.A.P.; Debacher, N.A.; Downs, A.J.; Cottet, L.; Mello, C.A.D. Removal of methylene blue from colored effluents by adsorption on montmorillonite clay. *J. Colloid Interface Sci.* **2009**, *332*, 46–53. [[CrossRef](#)]
20. Hameed, B.H.; Din, A.T.M.; Ahmad, A.L. Adsorption of methylene blue onto bamboo-based activated carbon: Kinetics and equilibrium studies. *J. Hazard. Mater.* **2007**, *141*, 819–825. [[CrossRef](#)]
21. Paşka, O.M.; Pacurariu, C.; Muntean, S.G. Kinetic and thermodynamic studies on methylene blue biosorption using corn-husk. *RSC Adv.* **2014**, *4*, 62621–62630. [[CrossRef](#)]
22. Hou, X.X.; Deng, Q.F.; Ren, T.Z.; Yuan, Z.Y. Adsorption of Cu²⁺ and methyl orange from aqueous solutions by activated carbons of corncob-derived char wastes. *Environ. Sci. Pollut. Res.* **2013**, *20*, 8521–8534. [[CrossRef](#)] [[PubMed](#)]
23. Chen, Z.; Ren, W.; Gao, L.; Liu, B.; Pei, S.; Cheng, H.M. Three-dimensional flexible and conductive interconnected graphene networks grown by chemical vapour deposition. *Nat. Mater.* **2011**, *10*, 424–428. [[CrossRef](#)] [[PubMed](#)]
24. Zhu, Y.; Murali, S.; Cai, W.; Li, X.; Suk, J.W.; Potts, J.R.; Ruoff, R.S. Graphene and graphene oxide: Synthesis, properties, and applications. *Adv. Mater.* **2010**, *22*, 3906–3924. [[CrossRef](#)]
25. Singh, E.; Chen, Z.; Houshmand, F.; Ren, W.; Peles, Y.; Cheng, H.M.; Koratkar, N. Superhydrophobic graphene foams. *Small* **2013**, *9*, 75–80. [[CrossRef](#)]
26. Robinson, J.T.; Perkins, F.K.; Snow, E.S.; Wei, Z.; Sheehan, P.E. Reduced graphene oxide molecular sensors. *Nano Lett.* **2008**, *8*, 3137–3140. [[CrossRef](#)]
27. Wang, Y.; Shao, Y.; Matson, D.W.; Li, J.; Lin, Y. Nitrogen-Doped Graphene and Its Application in Electrochemical Biosensing. *ACS Nano* **2010**, *4*, 1790–1798. [[CrossRef](#)]
28. Zhu, Y.P.; Ren, T.Z.; Liu, Y.P.; Yuan, Z.Y. In situ simultaneous reduction-doping route to synthesize hematite/N-doped graphene nanohybrids with excellent photoactivity. *RSC Adv.* **2014**, *4*, 31754–31758. [[CrossRef](#)]
29. Wang, Y.; Wang, B.; Wang, J.; Ren, Y.; Xuan, C.; Liu, C.; Shen, C. Superhydrophobic and superoleophilic porous reduced graphene oxide/polycarbonate monoliths for high-efficiency oil/water separation. *J. Hazard. Mater.* **2018**, *344*, 849–856. [[CrossRef](#)]
30. Bi, H.; Xie, X.; Yin, K.; Zhou, Y.; Wan, S.; He, L.; Xu, F.; Banhart, F.; Sun, L.; Ruoff, R.S. Spongy graphene as a highly efficient and recyclable sorbent for oils and organic solvents. *Adv. Funct. Mater.* **2012**, *22*, 4421–4425. [[CrossRef](#)]
31. Liu, F.; Chung, S.; Oh, G.; Seo, T.S. Three-dimensional graphene oxide nanostructure for fast and efficient water-soluble dye removal. *ACS Appl. Mater. Interfaces* **2012**, *4*, 922–927. [[CrossRef](#)] [[PubMed](#)]
32. Zhao, G.; Li, J.; Ren, X.; Chen, C.; Wang, X. Few-layered graphene oxide nanosheets as superior sorbents for heavy metal ion pollution management. *Environ. Sci. Technol.* **2011**, *45*, 10454–10462. [[CrossRef](#)] [[PubMed](#)]
33. Li, F.; Jiang, X.; Zhao, J.; Zhang, S. Graphene oxide: A promising nanomaterial for energy and environmental applications. *Nano Energy* **2015**, *16*, 488–515. [[CrossRef](#)]
34. Sun, H.; Zhu, Z.; Liang, W.; Yang, B.; Qin, X.; Zhao, X.; Pei, C.; La, P.; Li, A. Reduced graphene oxide-coated cottons for selective absorption of organic solvents and oils from water. *RSC Adv.* **2014**, *4*, 30587–30591. [[CrossRef](#)]
35. Sun, H.; Cao, L.; Lu, L. Magnetite/reduced graphene oxide nanocomposites: One step solvothermal synthesis and use as a novel platform for removal of dye pollutants. *Nano Res.* **2011**, *4*, 550–562. [[CrossRef](#)]
36. Yin, H.; Zhao, S.; Wan, J.; Tang, H.; Chang, L.; He, L.; Zhao, H.; Gao, Y.; Tang, Z. Three-dimensional graphene/metal oxide nanoparticle hybrids for high-performance capacitive deionization of saline water. *Adv. Mater.* **2013**, *25*, 6270–6276. [[CrossRef](#)]
37. Liu, T.; Chen, S.; Liu, H. Oil Adsorption and Reuse Performance of Multi-Walled Carbon Nanotubes Taoener. *Procedia Eng.* **2015**, *102*, 1896–1902. [[CrossRef](#)]
38. Zhao, J.; Ren, W.; Cheng, H.M. Graphene sponge for efficient and repeatable adsorption and desorption of water contaminations. *J. Mater. Chem.* **2012**, *22*, 20197–20202. [[CrossRef](#)]
39. Wu, R.; Yu, B.; Liu, X.; Li, H.; Wang, W.; Chen, L.; Bai, Y.; Ming, Z.; Yang, S.T. One-pot hydrothermal preparation of graphene sponge for the removal of oils and organic solvents. *Appl. Surf. Sci.* **2016**, *362*, 56–62. [[CrossRef](#)]
40. Hong, J.Y.; Sohn, E.H.; Park, S.; Park, H.S. Highly-efficient and recyclable oil absorbing performance of functionalized graphene aerogel. *Chem. Eng. J.* **2015**, *269*, 229–235. [[CrossRef](#)]
41. Fernández-Merino, M.J.; Guardia, L.; Paredes, J.I.; Villar-Rodil, S.; Solís-Fernández, P.; Martínez-Alonso, A.; Tascón, J.M.D. Vitamin C is an ideal substitute for hydrazine in the reduction of graphene oxide suspensions. *J. Phys. Chem. C* **2010**, *114*, 6426–6432. [[CrossRef](#)]
42. Pei, S.; Cheng, H.M. The reduction of graphene oxide. *Carbon N. Y.* **2012**, *50*, 3210–3228. [[CrossRef](#)]
43. Gao, J.; Liu, F.; Liu, Y.; Ma, N.; Wang, Z.; Zhang, X. Environment-friendly method to produce graphene that employs vitamin C and amino acid. *Chem. Mater.* **2010**, *22*, 2213–2218. [[CrossRef](#)]

44. Tung, V.C.; Allen, M.J.; Yang, Y.; Kaner, R.B. High-throughput solution processing of large-scale graphene. *Nat. Nanotechnol.* **2009**, *4*, 25–29. [[CrossRef](#)] [[PubMed](#)]
45. Wang, H.; Robinson, J.T.; Li, X.; Dai, H. Solvothermal Reduction of Chemically Exfoliated Graphene Sheets. *J. Am. Chem. Soc.* **2009**, *131*, 9910–9911. [[CrossRef](#)]
46. Feng, Y.; Yao, J. Design of Melamine Sponge-Based Three-Dimensional Porous Materials toward Applications. *Ind. Eng. Chem. Res.* **2018**, *57*, 7322–7330. [[CrossRef](#)]
47. Oribayo, O.; Feng, X.; Rempel, G.L.; Pan, Q. Modification of formaldehyde-melamine-sodium bisulfite copolymer foam and its application as effective sorbents for clean up of oil spills. *Chem. Eng. Sci.* **2017**, *160*, 384–395. [[CrossRef](#)]
48. Chen, J.; You, H.; Xu, L.; Li, T.; Jiang, X.; Li, C.M. Facile synthesis of a two-tier hierarchical structured superhydrophobic-superoleophilic melamine sponge for rapid and efficient oil/water separation. *J. Colloid Interface Sci.* **2017**, *506*, 659–668. [[CrossRef](#)]
49. Zhang, Y.; Zhang, Q.; Zhang, R.; Liu, S.; Zhou, Y. A superhydrophobic and elastic melamine sponge for oil/water separation. *New J. Chem.* **2019**, *43*, 6343–6349. [[CrossRef](#)]
50. Wu, D.; Fang, L.; Qin, Y.; Wu, W.; Mao, C.; Zhu, H. Oil sorbents with high sorption capacity, oil/water selectivity and reusability for oil spill cleanup. *Mar. Pollut. Bull.* **2014**, *84*, 263–267. [[CrossRef](#)]
51. Rabchinskii, M.K.; Dideikin, A.T.; Kirilenko, D.A.; Baidakova, M.V.; Shnitov, V.V.; Roth, F.; Konyakhin, S.V.; Besedina, N.A.; Pavlov, S.I.; Kuricyn, R.A.; et al. Facile reduction of graphene oxide suspensions and films using glass wafers. *Sci. Rep.* **2018**, *8*, 14154. [[CrossRef](#)] [[PubMed](#)]
52. Kumar, P.V.; Bardhan, N.M.; Tongay, S.; Wu, J.; Belcher, A.M.; Grossman, J.C. Scalable enhancement of graphene oxide properties by thermally driven phase transformation. *Nat. Chem.* **2014**, *6*, 151–158. [[CrossRef](#)] [[PubMed](#)]
53. Yan, J.A.; Xian, L.; Chou, M.Y. Structural and electronic properties of oxidized graphene. *Phys. Rev. Lett.* **2009**, *103*, 086802. [[CrossRef](#)] [[PubMed](#)]
54. Zhu, C.; Guo, S.; Fang, Y.; Dong, S. Reducing sugar: New functional molecules for the green synthesis of graphene nanosheets. *ACS Nano* **2010**, *4*, 2429–2437. [[CrossRef](#)] [[PubMed](#)]
55. Huang, J.; Yan, Z. Adsorption Mechanism of Oil by Resilient Graphene Aerogels from Oil-Water Emulsion. *Langmuir* **2018**, *34*, 1890–1898. [[CrossRef](#)]
56. Kabiri, S.; Tran, D.N.H.; Altalhi, T.; Losic, D. Outstanding adsorption performance of graphene-carbon nanotube aerogels for continuous oil removal. *Carbon N. Y.* **2014**, *80*, 523–533. [[CrossRef](#)]
57. Li, H.; Liu, L.; Yang, F. Covalent assembly of 3D graphene/polypyrrole foams for oil spill cleanup. *J. Mater. Chem. A* **2013**, *1*, 3446–3453. [[CrossRef](#)]
58. Han, Z.; Tang, Z.; Li, P.; Yang, G.; Zheng, Q.; Yang, J. Ammonia solution strengthened three-dimensional macro-porous graphene aerogel. *Nanoscale* **2013**, *5*, 5462–5467. [[CrossRef](#)]
59. Xu, Y.; Sheng, K.; Li, C.; Shi, G. Self-Assembled Graphene Hydrogel via a One-Step Hydrothermal Process. *ACS Nano* **2010**, *4*, 4324–4330. [[CrossRef](#)]
60. Wu, C.; Huang, X.; Wu, X.; Qian, R.; Jiang, P. Mechanically flexible and multifunctional polymer-based graphene foams for elastic conductors and oil-water separators. *Adv. Mater.* **2013**, *25*, 5658–5662. [[CrossRef](#)]
61. Saito, R.; Hofmann, M.; Dresselhaus, G.; Jorio, A.; Dresselhaus, M.S. Raman spectroscopy of graphene and carbon nanotubes. *Adv. Phys.* **2011**, *60*, 413–550. [[CrossRef](#)]
62. Ferrari, A.C.; Meyer, J.C.; Scardaci, V.; Casiraghi, C.; Lazzeri, M.; Mauri, F.; Piscanec, S.; Jiang, D.; Novoselov, K.S.; Roth, S.; et al. Raman spectrum of graphene and graphene layers. *Phys. Rev. Lett.* **2006**, *97*, 187401. [[CrossRef](#)] [[PubMed](#)]
63. Pimenta, M.A.; Dresselhaus, G.; Dresselhaus, M.S.; Cançado, L.G.; Jorio, A.; Saito, R. Studying disorder in graphite-based systems by Raman spectroscopy. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1276–1291. [[CrossRef](#)] [[PubMed](#)]
64. Gao, X.; Jang, J.; Nagase, S. Hydrazine and thermal reduction of graphene oxide: Reaction mechanisms, product structures, and reaction design. *J. Phys. Chem. C* **2010**, *114*, 832–842. [[CrossRef](#)]
65. Chen, C.; Kong, W.; Duan, H.M.; Zhang, J. Theoretical simulation of reduction mechanism of graphene oxide in sodium hydroxide solution. *Phys. Chem. Chem. Phys.* **2014**, *16*, 12858–12864. [[CrossRef](#)] [[PubMed](#)]