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POSSIBILITIES OF OBTAINING NANOCOMPOSITE MATERIALS AS ADSORBENTS FOR WASTE WATER TREATMENT

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Abstract: *The volume of waste water worldwide reaches about 440 km^3/year, which is why the purification of the same is among the important and widespread technological processes. One of the most serious problems regarding wastewater is related to its contamination with heavy metals and dyes generated by various industries. The currently widely applied technologies for their purification are often either very expensive, show low efficiency with respect to some pollutants, or cannot meet the established ecological and sanitary norms. Of the conventional water purification methods, adsorption remains the preferred method based on the interaction between adsorbents in the solid phase and adsorbates in the liquid or gas phase. Despite its advantages, this method also has disadvantages (such as low selectivity and low adsorption capacity), which scientists are trying to overcome by offering new more efficient and economically advantageous adsorbents. In recent years, nanotechnology has attracted a lot of attention in various fields, including wastewater treatment. The combination of the advantages of nanotechnology and the classical methods of silicate technology is an innovative approach for obtaining new and composite materials that combine the unique functional properties of nanomaterials with the properties of ceramic materials.*
Keywords: *Waste water, Treatment, Adsorbents, Nanocomposite materials.*

INTRODUCTION

The intense industrial development has significant impact on the environment. Modern production facilities lead to formation of substantial amount of wastes contaminated with wide variety of organic and inorganic substances. One of the most severe problems related to waste waters is their contamination with heavy metals. At present, the widely used purification technologies are either very expensive or cannot meet the established ecological and sanitary standards. Thus, due to the accumulation of heavy metals in the environment and because of the adoption of new ecological standards, there has recently been a growing interest towards development of improved technologies for their purification (Ninova, V., Nikolova, N., & Marinov, M., 2002). Among the conventional methods, adsorption remains the preferred method due to its low cost and good efficiency (Bhatnagar, A., & Sillanpää, M., 2010). Despite its advantages, this method has certain drawbacks (e.g. low selectivity and low adsorption capacity) which researchers are trying to overcome by proposing new efficient and economically feasible adsorbents (Bryan, M., Chai, P., Law, J., & Mahmoudi, E., 2022).

The porous ceramic materials are quite important in various fields of application, e.g. heat insulation materials, in filtration processes, preparation of biomedical and catalytic substrates, as well as dielectric materials in capacitors.

The aim of the present paper is to review the possibilities for preparation of ceramic composite materials that could be used as adsorbents for purification of waste waters from various contaminants like dyes and some heavy metals.

EXPOSITION

The amount of waste waters in the world is estimated to be about 440 kм^3/year. Thus, their purification is one of the most widely spread processes. Dyes are some of the most harmful contaminants of water basins. Hey are used on a large scale in a wide variety of industries (textile, cosmetics, gasoline, plastics) and dye production in the world is estimated to be about 800 000 tons per year, 15% of which remain untreated. (Lim, C., Bay, H., Neoh, C., Aris, A., Abdull Majid, Z., & Ibrahim, Z., 2013). The conventional methods of treatment like precipitation and coagulation are neither economically feasible, nor environment friendly due to the high operative costs, low efficiency towards some contaminants, the necessity to use chemical reagents and the generation of toxic products and large amounts of wastes at the end of the process. Besides, due to their complex aromatic structure, the dyes are exceptionally resistant to photodegradation, biodegradation, oxidation, high temperature, etc. (Soleimani, H., Mahvi, A., Yaghmaeian, K., Abbasnia, A., Sharafi, K., Alimohammadi, M., & Zamanzadeh, M., 2019).

Among the conventional methods, adsorption remains the preferred method of purification because of its relatively low cost and good efficiency the (Bhatnagar, A., & Sillanpää, M., 2010). The process of adsorption is actually adhesion of gas, liquid or solution on the surface of a solid-state material (Fig.1). The substance on whose surface molecules is adsorbed is called adsorbent. The second component taking part in the reaction is called adsorbate – gas, liquid or component of some solution which is adsorbed onto adsorbent's surface.

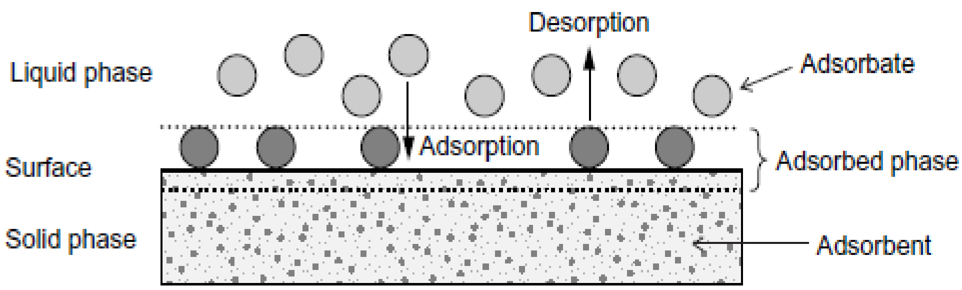


Fig. 1 General terms in adsorption (Worch, 2012)

The main factors affecting the adsorption process and the basis on which the nature of the process is determined are as follows:

1. Nature of the adsorbent and the adsorbate;
2. Adsorbent's surface;
3. Activation of the adsorbent;
4. Experimental conditions: temperature, pressure, period of residence, etc.

Adsorption is a surface phenomenon stipulated by the interaction between the adsorbents in solid state and adsorbates in liquid or gaseous state. Despite its advantages, his method has some drawbacks (e.g. low selectivity and low adsorption capacity) which researchers are trying to overcome by proposing new more efficient and economically feasible adsorbents.

The adsorbents should comply with a number of requirements including being active, stable, available, cheap, easily regenerating and, most important, the exchange ions should be harmless and not cause secondary water pollution. The main requirement for a material to be a good adsorbent is to have well developed surface. The most widely used adsorbents in industrial practice are active carbon, mesoporous silicates, natural zeolites and synthetic zeolites. Each particle of these adsorbents is an agglomeration of porous microcrystals interconnected by macropores. To achieve high adsorption capacity, substances with highly developed surface are used. He efficiency, capacity and reusability of the adsorption material depend on the functional groups on adsorbent's surface. (Ninova, V., Nikolova, N., & Marinov, M., 2002). Researches have shown that, due to their high ratio surface-to-volume, the nanomaterials are better than the conventional adsorbents. A large number of different materials were investigated as adsorbents but lately the researchers focus their attention mainly on graphene and its derivatives (Bryan, M., Chai, P., Law, J., & Mahmoudi, E., 2022).

In recent years, the nanotechnology has attracted much attention, including in the treatment of waste waters. Nanotechnology is a one of the most modern and rapidly developing field of science and practice worldwide. It is based on the specific properties which nanomaterials have. The nanosized particles and nanostructured materials become extremely important for modern engineering, microelectronics, ceramics, catalysis, medicine, etc. (Fig.2) (Georgieva, A., Yovkova, F., Panayotova, K., Georgieva, M., Minova, M., 2022).

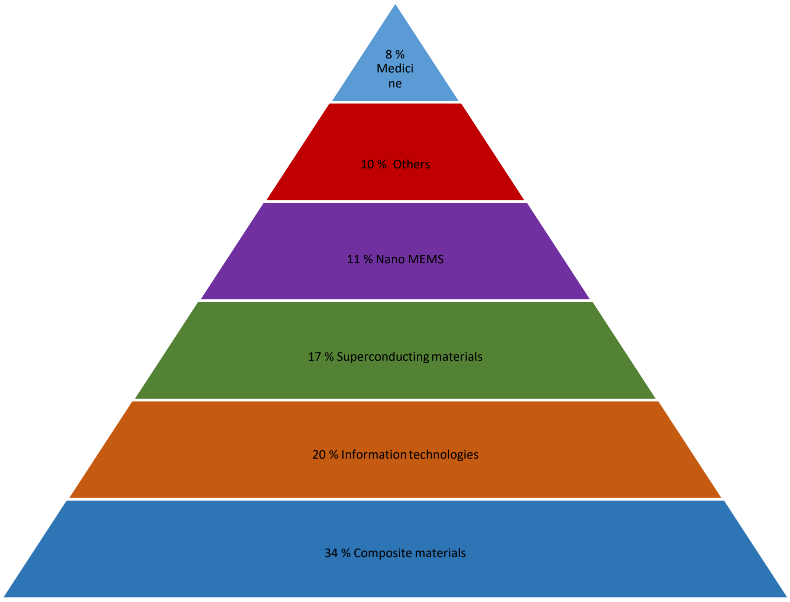


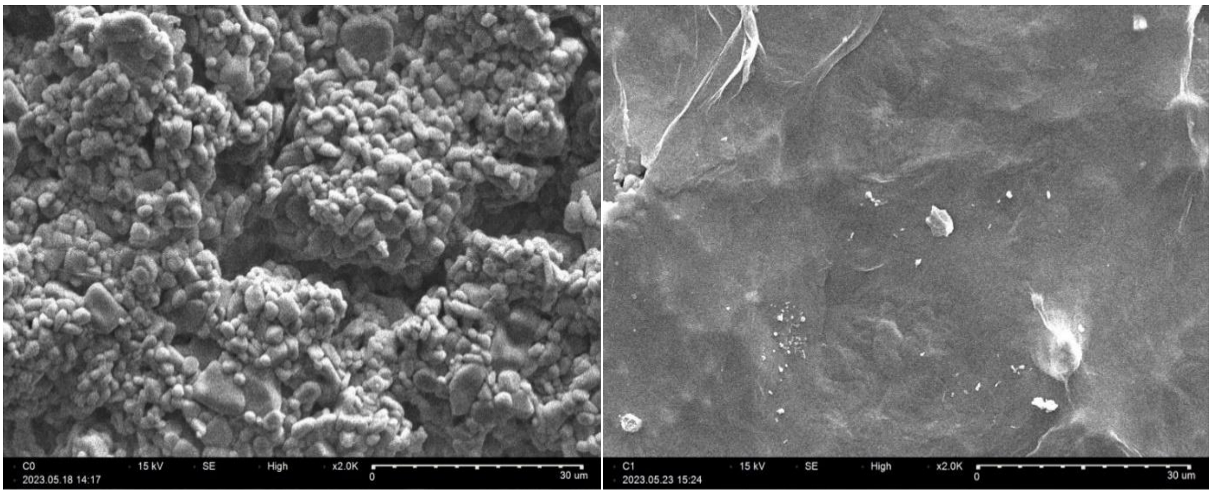
Fig. 2 aspects of application of nanosized particles and nanostructured materials

With its outstanding properties, including mechanical strength, thermal and electrical conductivity, graphene is a very good candidate as an adsorbent, but it tends to transform into graphite through van der Waals interactions. However, if graphene is oxidized it transforms into graphene oxide – a material with very high ratio surface-to-volume, oxygen containing functional groups (epoxy, carboxyl and hydroxyl ones) and very high water solubility (Ali, I., Basheer, A., Mbianda, X., Burakov, A., Galunin, E., Burakova, I., Mkrtchyan, E., Tkachev, A., Grachev, V., 2019). The problem with the graphene oxide is that it repels he anion molecules, thus preventing them from adsorbing on its surface. Of course, this disadvantage can be surmounted by functionalization of graphene oxide and preparation of composite materials with very high ratio surface-to-volume, excellent stability and reinforced active centers. This is exceptionally important since the adsorption efficiency is controlled by the type and force of the interaction between the functional groups of the adsorbent and the adsorbate. One of the advantages of graphene oxide is that it is easily dispersed in water and other organic solvents, as well as in various matrices, due to the presence of oxygen containing functional groups in it. This is still a very important property for the mixing of the material with ceramic or polymeric matrices when the aim is to improve their electrical, mechanical and other properties.

In the production of ceramic and composite materials with specific properties, nanotechnology plays a significant role for the preparation of the initial materials in finely dispersed state that not only intensifies the process of synthesis but also leads to improvement and reproducibility of products' properties. Combining the advantages of nanotechnology with classical silicate technology is an innovative approach for developing new composite materials that integrate the unique functional properties of nanomaterials with those of ceramic materials.

In recent years, a research team of the University “Prof.Dr. Asen Zlatarov”- Burgas works on the synthesis of ceramic nanocomposites containing nano-inclusions (with thickness of several nanometers) from graphene nanostructures or reduced graphene oxide (Georgieva, M., Georgieva, A., Panayotova, K., Yovkova, F., Markovska, I., 2023). A two-stage technology for preparation of composite ceramic materials of the type graphene/ceramic matrix has been applied and validated. For the characterization of the ceramic samples and the composite material obtained, the methods of infrared spectroscopy, X-ray phase analysis, BET analysis scanning and transmission electron microscopy and optical microscopy were basically used. First, fine-grain porous corundum ceramic materials were synthesized (Fig.3) by the method of solid state sintering of diffusion nature, at relatively low temperatures of 1500°C for corundum materials. It was achieved by adding graphene nanoplates (GNP) in concentration about 2 masses % and 3 mass % TiO_2. Some of the more important physicochemical properties of the corundum ceramics were determined. E.g. water absorption (WA), apparent density (ρ_{app}, g/cm^3) and apparent (opened) porosity (P_{app}, %). The results obtained indicated that the introduction of graphene – GNP in the initial blends in amounts of 2 mass % followed by high temperature sintering, the ceramic samples obtained showed sufficient density - 3.26 g/cm^3, water absorption - 10.43 % and high apparent porosity - 33.46 %. Therefore, the small amount of graphene structures introduced in the blends played the role of pore-forming agent. The adsorption-texture analyses carried out showed that the mesopores had sizes between 2 nm and 30 nm. In the next stage of the experiment, graphene oxide was obtained in nano-colloidal form (2 mg/ml, dispersion in H_2O) which was impregnated into the synthesized solid porous corundum samples to obtain composite ceramic material of the type NGO/Al_2O_3 (Fig.3).

The graphene nanostructures synthesized the reduced graphene oxide (RGO) and the graphene oxide in nanocolloid form (NGO) can be used for controlled preparation of ceramic composite materials of the type graphene/matrix. Studying the properties of the latter as new materials with explicit characteristics, it was concluded that they could be used as adsorbents for purification of waste waters from various contaminants like dyes and some heavy metals.



a) SEM of corundum sample - x2.0K; b) SEM of composite NGO/Al_2O_3 - x2.0K

Fig. 3. SEM images ceramic materials synthesized on the basis of corundum

The studies of such ceramic composites indicated that the introduction of small volume fractions of graphene nanoplates (GNP), graphene oxide in nanocolloid form (NGO) of reduced graphene oxide (RGO) might result in significant improvement of the fracture strength and the electric conductivity of the ceramic material. Due to the improved functionality and physical properties of these materials, the application of the composite in various industrial fields can be significantly widened. To enhance the overall performance characteristics of the matrix, the length and shape of the carbon nanofillers are typically adjusted to achieve a reinforcing effect, even when added in small quantities. The key issue by the preparation of these ceramic materials is the transfer of the extraordinary functionality of the carbon fillers to the composite's matrix. This can be done by achieving uniform dispersion, orientation of the fillers in the substrate and control of the interphase interactions at the boundary surfaces between the carbon fillers and the ceramic or polymer matrix (Porwal, H., Grasso, S., Reece, M., 2013).

CONCLUSION

A short review was made on the possibilities for obtainment of composite materials of the type graphene/ceramic matrix, which could be also applied as adsorbents for purification of waste waters from various pollutants like dyes and some heavy metals. Using a complicated approach and combining the advantages of nanotechnology and the classical methods of the silicate technology, new and composite materials can be synthesized that would combine the unique functional properties of the nanomaterials with the properties of the ceramic materials. The graphene nanostructures, reduced graphene oxide and graphene oxide in nanocolloid form can successfully be used for controlled preparation of ceramic composite materials. Studying the properties of the latter as new materials with explicit characteristics, it was concluded that they could be used as adsorbents for purification of waste waters from various contaminants like dyes and some heavy metals.

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