CYCLIC PHOTOCATALYTIC REGENERATION OF SORBENT, BASED ON CARBON NITRIDE ($g\text{-}C_3N_4$) INCORPORATED IN SILICA NET STRUCTURE

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Abstract

In this work, we present an advanced preparation method, of photoactive layered graphitic carbon nitride ($g\text{-}C_3N_4$) incorporated into the silica structure containing zinc ions. This new nanocomposite has enhanced sorption properties and photocatalytic activity due to presence of $g\text{-}C_3N_4$. Samples with 20 wt.% and 10 wt.% of $g\text{-}C_3N_4$ were prepared and successfully tested. Specific surface area of nanocomposites was increased from 36 m^2/g of pure carbon nitride $g\text{-}C_3N_4$ to 366 and 320 m^2/g of functional composites respectively. The material was prepared by vigorous stirring of aqueous solution of zinc acetate and $g\text{-}C_3N_4$ within ultrasonic field of power density of 1 kW/L. During the sonication, sodium water glass was added at once to synthesize $ZnO\text{-}m{\cdot}SiO_2$ nanoparticles by precipitation reaction. The dispersion was then rapidly frozen and subjected to vacuum freeze-drying process to obtain powder material, which is easier to handle and more suitable for tests. Prepared nanocomposites were subjected to tests of sorption and photocatalytic degradation of methylene blue dye. Furthermore, samples did undergo four successful cycles of sorption of methylene blue with starting concentration of 1 mg/L followed by photocatalytic regeneration. The sorption capacity of sample with 20 wt.% of $g\text{-}C_3N_4$ was 0.21 mg/g and after the fourth cycle of regeneration it was restored to 75 % of its original value. The sorption capacity of sample with 10 wt.% of $g\text{-}C_3N_4$ was 0.18 mg/g and after fourth cycle of regeneration it was restored to 90 % of its original value.

Keywords: Photocatalysis, photocatalytic regeneration, sorption, nanoparticles, graphitic carbon nitride

1. INTRODUCTION

An environmental pollution is one of the major threats nowadays. People are turning to more ecological solutions and the industry is under pressure to reduce the amount of released pollutants. For these reasons industry companies search for new economic and environmentally friendly solutions. An effective and environmentally friendly removal and disposal of pollutants is therefore the goal of many studies [1,2]. Photocatalytic and sorption processes are considered as a good way how to ecologically remove pollutants. Photocatalytic process would be ideally powered by solar energy, making it energy-saving. Beside decomposition of organic pollutants [3], the photocatalysis has many other uses such as production of hydrogen by water splitting [4], self-cleaning materials [5], water disinfection using antibacterial effects [6] and reduction of carbon dioxide [7] and nitrogen oxides [8].

Sorption processes are another way how to remove pollutants. They are based on the binding of substances on their surface, thereby reducing their concentration in the environment. Sorption processes are used for sanitization of oil spills [9], removal of heavy metals from water [10], removal of organic pollutants [11], carbon capture and storage [12] or storage of other substances, such as hydrogen [13]. After its saturation, the sorbent must be disposed or subjected to a regeneration process. Simply disposal of saturated sorbents could be expensive. For example, it is the most expensive and time-consuming part of removal of oil spills [9].

On the other hand, there is a regeneration process that restores sorption capacity of the sorbent and allows its further use. Regeneration of the saturated sorbent is performed mostly thermally and chemically [14,15]. Thermal processes are energy-intensive and therefore economically inappropriate. For chemical regeneration,

toxic or otherwise dangerous substances are often used. Therefore, there is an effort to develop and improve eco-friendly methods such as biological or photocatalytic regeneration [16,17].

If the sorbent also exhibits photocatalytic activity, it can be regenerated using electromagnetic radiation. The following photocatalytic reaction results in sorbate decomposition. Ideally the pollutants would be decomposed into substances with less sorbent affinity and washed away. Pardo et al. [17] prepared hydrogel containing titanium dioxide. The material was tested on sorption of methylene blue and antibiotics Ofloxacin and Ciprofloxacin and was subjected to photocatalytic regeneration under UV light irradiation. Sorption capacities were 96 mg/g for methylene blue, 84 mg/g for Ofloxacin and 63 mg/g for Ciprofloxacin when the starting concentrations of tested pollutants was 100 mg/L. Material preserved its sorption capacity for ten cycles of regeneration. Several other materials, such as zeolite [18], were modified by titanium dioxide and subjected to successful photocatalytic regeneration under UV irradiation. For better separability of saturated sorbent, it is very convenient to modify it with magnetic material [19]. The regeneration of Fe_3O_4/Bi_2S_3 sorbent with magnetic properties took place under simulated solar radiation (300 W xenon lamp). Magnetic properties then provided better handling of the material but after five regeneration cycles the sorption capacity has fallen to 25 % of the original value.

This work continues in the study of regeneration of graphitic carbon nitride incorporated into the silica structure containing zinc [20]. Following material has greater specific surface area, greater sorption capacities than ZnO-m·SiO_2/g-C_3N_4 nanocomposite [20] and did undergo four successful photocatalytic regeneration under UV light irradiation. Prepared sorbent was characterized by EDX, BET analysis, SEM and was subjected to test of sorption and photocatalytic regeneration.

2. EXPERIMENTAL

2.1. Materials and chemicals

Chemicals used for experiments are zinc acetate of 99 % purity purchased from PENTA s.r.o., sodium water glass 38-40 °Bé (Na_2SiO_3) with module of 3 purchased from company Vodní sklo, a.s. and melamine of 99 % purity purchased from Sigma-Aldrich spol. s.r.o. For all aqueous solutions, demineralized water was used.

2.2. Preparation of graphitic carbon nitride g-C_3N_4

Bulk graphitic carbon nitride was prepared the same way as in our previous work [21]. Melamine was heated in laboratory furnace in air from 20 °C to 550 °C with step of 2 °C per minute and lasted there for 4 hours. Material was then comminuted by grinding in agate mortar and further exfoliated by heating up to temperature of 500 °C with step of 2 °C per minute for next two hours. The specific surface area of prepared exfoliated graphitic carbon nitride was 157 m^2/g.

2.3. Preparation of modified graphitic carbon nitride g-C_3N_4

To prepare a sample with 20 wt.% of g-C_3N_4, 27 g of zinc acetate and 0.295 g of g-C_3N_4 were added to 75 ml of demineralized water and homogenized in the ultrasonic field. To prepare a sample with 10 wt.% of g-C_3N_4, 0.131 g of g-C_3N_4 was used. 225 ml of demineralized water was then mixed with 2.57 g of water glass (the fraction of solids was 39.67 wt.%). The mixture was homogenized in an ultrasonic field with power density of 1 kW/L and it was continuously stirred at 500 RPM. After five minutes, a dispersion of g-C_3N_4 and zinc acetate was added at once. The mixture was further stirred at 500 RPM in the ultrasonic field for fifteen minutes. The residue zinc acetate was then removed by washing the material. The mixture was transferred to a two-liter cylindrical container which was filled by demineralized water to its maximum. After two hours of sedimentation, the clear liquid above the sediment was carefully removed and the cylinder was again filled to the maximum

by demineralized water. This washing cycle was repeated five times. The sedimented dispersion was then quickly frozen and subjected to vacuum sublimation.

2.4. EDAX and SEM analysis

The composition of nanocomposite was determined by EDX analysis on scanning electron microscope SEM FEI Quanta 650 FEG. This scanning electron microscope was used to capture SEM images of powdered sample.

2.5. Specific surface area

Dynamic BET analysis was performed on Qsurf HORIBA SA9601 to measure specific surface area (SSA). Powder material was degassed for 5 hours at 150 °C and then subjected to six-point analysis.

2.6. Continual measuring of adsorption of simulant dye

We used reactor for continuous dye adsorption measurement. This method applies the principle of dye concentration measurement from patent application "Continuous measurement of photocatalysis of dye simulants" [22]. The advantage is a fast in situ measurement, without the need of taking samples and therefore compromising the system. Setup was the same as described in [20]. The decrement of the dye concentration was calculated from measurement of diffused and backscattered light intensity from a laser located at the top of the measuring vessel. Ocean Optics USB4000-UV-VIS was used as a detector. Sorption process took place at the temperature of 20 °C, in the dark environment and under continuous stirring until the sorbent was saturated. 1 mg/L of methylene blue was used as starting concentration of simulant dye.

3. RESULTS AND DISCUSSION

Nanocomposite sorbent based on graphitic carbon nitride incorporated into silicate structure containing zinc was successfully prepared and tested on sorption of methylene blue and photocatalytic regeneration. The samples were prepared in two variants: 1. ECN20 with 20 wt.% of g-C_3N_4 and 2. ECN10 with 10 wt.% of g-C_3N_4. The SSA, which has an important role in sorption and photocatalytic processes, was determined to be 366 m^2/g for ECN20 and 320 m^2/g for ECN10. The SSA of prepared samples is higher than the SSA of previously prepared sorbent capable of photocatalytical regeneration [20] with value of 238 m^2/g.

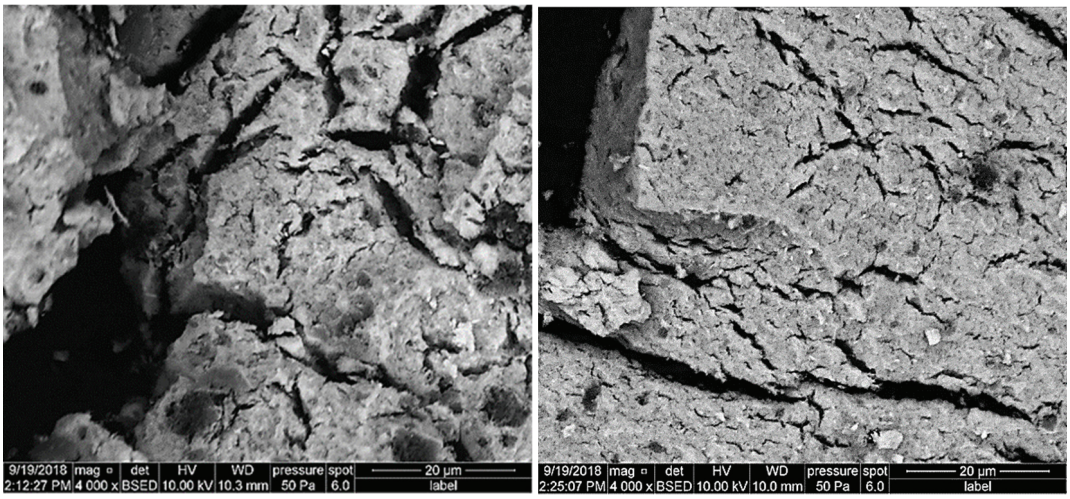

Figure 1 SEM images of ECN20 (left) and ECN10 (right)

Images (**Figure 1**) from scanning electron microscope showed ragged morphology of the samples causing high values of the SSA. The EDX analysis (**Figure 2**) confirmed final content of both samples to be 18.14 wt.%

for ECN20 and 8.23 wt.% for ECN10. Lower content than the estimated was probably caused by imperfect incorporation of g-C_3N_4 during synthesis.

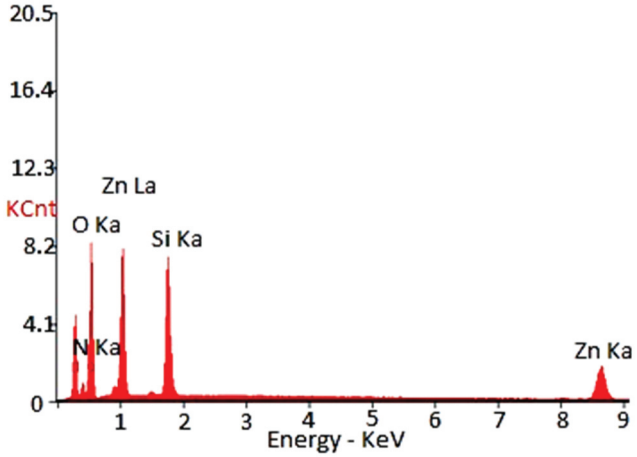

Figure 2 EDX element analysis of ECN20 used for calculation of g-C_3N_4 content (18.14 wt.%)

Samples were subjected to repeated sorption of methylene blue with starting concentration of 1 mg/L and photocatalytic regeneration process. The regeneration process consisted of several steps. At first, the saturated sorbent was separated from the methylene blue residue by centrifugation. The sediment was then moved into beaker and filled up to 50 ml with deionized water and subjected to photocatalytical decomposition of sorbed methylene blue. Photocatalytic regeneration was performed under LED UV irradiation source with the maximum of light emission located at 365 nm. After decomposition, the sample was centrifugated again to remove by-products and then it was ready for next sorption process. Sorption characteristics are shown on **Figure 3** and **Figure 4**. Sorption capacity of ECN10 was 0.18 mg/g and 90 % of it was regenerated after fourth cycle. The decrement of sorption capacity was due to loses of sorbent during manipulation or stronger interactions were created between sorbent and methylene blue due to deformation and enclosing of some pores.

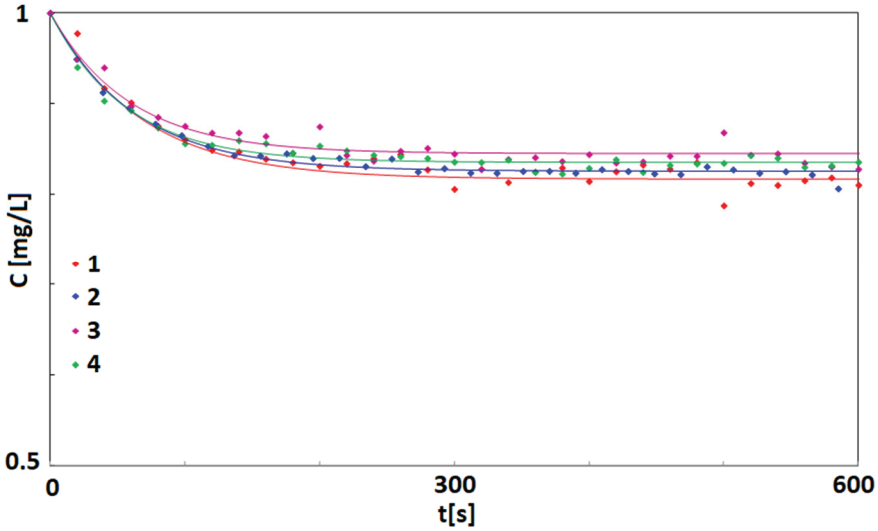

Figure 3 Sorption kinetics of methylene blue sorption process on the ECN10 for four cycles (different colours) of photocatalytic regeneration. Numbers 1 to 4 indicate the order of sorption process.

Sorption capacity of ECN20 was 0.21 mg/g and about 75 % of it was available after fourth cycle. The decrement of sorption capacity of ECN20 is greater than of ECN10 due to greater content of g-C_3N_4 which probably serves as centre for stronger interactions.

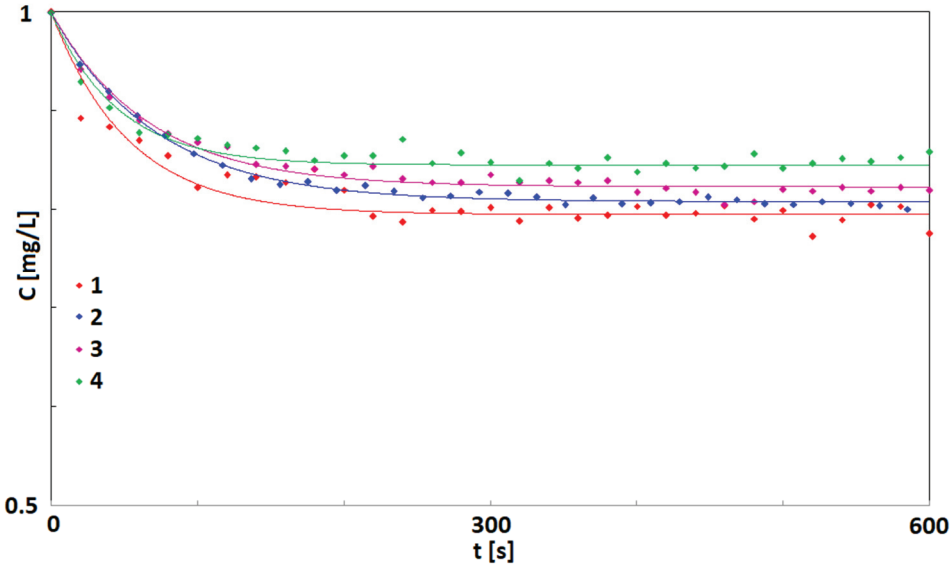

Figure 4 Sorption kinetics of methylene blue sorption on the ECN20 for four cycles (different colours) of photocatalytic regeneration. Numbers 1 to 4 indicate the order of sorption process.

Rate constants of adsorption tests were calculated from linear parts of acquired data for both samples. The rate constants were 0.015 s^{-1} for ECN10 and 0.019 s^{-1} for ECN20. These rate constants are greater than previously tested material [20] with the value of 0.004 s^{-1}. Modified nanocomposite showed better performance in photocatalytic regeneration and sorption process of methylene blue than previous nanocomposite ÚZnO-m·SiO_2/g-C_3N_4 [20] and was tested with four regeneration cycles.

4. CONCLUSION

Nanocomposite sorbent based on graphitic carbon nitride incorporated into silicate structure containing zinc was successfully prepared and tested for sorption of methylene blue and photocatalytic regeneration. The EDX analysis confirmed estimated composition and SEM images showed ragged morphology of both prepared samples, which caused the great values of the specific surface area. The specific surface area of sample with 20 wt.% of g-C_3N_4 was 366 m^2/g and was greater than at the sample with 10 wt.% of g-C_3N_4 with the value of 320 m^2/g.

Both samples were successfully regenerated four times by UV LED light source. Greater content of g-C_3N_4 led to greater decrease in sorption capacity. The sorption capacity of ECN20 was 0.21 mg/g and after the fourth cycle of regeneration it was restored to 75 % of its original value. The sorption capacity of ECN10 was 0.18 mg/g and after fourth cycle of regeneration it was restored to 90 % of its original value. Although both samples were successfully regenerated, the sample ECN10 performed better in the photocatalytic regeneration process under the UV light irradiation.

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REFERENCES

[1] NATH, R. K., ZAIN, M. F. M. and JAMIL M. An environment-friendly solution for indoor air purification by using renewable photocatalysts in concrete: A review. *Renew. Sustain. Energy Rev.* 2016. vol. 62, pp. 1184-1194.

[2] MOLINARI, A., SARTI, E., MARCHETTI, N. and PASTI L. Degradation of emerging concern contaminants in water by heterogeneous photocatalysis with $Na_4W_{10}O_{32}$. *Appl. Catal. B Environ.* 2017. vol. 203, pp. 9-17.

[3] SVOBODA, L., DVORSKÝ, R., PRAUS, P., MATÝSEK, D. and BEDNÁŘ, J. Synthesis of ZnO nanocoatings by decomposition of zinc acetate induced by electrons emitted by indium. *Applied Surface Science*. 2016. vol. 388, p. 491-496.

[4] ISMAIL, A. A. and BAHNEMANN, D. W. Photochemical splitting of water for hydrogen production by photocatalysis: A review. *Sol. Energy Mater. Sol. Cells.* 2014. vol. 128, pp. 85-10.

[5] FAN, Y. Photocatalysis and self-cleaning from g-C_3N_4 coated cotton fabrics under sunlight irradiation. *Chem. Phys. Lett.* 2018. vol. 699, pp. 146-154.

[6] HELALI, S. Solar photocatalysis: A green technology for E. coli contaminated water disinfection. Effect of concentration and different types of suspended catalyst. *J. Photochem. Photobiol. A Chem.* 2014. vol. 276, pp. 31-40.

[7] XIONG, Z., LEI, Z., LI, Y., DONG, L., ZHAO, Y. and ZHANG, J. A review on modification of facet-engineered TiO2 for photocatalytic CO2 reduction. *J. Photochem. Photobiol. C Photochem. Rev.* 2018. vol. 36, pp. 24-47.

[8] ÂNGELO, J., ANDRADE, L., MADEIRA, L. M. and MENDES A. An overview of photocatalysis phenomena applied to NOx abatement, *J. Environ. Manage.* 2013. vol. 129, pp. 522-539.

[9] BHARDWAJ, N. and BHASKARWAR, A. N.. A review on sorbent devices for oil-spill control. *Environ. Pollut.* 2018.

[10] LÓPEZ-DELADO, A., PÉREZ, C. and LÓPEZ, F. A. Sorption of heavy metals on blast furnace sludge. *Water Res.* 1998 vol. 32, no. 4, pp. 989-996.

[11] ZHU, R., ZHU, GE, J., F. and YUAN, P. Regeneration of spent organoclays after the sorption of organic pollutants: A review. *J. Environ. Manage.* 2009 vol. 90, no. 11, pp. 3212-3216.

[12] THEO, W. L., LIM, J. S., HASHIM, H., MUSATFFA, A. A. and HO, W. S.. Review of pre-combustion capture and ionic liquid in carbon capture and storage. *Appl. Energ.* 2016 vol. 183, pp. 1633-1663.

[13] HUANG, J. Revealing contribution of pore size to high hydrogen storage capacity. *Int. J. Hydrogen Energy*. 2018 vol. 43, no. 39, pp. 18077-18082.

[14] SALVADOR, F., MARTIN-SANCHEZ, N., SANCHEZ-HERNANDEZ, R., SANCHEZ-MONTERO, M. J. and IZQUIERDO, C. Regeneration of carbonaceous adsorbents. Part I: Thermal Regeneration. *Microporous Mesoporous Mater.* 2015. vol. 202, pp. 259-276.

[15] LIU, D. Electrochemical regeneration of a graphite adsorbent loaded with Acid Violet 17 in a spouted bed reactor. *Chem. Eng. J.* 2016. vol. 304, pp. 1-9.

[16] KLIMENKO, N., SMOLIN, S., GRECHANYK, S., KOFANOV, V., NEVYNNA, L. and SAMOYLENKO, L. Bioregeneration of activated carbons by bacterial degraders after adsorption of surfactants from aqueous solutions. *Colloids Surfaces A Physicochem. Eng. Asp.* 2003 vol. 230, no. 1-3, pp. 141-158.

[17] PARDO, A. Self-regenerating photocatalytic hydrogel for the adsorption and decomposition of methylene blue and antibiotics in water. *Environ. Technol. Innov.* 2018. vol. 11, pp. 321-327.

[18] LIU, S., LIM, M. and AMAL, R..TiO_2-coated natural zeolite: Rapid humic acid adsorption and effective photocatalytic regeneration. *Chem. Eng. Sci.* 2014. vol. 105, pp. 46-52.

[19] ZHU, H., JIANG, R., LI, J., FU, Y., JIANG, S. and YAO, J. Magnetically recyclable Fe_3O_4/Bi_2S_3 microspheres for effective removal of Congo red dye by simultaneous adsorption and photocatalytic regeneration. *Sep. Purif. Technol.* 2017. vol. 179, pp. 184-193.

[20] MANČÍK, P., BEDNÁŘ, J., SVOBODA, L., DVORSKÝ, R. and MATÝSEK, D. Photocataylytic Reactivation of g-C_3N_4 Based Nanosorbent. In *NANOCON 2017 - 9th International Conference on Nanomaterials - Research & Application*. Ostrava: TANGER, 2017, pp. 289-294.

[21] SVOBODA, L., PRAUS, P., and LIMA, M. J. Graphitic carbon nitride nanosheets as highly efficient photocatalysts for phenol degradation under high-power visible LED irradiation. *Materials Research Bulletin*. 2018. vol. 100, pp. 322-332.

[22] DVORSKÝ, R., BEDNÁŘ, J., SVOBODA, L. and MANČÍK, P. Přihláška vynálezu: “Způsob kontinuálního měření fotokatalýzy barvivových simulantů, PV 2018-421, 2018.