Bisphenol A Removal by Graphene Oxide Applied in Different Processes

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Highlights:

- GO was more effective under visible light than UV irradiation.
- Graphene oxide enhanced the 3D-EO process in BPA removal.
- BPA could be removed by 93% using 3D-EO.
- Removal of 3D-EO was fitted well by pseudo first order kinetic modeling.
- This is the first study conducted with 3D-EO enhanced by GO in BPA removal.

Abstract: Bisphenol A (BPA) is a commonly used plasticizer incorporated into the parent plastics during manufacturing. It is classified as an emerging contaminant that is continually detected in aquatic environments and is listed as an endocrine disrupting chemical confirmed to be associated with cardiovascular disease and reproductive disorder. The hazardous aspects of BPA require the development of innovative methods for its degradation. Among these techniques, adsorption and electrochemical degradation are considered to be particularly attractive due to their high efficiency, versatility and environmental friendliness, since they do not require any other chemicals. The use of graphene oxide (GO) was investigated as an adsorbent and as a particle electrode for the removal of BPA from aqueous solutions. The adsorptive behaviors of GO toward BPA were investigated in batch mode under darkness, visible light and UV light conditions. GO was used as particle electrode in a three-dimensional electro-oxidation (3D-EO) process established by an Ru/TiO_2 anode and the effects of current density values ranging from 10 to 50 mA/cm^2 were investigated. The obtained results revealed that the 3D electrochemical degradation process achieved a higher BPA removal efficiency than adsorption, showing that 3D-EO with a graphene oxide particle electrode may significantly improve BPA removal efficiency.

1   Introduction

As plastic particles are found in terrestrial ecosystems and the ocean, they pose various threats to biodiversity as well as human health. Their worldwide annual

production is expected to increase to 966 million tons in 2050 [1]. This increase in plastic production will lead to an increase in the global amount of discarded plastics that will eventually reach and persist in the environment.

Used plastics do not remain as they are but undergo degradation and fragmentation processes through physical, chemical and biological drivers, such as ultraviolet radiation, temperature change and mechanical abrasion, resulting in particles of a size smaller than 5 mm [2]. Due to their small size, they are easily ingested by a wide range of organisms and pose great risks, such as pathological stress, reproductive complications and reduced growth rate [3]. Furthermore, hazardous chemicals associated with micro-plastics may be released into the surrounding environment during the fragmentation of plastics. These compounds are potentially harmful additives and are known to disrupt the estrogenic and endocrine activity in vertebrate and invertebrate species [4].

Bisphenol A (BPA), one of the most commonly used plasticizers, is incorporated into the parent plastics during the manufacturing processes to give tensile strength or flexibility and is reported among the most commonly found anthropogenic substances in environmental samples [5]. It has been confirmed to be associated with obesity, cardiovascular disease, reproductive disorder, and breast cancer. It is known that plasticizers may have biological effects already at concentrations in the µg/L or mg/L range [6].

As the removal of BPA is crucial, many treatment processes have been developed, including biodegradation [7-9], photodegradation [10], nanofiltration [11] and reverse osmosis [12]. These methods are not fully successful in BPA removal and have some drawbacks, such as high cost, the need for further treatment, the formation of hazardous by-products, low efficiency, and applicability for a limited concentration range. Among these methods, adsorption is considered to be one of the most effective methods for BPA removal and many researchers have studied the adsorption of BPA with different materials in the last decades [13,14].

The increasing use of carbon-based adsorbents as photocatalyst support brought about the development of the carbocatalysis term. Carbocatalysis has become more important with the widespread use of graphene (G). Over the last few years, carbon-based nanocomposites, especially graphene and graphene oxide (GO), have started to attract attention. GO is used in many different industries especially for the adsorption of pollutants due to its many advantages, such as thermal stability, electrical conductivity, high pore volume and surface area [15]. The most frequently studied methods for degradation of persistent organic pollutants (POPs) are catalytic applications in which the effect of both UV radiation and visible light are assessed. Furthermore, the GO composite used in BPA

degradation is found to be effective under visible light [16-18]. The study conducted by Xu, *et al.* [18] showed that 1 mg/L of bisphenol A can be reduced by 96% after 1 hour of treatment under visible light.

In this study, GO was synthesized using the modified Hummers method [19]. Synthesized GO was characterized and used to remove BPA from water under visible light, UV light and darkness as well as electro-oxidation (EO) and EO with GO.

2   Materials and Method

2.1   Experimental Set-up

All chemicals used in this study were purchased from Merck (Turkey). Experimental studies in darkness and under visible light were carried out with 100 mL sample volume, shaking was performed using a GFL brand horizontal shaker placed in a WTW incubator to maintain the temperature constant at 20 °C. LED lights with a wavelength of 7000 K were operated as light source in the degradation experiments. For the experiments under UV light, 100 mL of sample volume was stirred with a WiseStir (MSH-20A) magnetic stirrer placed under four UV light sources with 8 W of power.

The experiments for the EO studies were conducted in a reactor with dimensions of 5 cm x 2 cm x 15 cm and a sample volume of 100 mL. A GW GPC-3060i laboratory direct current (DC) power supply was used to apply different current densities between the Ru/TiO_2 and TiO_2 electrodes, respectively used as anode and cathode. All EO and 3D-EO experiments were operated with a magnetic stirrer. A Hettich Rotofix centrifuge was used to separate the GO in all the samples from the different processes before BPA analysis using a gas chromatographer equipped with a mass detector.

### 2.2   Graphene Oxide Synthesizing

The graphene oxide (GO) used in this study was synthesized by the modified Hummer method [19]. According to this method, a 9:1 mixture of concentrated sulfuric acid/phosphoric acid (360: 40 mL) is placed in a beaker that is placed in an oil bath. Graphite (3.0 g) and potassium permanganate (18.0 g) are added slowly. The mixture is stirred at 40-45 °C for 16 hours. The mixture is then cooled to room temperature by pouring onto 400 mL of ice. Finally, 30% hydrogen peroxide (3 mL) is added. After obtaining the GO from the acidic solution, the GO is washed with distilled water, 35% hydrochloric acid and ethanol. The solution is placed in centrifuge tubes and centrifuged for 45 min at 3000 rpm. Washing and centrifugation is repeated three times.

The synthesized GO is stored in ethanol before the degradation studies. For characterization, the zeta potential and particle size were measured using a Malvern Zeta Sizer Z90 and TEM analysis was done in the Central Laboratory of Gebze Technical University, Turkey.

3   Results and Discussion

Although to date several methods have been developed to synthesize GO, the most widely used method is the modified Hummer method, which is based on the chemical reduction of GO. In this method, oxidation of natural graphite with strong oxidants ($KMnO_4$, HNO_3, etc.) is used to obtain GO, after which the obtained GO is exfoliated. The synthesis method is given in detail in Section 2.2. Measurements were done for characterization and TEM analysis and to determine particle size and zeta potential.

According to the particle size distribution and zeta potential measurements was found to be 160 nm. The zeta potential was determined as lower than -30 mV for all pH values except pH 2, which showed that the stability of the synthesized GO was good (Figure 1).
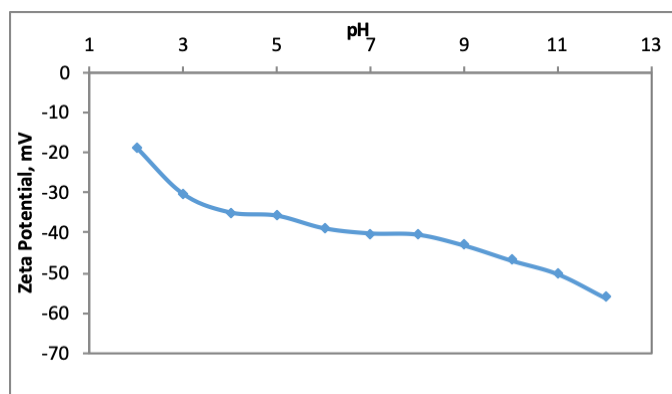


Figure 1   Zeta potential result of GO.

Values of -30 mV and lower for the zeta potential are generally considered to be critical to represent the stability of a dispersion [20]. The TEM imaging and the morphological change of GO are given in Figure 2. GO was present in relatively flat plates. This is mostly due to electrostatic pushing. In this study, the application of different processes was compared and the influent parameters were investigated. The effects of darkness, visible light, UV light, EO with Ru/TiO_2 electrodes and three-dimensional electrodes were researched. The independent variables were kept the same, i.e. a GO concentration of 300 mg/L, a BPA

concentration of 25 mg/L and a reaction time of 30 minutes. The results are presented in Figure 3.
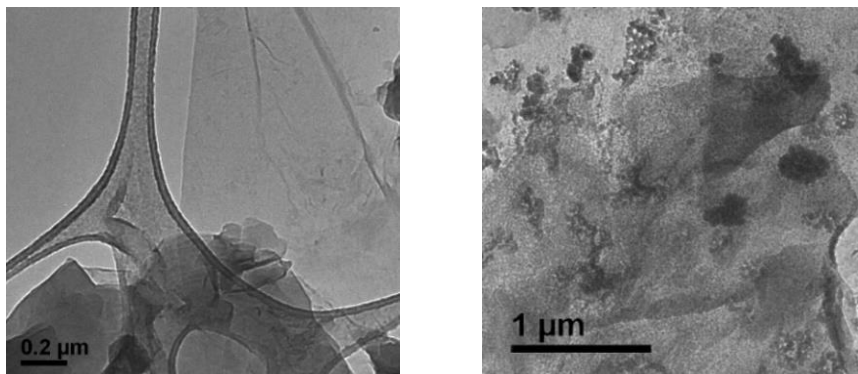

Figure 2   TEM imaging of GO.

The effect of light can be seen in Figure 3. While the removal efficiency obtained in darkness was 18%, UV light did not affect the removal. The removal efficiency obtained with visible light was 21%, but the increase in removal was not significant. In order to enhance the removal efficiency, the EO process was investigated.
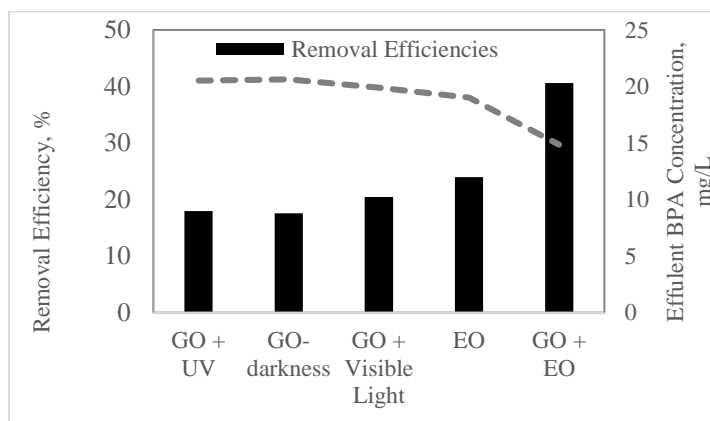
Figure 3   Comparison of different processes.

When a current density of 25 mA/cm^2 was applied, the removal efficiency of EO with Ru/TiO$_2$ electrodes increased to 24%. The usage of three-dimensional electrodes with GO in EO increased the removal to 40%. Based on this information, EO with three-dimensional electrodes was selected as the most effective process among the studied processes.

To investigate the effect of current density on BPA removal, different current densities and reaction times were applied (Figure 4). An increase in reaction time led to an increase BPA removal. In the first 10 minutes, the removal was around 20% for all current densities. This can mainly be explained by the low production of oxidative species such as hydroxyl radicals in EO during the first minutes.
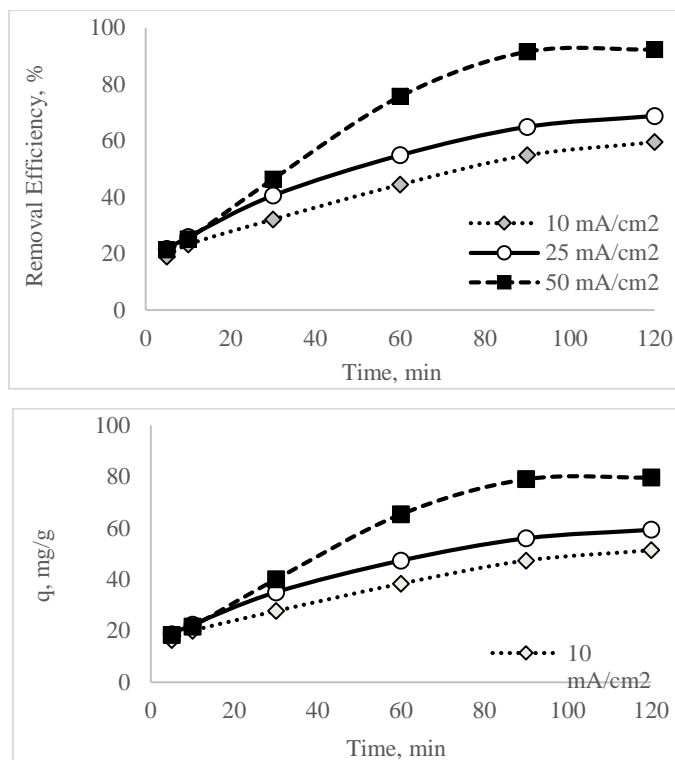
Figure 4 BPA removal efficiency and adsorption capacities for different current densities in the 3D-EO process.

When the reaction time is increased, more of these oxidative species can be produced in the water. The similarity in removal efficiency for different current densities can be attributed to the effect of adsorption but not of oxidation. At reaction time longer than 10 minutes, the effect of oxidative species can be seen.

An increase in current density from 10 to 25 mA/cm^2 led to an enhancement of the removal efficiency of around 10%. However, when the current density was 50 mA/cm^2, the removal efficiency reached 93% at 90 minutes while it was 73% for 25 mA/cm^2. Similar results were seen for the adsorption capacity.

3.1   Kinetic Modeling

Pseudo first order kinetic model is widely used to represent adsorption. The equation can be linearized in Eq. (1) as follows [21]:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 \tag{1}$$

The equation for the pseudo second order kinetic model is in Eq. (2) as follows [21],

$$\frac{t}{q_t} = 1/(k_2 q_e^2) + 1/q_e t \tag{2}$$

Intraparticle diffusion modeling was first developed by Weber and Morris. The equation can be linearized in Eq. (3) as follows:

$$q_t = k_3 t^{1/2} + \tag{3}$$

In all equations qe and qt are the adsorption capacities at equilibrium and at time t, k_1, k_2, k_3 are the kinetic constants of the model.

The results from pseudo first order, pseudo second order and intraparticle modeling can be seen in Figure 5. The calculated kinetic constants and regression coefficients are given in Table 1.

Table 1   Kinetic Modeling Results

	10 mA/cm^2	25 mA/cm^2	50 mA/cm^2
Pseudo first order kinetic			
k_1	0.016	0.016	0.012
R^2	0.996	0.995	0.956
Pseudo second order kinetic			
q_e, mg/g	59	68	104
k_2	0.044	0.048	0.029
R^2	0.969	0.985	0.967
Intraparticle modeling			
k_3	4.14	4.91	7.87
R^2	0.995	0.993	0.974

When the regression coefficients of the three models are examined it can be seen that the regression coefficients of the three models are all higher than 0.95. Except for 50 mA/cm^2, the results are more suitable for pseudo first order kinetic modeling, while they are suitable for intraparticle modeling at 50 mA/cm^2 current density. Consequently, it can be said that the results for the different current densities are suitable for both pseudo first order kinetics and intraparticle modeling. This can be explained by the fact that not only the physisorption but also the intraparticle diffusion is involved in the adsorption under different current densities.
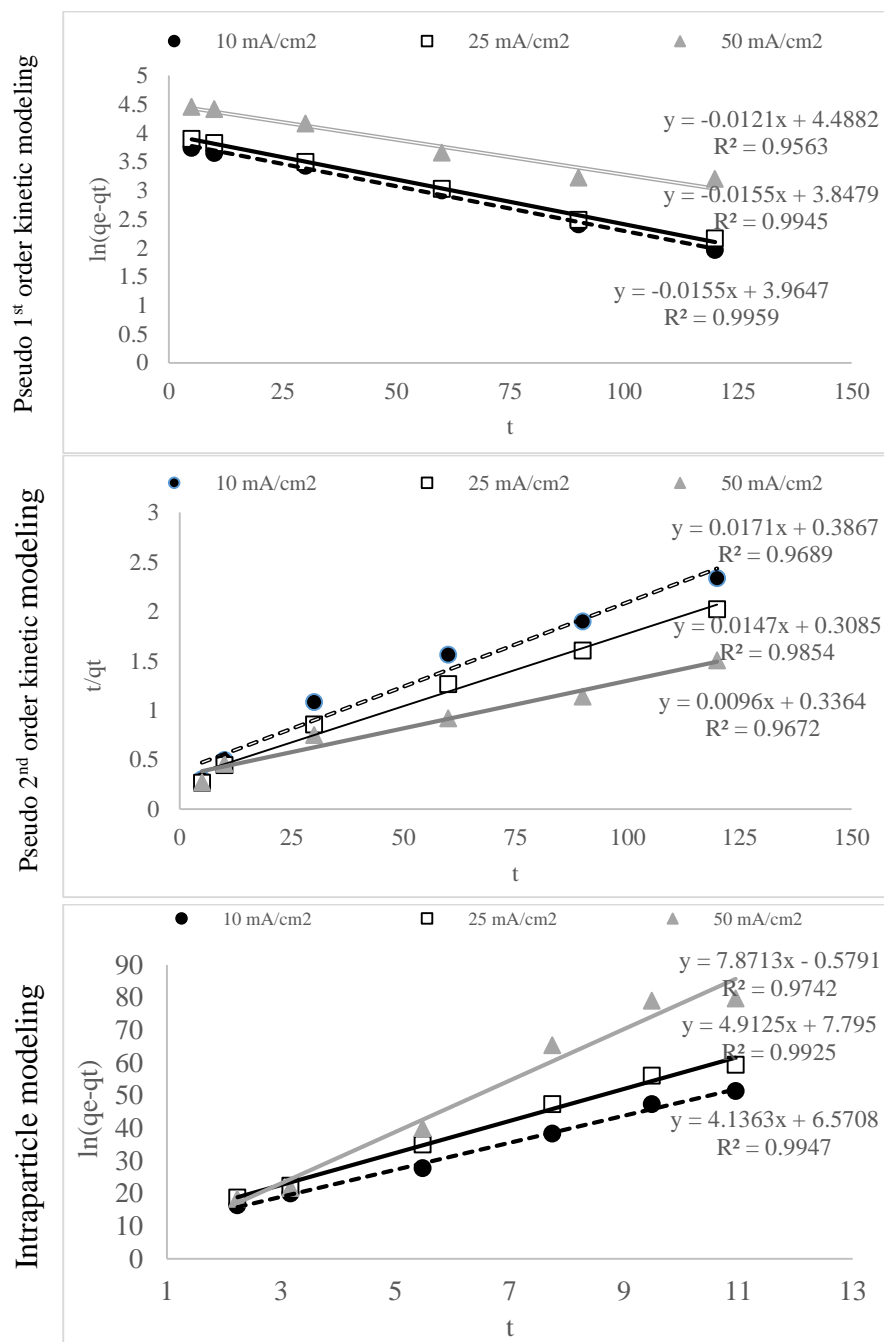
Figure 5 Kinetic modeling of the 3D-EO process results.

4   Conclusion

In this study, a comparison was made between different processes with graphene oxide (GO) synthesized according to the modified Hummer method. It was observed that GO was more effective under visible light, while the effect of UV light was negligible. The BPA removal obtained under visible light was found to be quite low (24%). Therefore, electro-oxidation (EO) using Ru/TiO_2 electrodes and using three-dimensional electrodes (graphene oxide) was investigated. Compared with EO, BPA removal by 3D-EO was found to be increased.

Several current densities in the 3D-EO process were investigated. The initial concentration of 25 mg/L for BPA was reduced with 93% removal efficiency at a current density of 50 mA/cm^2 and 90 minutes reaction time. The increase in BPA removal by 3D-EO shows that apart from the oxidative species produced by electro-oxidation, the adsorption process is also available. According to the results of kinetic modeling, both pseudo first order kinetic and intraparticle modeling were found to be suitable, which indicates that physisorption and intraparticle diffusion play a role in the adsorption process. The effect of different BPA and GO concentrations on the degradation can also be studied. With the aim of cost reduction of EO by employing three-dimensional electrodes, investigations on the use different electrodes, such as Pt/TiO_2 and metal-doped graphene oxide, can be done as further study. To determine the effect of adsorption and oxidative species on the three-dimensional electro-oxidation process, further studies can be performed.

Acknowledgements

References

[1]   Song N.S., Co H.J. & Kim S.K., *Occurrence of Microplastics in Commercial Seafood from Korea and Human Exposure*, Micro 2018: Fate and İmpact of Microplastics: Knowledge, Action and Solutions, pp. 31-32, 2018.

[2]   Barnes, D.K., Galgani, F., Thompson, R.C. & Barlaz, M., *Accumulation and Fragmentation of Plastic Debris in Global Environments*, Philos Trans R Soc Lond B Biol. Sci., **364**(1526), pp. 1985-98, Jul 27, 2009.

[3]   Fossi, M.C., Marsili, L., Baini, M., Giannetti, M., Coppola, D., Guerranti, C., Caliani, I., Minutoli, R., Lauriano, G., Finoia, M.G., Rubegni, F., Panigada, S., Berube, M., Ramirez, J.U. & Panti, C., *Fin Whales and Microplastics: The Mediterranean Sea and the Sea of Cortez Scenarios*, Environmental Pollution, **209**, pp. 68-78, Feb, 2016.

[4]   Sohoni, P. & Sumpter, J.P., *Several Environmental Oestrogens are also Anti-Androgens*, Journal of Endocrinology, **158**(3), pp. 327-339, Sep, 1998.

[5]   Flores, A.S., Gwon, E.M., Sim, D.M., Nisola, G., Galera, M.M., Chon, S.S., Chung, W.J., Pak, D.W. & Ahn, Z.S., *Performance Evaluation of Pilot Scale Sulfur-Oxidizing Denitrification for Treatment of Metal Plating Wastewater*, J. Environ Sci Health A Tox Hazard Subst Environ Eng,, **41**(1), pp. 101-16, 2006.

[6]   Oehlmann, J., Schulte-Oehlmann, U., Kloas, W., Jagnytsch, O., Lutz, I., Kusk, K.O., Wollenberger, L., Santos, E.M., Paull, G.C., Van Look, K.J.W. & Tyler, C.R., *A Critical Analysis of the Biological Impacts of Plasticizers on Wildlife*, Philosophical Transactions of the Royal Society B-Biological Sciences, **364**(1526), pp. 2047-2062, Jul 27, 2009.

[7]   Mohapatra, D.P., Brar, S.K., Tyagi, R.D. & Surampalli, R.Y., *Degradation of Endocrine Disrupting Bisphenol a During Pre-Treatment and Biotransformation of Wastewater Sludge*, Chemical Engineering Journal, **163**(3), pp. 273-283, Oct 1, 2010.

[8]   Zhang, H.W., Wang, Y.F., Wang, J. & He, Y.Q., *Mechanism of Bisphenol A Removal by a Submerged Membrane Bioreactor in the Treatment of Synthetic Municipal Sewage: Staged Analyses*, Desalination and Water Treatment, **57**(26), pp. 12364-12374, Jun 2, 2016.

[9]   Chen, J.H., Huang, X. & Lee, D.J., *Bisphenol A Removal by a Membrane Bioreactor*, Process Biochemistry, **43**(4), pp. 451-456, Apr, 2008.

[10]   Wang, R.C., Ren, D.J., Xia, S.Q., Zhang, Y.L. & Zhao, J.F., *Photocatalytic Degradation of Bisphenol a (BPA) Using Immobilized TiO_2 and UV Illumination in a Horizontal Circulating Bed Photocatalytic Reactor (HCBPR)*, Journal of Hazardous Materials, **169**(1-3), pp. 926-932, Sep 30, 2009.

[11]   Zielinska, M., Bulkowska, K., Cydzik-Kwiatkowska, A., Bernat, K. & Wojnowska-Baryla, I., *Removal of Bisphenol A (BPA) from Biologically Treated Wastewater by Microfiltration and Nanofiltration*, International Journal of Environmental Science and Technology, **13**(9), pp. 2239-2248, Sep, 2016.

[12]   Yuksel, S., Kabay, N. & Yuksel, M., *Removal of Bisphenol a (BPA) from Water by Various Nanofiltration (NF) and Reverse Osmosis (RO)*

Membranes, Journal of Hazardous Materials, **263**, pp. 307-310, Dec 15, 2013.

[13] López-Ramón, M.V., Ocampo-Pérez, R., Bautista-Toledo, M.I., Rivera-Utrilla, J., Moreno-Castilla, C. & Sánchez-Polo, M., *Removal of Bisphenols A and S by Adsorption on Activated Carbon Clothes Enhanced by the Presence of Bacteria*, Science of the Total Environment, **669**, pp. 767-779, June 15, 2019.

[14] Ndagijimanaa, P., Liu, X., Li, Z., Yu, G. & Wang, Y., *Optimized Synthesis Of A Core-Shell Structure Activated Carbon and its Adsorption Performance for Bisphenol A*, Science of the Total Environment, **689**, pp. 457-498, Nov 1, 2019.

[15] Feng, Y., Yao, T.J., Yang, Y., Zheng, F.R., Chen, P., Wu, J. & Xin, B.F., *One-Step Preparation of Fe2O3/Reduced Graphene Oxide Aerogel as Heterogeneous Fenton-Like Catalyst for Enhanced Photo-Degradation of Organic Dyes*, Chemistryselect, **3**(31), pp. 9062-9070, Aug 23, 2018.

[16] Chen, F.Y., An, W.J., Liu, L., Liang, Y.H. & Cui, W.Q., *Highly Efficient Removal of Bisphenol a by a Three-Dimensional Graphene Hydrogel-Agbr@Rgo Exhibiting Adsorption/Photocatalysis Synergy*, Applied Catalysis B-Environmental, **217**, pp. 65-80, Nov 15, 2017.

[17] Simsek, E.B., Kilic, B., Asgin, M. & Akan, A., *Graphene Oxide Based Heterojunction Tio2-Zno Catalysts with Outstanding Photocatalytic Performance for Bisphenol-A, Ibuprofen and Flurbiprofen*, Journal of Industrial and Engineering Chemistry, **59**, pp. 115-126, Mar 25, 2018.

[18] Xu, L., Yang, L., Johansson, E.M.J., Wang, Y.H. & Jin, P.K., *Photocatalytic Activity and Mechanism of Bisphenol a Removal Over Tio2-X/Rgo Nanocomposite Driven by Visible Light*, Chemical Engineering Journal, **350**, pp. 1043-1055, Oct 15, 2018.

[19] Marcano, D.C., Kosynkin, D.V., Berlin, J.M., Sinitskii, A., Sun, Z.Z., Slesarev, A., Alemany, L.B., Lu, W. & Tour, J.M., *Improved Synthesis of Graphene Oxide*, Acs Nano, **4**(8), pp. 4806-4814, Aug, 2010.

[20] Li, M.J., Liu, C.M., Xie, Y.B., Cao, H.B., Zhao, H. & Zhang, Y., *The Evolution of Surface Charge on Graphene Oxide during the Reduction and Its Application in Electroanalysis*, Carbon, **66**, pp. 302-311, Jan, 2014.

[21] Lagergreen, S., *Zur Theorie Der Sogenannten Adsorption Gelöster Stoffe, Zeitschrift für Chemie und Industrie der Kolloide*, **2**(1), pp. 15-15, July 01, 1907. (Text in Deutsch)