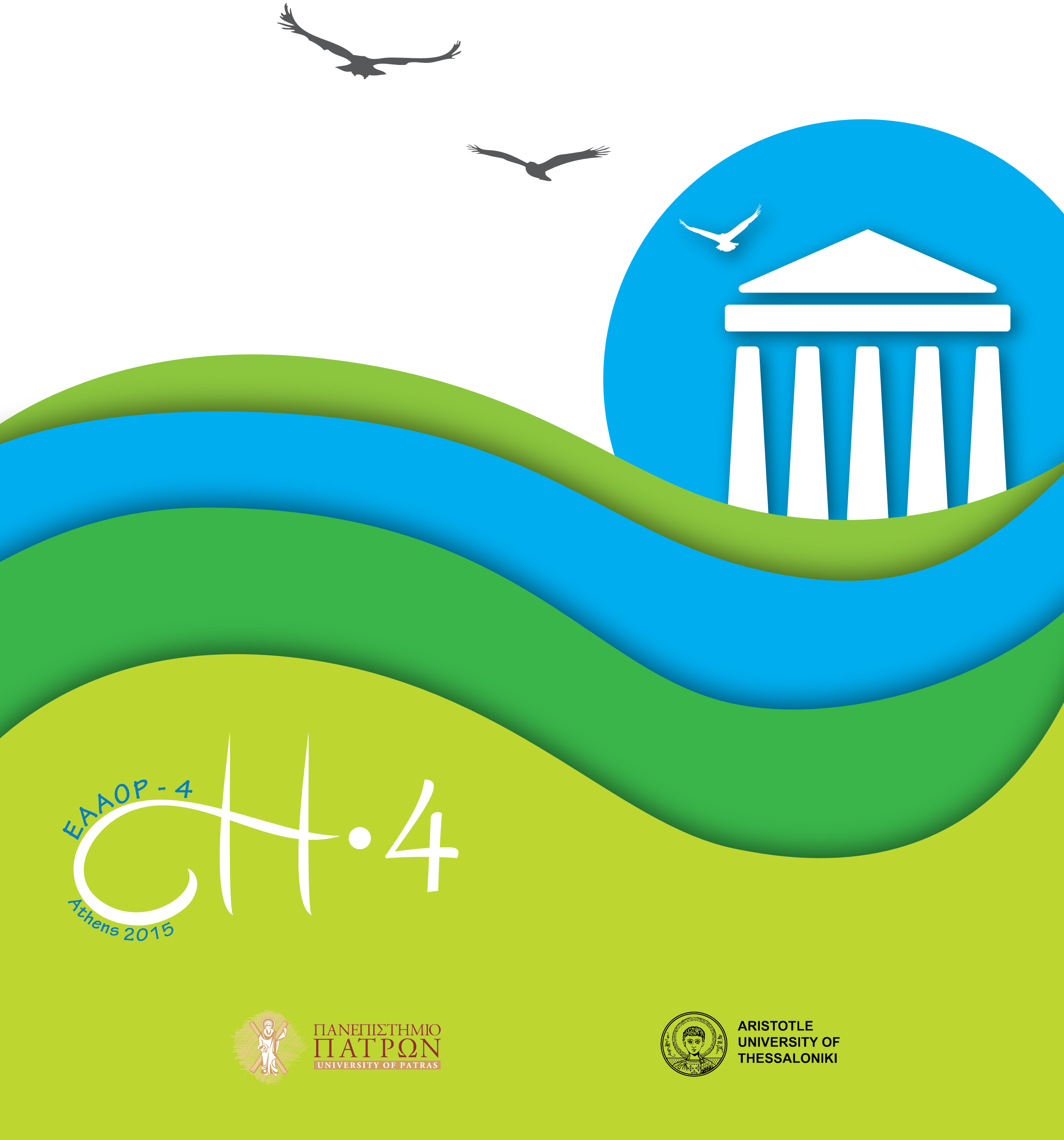
EUROPEAN CONFERENCE ON ENVIRONMENTAL APPLICATIONS OF ADVANCED OXIDATION PROCESSES

21-24 OCTOBER 2015, ATHENS - GREECE

CONFERENCE



EAAOP - 4

Athens 2015

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WELCOME TO EAAOP 4 CONFERENCE

On behalf of the Organizing and International Scientific Committees, we are glad to invite you to attend the 4th European Conference on Environmental Applications of Advanced Oxidation Processes – EAAOP4 – that will be held in Athens, Greece, on October 21-24, 2015.

The objective of the conference is to bring together scientists, engineers and other environmental professionals to present their findings and discuss future trends and directions concerning various Environmental Applications of Advanced Oxidation Processes (AOPs).

The presentations will focus on the scientific and technological advances of AOPs for the remediation of surface water, drinking water, groundwater, municipal and industrial wastewater, air and soil contaminated with various recalcitrant compounds, either alone or in conjunction with other processes.

This is the fourth event of the well-established EAAOP conferences with the previous three having been held in Chania, Greece (2006), Nicosia, Cyprus (2009) and Almeria, Spain (2013).

The Organizing Committee truly hopes that the EAAOP 4 program will reflect the high commitment and exceptional profile of the international community working in this field. Young researchers are called to participate and to interact closely with senior scientists, companies and stakeholder representatives, engaging open and vivid discussions throughout the whole meeting. Invited lectures, oral presentations and poster sessions will take place at the premises of luxurious TITANIA Hotel, while an appealing social program is being planned to provide you with a taste of genuine Hellenic hospitality.

Following the conference, the Scientific Committee shall invite the authors of selected contributions to submit full papers for publication in special issues of various journals.

Looking forward to meeting you in Athens in October 2015 (21-24 October 2015).

On behalf of the Organizing and Scientific Committees,

Dionissios Mantzavinos
Ioannis Poulios
Organizing Chairs

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Removal of Beta-Blockers from Aqueous Media by Adsorption onto Graphene Oxide

PP2- 10

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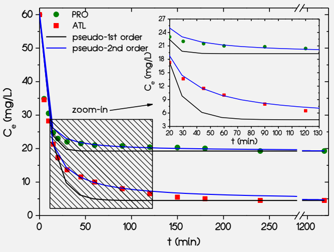


The aim of this study is the adsorption evaluation of graphene oxide (GhO) as adsorbent material for the removal of beta-blockers existed in wastewaters. The two model drug molecules were atenolol (ATL) and propranolol (PRO). After the characterization of GhO surface with SEM images, FTIR spectroscopy was used in order to confirm some possible adsorption interaction between drugs and adsorbent. The adsorption equilibrium data were fitted to Langmuir, Freundlich and Langmuir-Freundlich model calculating the maximum adsorption capacity (67 and 116 mg/g for PRO and ATL (25 °C), respectively). The temperature effect on adsorption was tested and the thermodynamic parameters were calculated. Finally, desorption of drugs from GhO was evaluated by using both aqueous eluants (pH 2- 10) and organic solvents.

1. Introduction

Beta-blockers are a class of pharmaceutical compounds, among others, that are not effectively removed during wastewater treatment, while they are detected in various environmental water samples [1]. Since the traditional water and wastewater treatment technologies are not able to remove compounds like beta-blockers from the water, different treatment options are under discussion to eliminate them. Recent studies have studied photocatalytic degradation for the removal of beta-blockers, ozonation or adsorption with several materials such as activated carbon or carrageenans. Of the above mentioned methods, adsorption appears to be a very promising technique for the removal of pharmaceuticals, because of its convenience once applied into current water treatment processes [2].

Graphene and graphene oxide are recently used as adsorbents to remove different groups of pollutants [3]. Despite the attention paid to graphene-based materials over recent years there are still only a handful of studies focusing on its use as sorbents for removal of pharmaceutical compounds [4].

In the present study, graphene oxide was synthesized and used for the adsorption/removal of beta-blockers from aqueous media. Due to the high environmental loading, ATL and PRO were used as model compounds. Although they both act on beta-adrenergic receptors (β -ARs), they can differ greatly in their specificity and lipophilic properties [5]. For example, PRO has a relatively high log(K_{0w}) of 3.48, whereas ATL has a considerably lower log(K_{0w}) of 0.23. In addition, structural differences may reflect differences in their adsorption, because PRO possesses an extra benzene ring, which is by far more inactive compared to the second amino group of ATL. Based on the above, their removal characteristics were investigated and compared in detail based on the differences in their physicochemical properties and chemical structures. The effects of different adsorption conditions on ATL and PRO removal were also studied: solution pH, temperature, and adsorption time. Finally, the adsorption isotherms and kinetics of the adsorbents were studied and discussed in order to understand the adsorption behavior. To the best of our knowledge, this is the first report in which the removal of beta-blockers from aqueous media was evaluated and compared by using graphene-based materials as sorbents.

2. Materials and Methods

2.1. Synthesis of graphene oxide (GhO)

GhO was synthesized with the modified Hummers method [6]. Commercial graphite powder (10 g) was stirred in 230 mL of concentrated sulfuric acid (temperature of solution was 0 °C). Then, potassium permanganate (30 g) was slowly added to the suspension. The rate of addition was controlled to prevent the rapid rise in the temperature of the suspension, which should be less than 20 °C. The reaction mixture was then cooled to 2 °C. After removal of the ice -bath, the mixture was stirred at room temperature for 30 min. Distilled water (230 mL) was slowly added to the reaction vessel, keeping the solution temperature less than 98 °C. The diluted suspension was stirred for additional 15 min, was further diluted with 1.4 L of distilled water and then 100 mL of a 30 wt% solution of hydrogen peroxide was added. The mixture was left overnight. The GhO particles settled at the bottom were separated from the excess liquid by decantation. The remaining suspension was transferred to dialysis tubes (Sigma Co). Dialysis was carried out until no precipitate of $BaSO_4$ was detected by addition of aqueous solution of $BaCl_2$. Then, the wet form of graphite oxide was separated by centrifugation. The gel-like material was freeze dried and a fine dark brown powder of the initial GhO was obtained.

2.2. LC-DAD-ESI/MS analysis

The LC-MS system consisted of a SIL 20A auto sampler with the volume injection set to 20mL and LC-20AB pump both from Shimadzu (Kyoto, Japan). The separation of the analytes was contacted by a C18 (Restek) analytical column 150 4.6 mm with 5mm particle size (Restek, USA). The samples were analyzed using the ESI interface in positive ionization (PI) mode. For the analysis in PI mode a gradient elution was performed by a binary gradient composed of solvent A (water with 0.1% formic acid) and solvent B (methanol with 0.1% formic acid) according to the following program: initial conditions 90% A, kept constant for 2.5 min then decreased to 70%, decreased to10% in 5 min, returns to the initial conditions after 7 min and re-equilibration time was set at 3 min.

2.3. Characterization techniques

Scanning electron microscopy (SEM) images were also taken with accelerating voltage of 15.00 kV (model Zeiss Supra 55 VP, Jena, Germany). For Fourier Transform Infrared Spectroscopy (FTIR) a Perkin-Elmer FT-IR spectrometer was used (model FTIR-2000, Perkin Elmer, Dresden, Germany). Infrared (IR) absorbance spectra were obtained between 450 and 4000 cm-1 at a resolution of 4 cm-1 using 20 co-added scans.

2.4. Adsorption– desorption experimental design

Batch experiments were carried out using 1 g/L of adsorbent (m = 0.01 g of adsorbent's mass were added to V = 10 mL of water in a conical flask).

3. Results and Discussion

3.1. SEM images

SEM was used to characterize the synthesized GhO. As it can be seen in Fig. 1a (next page), GhO formed the sheet-like structure and had a smooth surface without holes onto its surface. Partial agglomeration was also observed. No significant changes were observed after PRO or ATL adsorption (Figs. 1b, 2c). GhO retained its structure and surface morphology.

3.2 FTIR spectroscopy

Figs. 2ab present the FTIR spectrum of GhO before and after adsorption of (a) ATL and (b) PR.

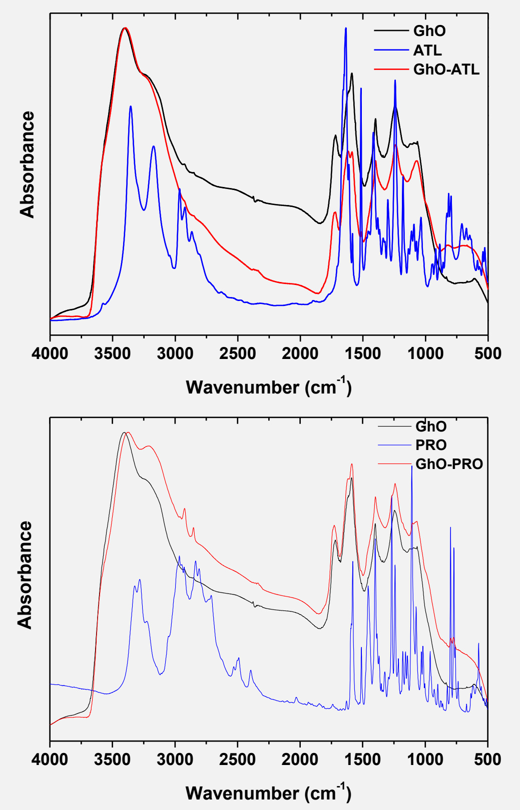


Figure 2. FT-IR spectra of GhO before and after adsorption of (a) ATL and (b) PRO

3.3. Effect of pH

One of the most important factors which influence the adsorption behavior of any adsorbent material is the pH of the solution. Fig. 3 demonstrates the effect of pH on the adsorption.

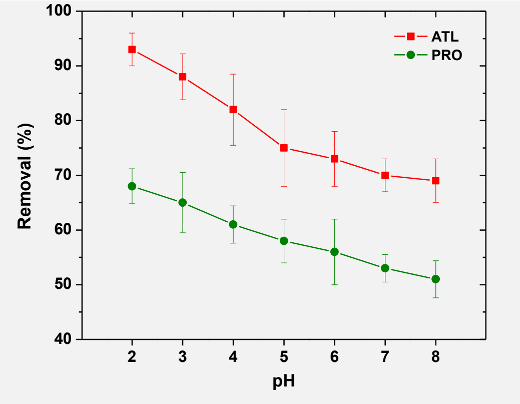
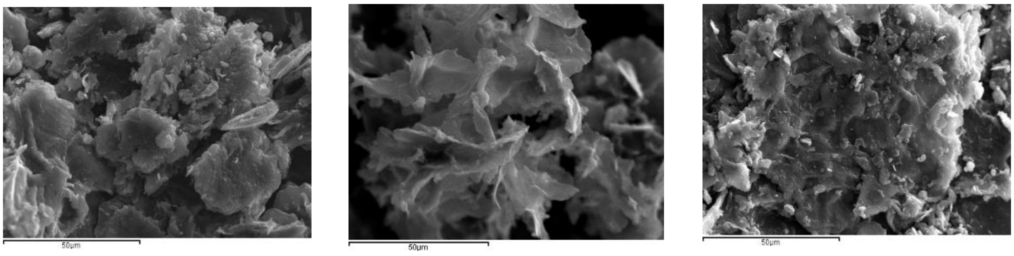


Figure. 3. Effect of pH on adsorption.



(a) (b) (c)

Figure 1. SEM micrographs of:(a) GhO; (b) GhO-PRO; (c) GhO-ATL.

3.4. Adsorption kinetics

The kinetic data were fitted to pseudo-first and -second order equations. This was done in order to determine the time period where the adsorption process was completed. The best correlation coefficient was found to be that of pseudo-second order equation (R2 = 0.994-0.996) (Table 1).

Table 1. Equilibrium parameters for the adsorption of atenolol and propranolol onto graphene oxide.

		Langmuir equation			Freundlich equation			L-F equation			
	T	Q_m	K_L	R^2	K_F	n	R^2	Q_m	K_{LF}	b	R^2
Beta-blocker	°C	mg/g	L/mg		$mg^{1-1/n}$ $L^{1/n}$ g^{-1}			mg/g	$(L/mg)^{1/b}$		
ATL	25	95	0.351	0.982	32.82	3.49	0.959	116	0.338	1.51	0.998
	45	102	0.466	0.977	38.16	3.60	0.963	127	0.400	1.61	0.998
	65	113	0.755	0.970	48.36	3.81	0.961	143	0.532	1.72	0.996
PRO	25	69	0.074	0.997	11.67	2.61	0.947	67	0.069	0.95	0.999
	45	72	0.090	0.997	13.54	2.69	0.960	77	0.101	1.12	0.999
	65	74	0.102	0.996	14.88	2.78	0.958	79	0.115	1.15	0.999

4. Conclusions

The present investigation evaluated the efficiency of two beta-blocker (ATL and PRO) removal, using GhO as adsorbent. Taking into consideration all the above obtained results, it can be concluded that GhO could prove to be a promising and effective adsorbent for the removal of beta-blockers from aqueous solutions.

Acknowledgements

The support for this study was received from the Greek Ministry of Education and Religious Affairs through Operational Program “Education and Lifelong Learning” of the National Strategic Reference Framework (NSRF) - Research Funding Program “Excellence II (Aristeia II, No 4199)”, which is gratefully appreciated.

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Introduction

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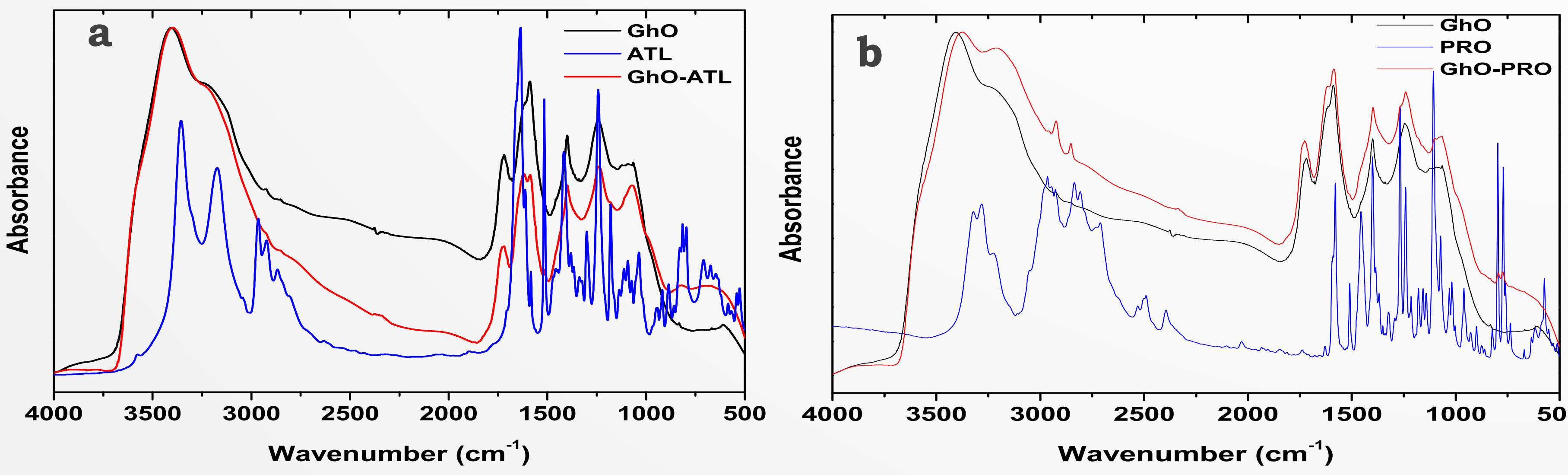
Experimental

GhO was synthesized with the modified Hummers method. Commercial graphite powder (10 g) was stirred in 230 mL of concentrated sulfuric acid (temperature of solution was 0 °C). Then, potassium permanganate (30 g) was slowly added to the suspension. The rate of addition was controlled to prevent the rapid rise in the temperature of the suspension, which should be less than 20 °C. The reaction mixture was then cooled to 2 °C. After removal of the ice-bath, the mixture was stirred at room temperature for 30 min. Distilled water (230 mL) was slowly added to the reaction vessel, keeping the solution temperature less than 98 °C. The diluted suspension was stirred for additional 15 min, was further diluted with 1.4 L of distilled water and then 100 mL of a 30 wt% solution of hydrogen peroxide was added. The mixture was left overnight. The GhO particles settled at the bottom were separated from the excess liquid by decantation. The remaining suspension was transferred to dialysis tubes (Sigma Co). Dialysis was carried out until no precipitate of $BaSO_4$ was detected by addition of aqueous solution of $BaCl_2$. Then, the wet form of graphite oxide was separated by centrifugation. The gel-like material was freeze dried and a fine dark brown powder of the initial GhO was obtained.

Results and discussion

FT-IR spectra of GhO before and after adsorption of (a) ATL and (b) PRO



References

[1] Transformation Products of Emerging Contaminants in the Environment: Analysis, Processes, Occurrence, Effects and Risks. D.A., Lambropoulou, L.M.L., Nollet,. UK, John Wiley and Sons Ltd., 2014.
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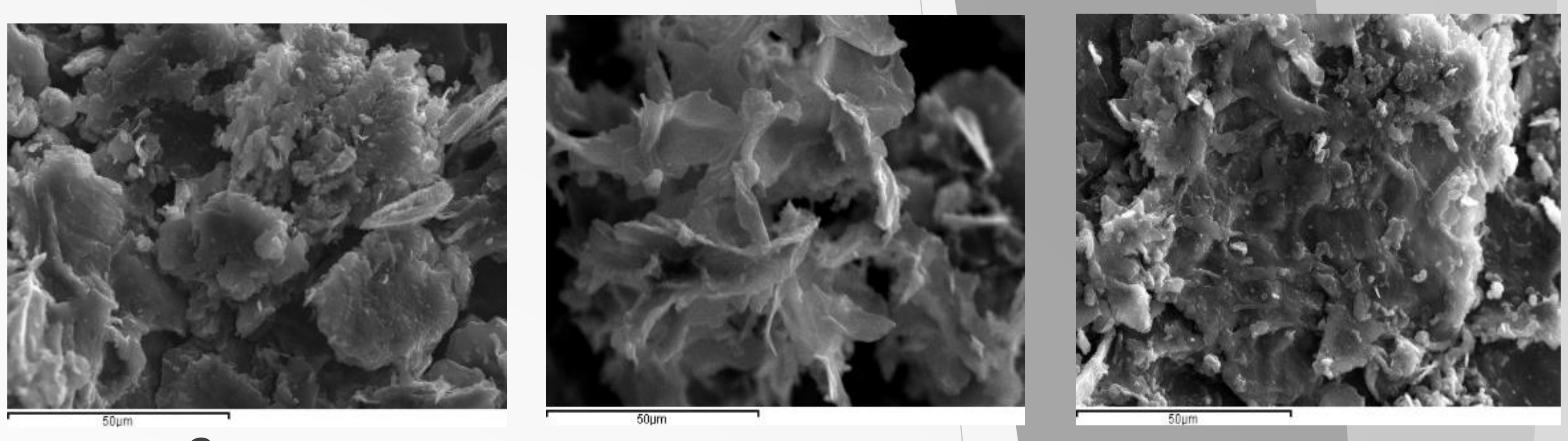
SEM micrographs of:(a) GhO (b) GhO-PRO (c) GhO-ATL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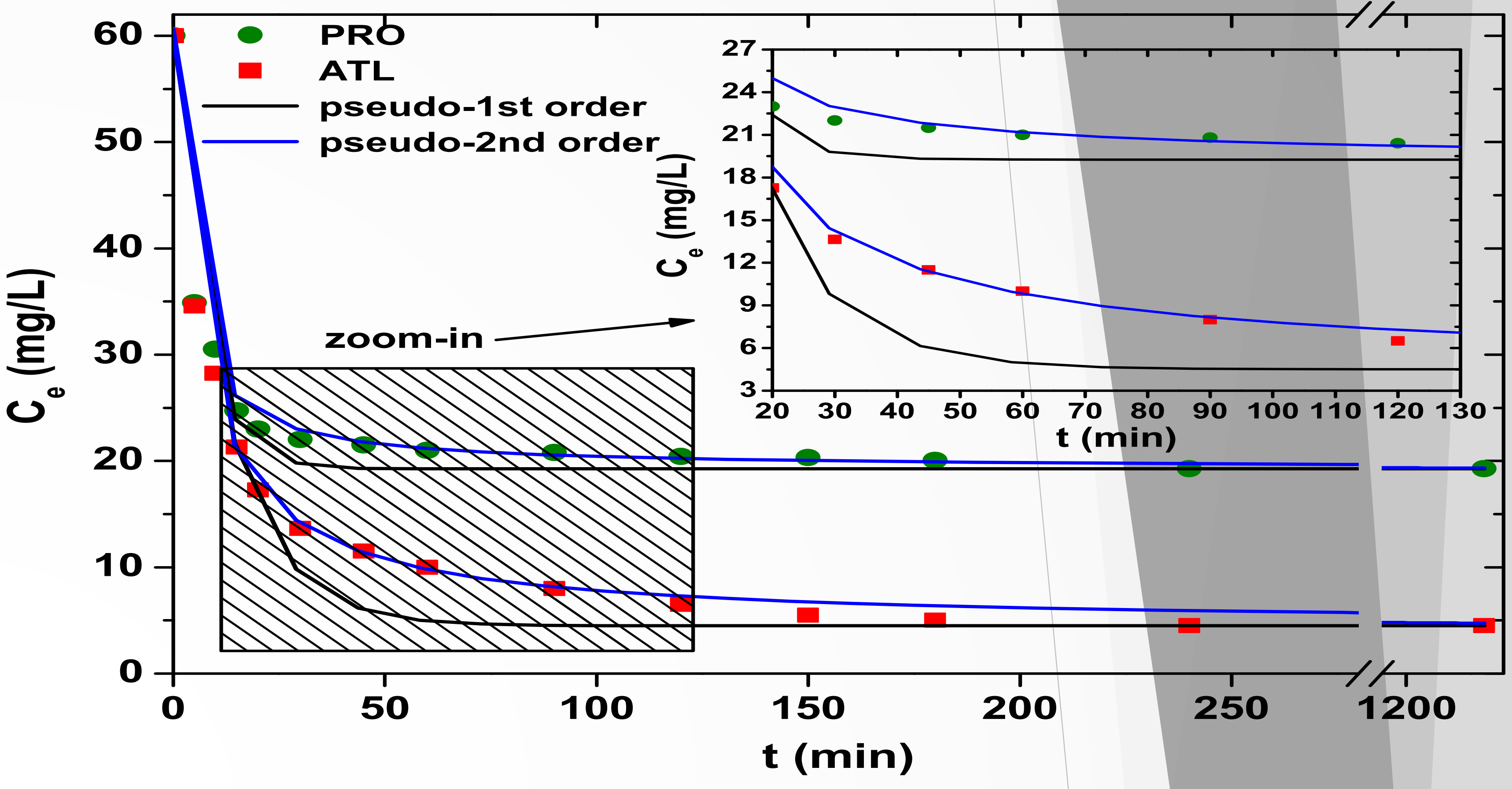
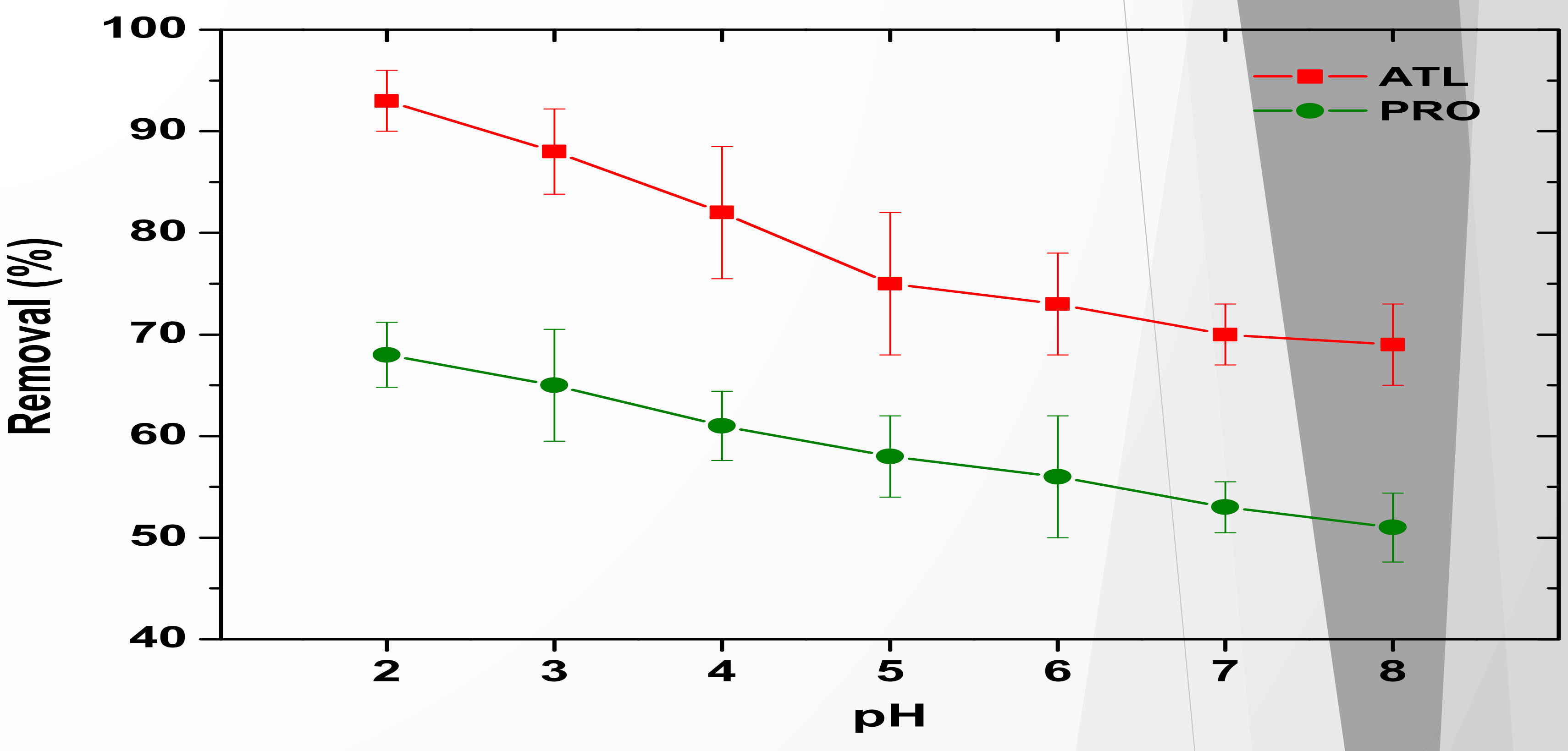
Effect of contact time on adsorption of ATL and PRO onto GhO



Effect of pH on adsorption



Conclusions

- ❖ **Sem images indicated that GhO formed the sheet-like structure and had a smooth surface without holes onto its surface. Additionally, GhO retained its structure and surface morphology after PRO or ATL adsorption.**
- ❖ **Under optimal adsorption conditions (pH 2) , the removal is approximately 85% for ATE and 70% for PRO.**
- ❖ **The best correlation coefficient was found to be that of pseudo-second order equation.**
- ❖ **The maximum adsorption capacity was 67 and 116 mg/g (25 °C) for PRO and ATL respectively.**
- ❖ **Finally, GhO proved to be a promising and effective adsorbent for the removal of beta-blockers from aqueous solutions.**

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