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Removal of beta-blockers from aqueous media by adsorption onto graphene oxide

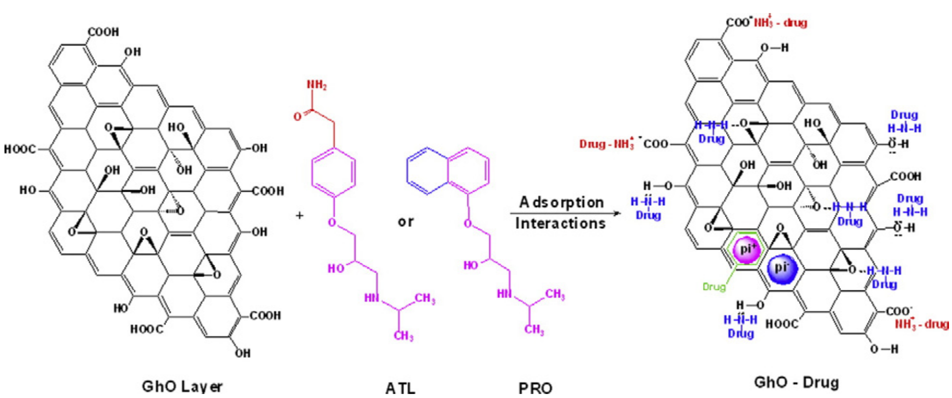
George Z. Kyzas [a], Anastasia Koltsakidou [b], Stavroula G. Nanaki [a], Dimitrios N. Bikiaris [a], Dimitra A. Lambropoulou [b,*]

[a] *Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Greece*
[b] *Laboratory of Environmental Pollution Control, Department of Chemistry, Aristotle University of Thessaloniki, GR–541 24 Thessaloniki, Greece*

HIGHLIGHTS

- Removal of beta-blockers by graphene oxide (GhO) from aqueous samples
- Detailed adsorbent characterization and adsorption studies
- Kinetic studies are performed and adsorption isotherms are determined and modeled.
- GhO was proved to be an effective adsorbent for removal of atenolol and propranolol.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of the present study is the evaluation of graphene oxide (GhO) as adsorbent material for the removal of beta-blockers (pharmaceutical compounds) in aqueous solutions. The composition and morphology of prepared materials were characterized by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). Atenolol (ATL) and propranolol (PRO) were used as model drug molecules and their behavior were investigated in terms of GhO dosage, contact time, temperature and pH. Adsorption mechanisms were proposed and the pH-effect curves after adsorption were discussed. The kinetic behavior of GhO-drugs system was analyzed after fitting to pseudo-first and -second order equations. 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 carrying out the equilibrium adsorption experiments at three different temperatures (25, 45, 65 °C). Then, the thermodynamic parameters of enthalpy, free energy and entropy were calculated. Finally, the desorption of drugs from GhO was evaluated by using both aqueous eluants (pH 2–10) and organic solvents.

* Corresponding author.
E-mail address: dlambro@chem.auth.gr (D.A. Lambropoulou).

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1. Introduction

Nowadays, the consumption of human pharmaceutical compounds is being continuously increased worldwide (Schumock et al., 2014). Since these compounds are excreted from the human body with little or no changes to the chemical structure, they frequently show up in urban wastewaters and many of them can further spread through the water cycle, even reaching drinking water, due to their hydrophilic character and low removal at wastewater treatment plants (WWTPs) (Stamatis and Konstantinou, 2013; Verlicchi et al., 2012; Lambropoulou and Nollet, 2014).

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 (Fatta-Kassinos et al., 2011; Verlicchi et al., 2012; Godoy et al., 2015). Beta-blockers, also called beta-adrenergic antagonists, are used mainly for the treatment of heart rhythm disorders, angina pectoris, hypertension, tachycardia or acute myocardial infarction (Brunetto Mdel et al., 2015). In this study, two model compounds were selected; atenolol and propranolol (Fig. 1). Both atenolol (denoted as ATL) and propranolol (denoted as PRO) are used against cardiovascular diseases; ATL is a b1-receptor selective antagonist, while PRO is a non-selective beta-blocker (Arvand et al., 2008; Benner et al., 2008). ATL is characterized by a half-life up to 166 days (Liu and Williams, 2007; Yamamoto et al., 2009) attesting its persistence within the environment. Because of this persistence, ATL has been detected in various environmental samples with concentrations varying from non-detected to 11 μg/L (Celle-Jeanton et al., 2014; Verlicchi et al., 2012; Godoy et al., 2015). As far as PRO is concerned, its elimination in sewage treatment plants has been reported as poor (Hoffman and Lefkowitz, 1996), while its detection in surface waters and wastewaters has been reported by several researchers (Bound and Voulvoulis, 2006; Ternes, 1998; Celle-Jeanton et al., 2014; Godoy et al., 2015). In addition, several studies focusing on the toxicological potential of PRO show that it could be of environmental relevance (Cleuvers, 2005; Huggett et al., 2002; Maszkowska et al., 2014; Rivera-Utrilla et al., 2013; Robinson et al., 2007). For example a 4-week exposure experiment by Huggett et al. (2002) (Huggett et al., 2002) showed that a concentration of 500 ng/L PRO has an effect on the reproduction and steroid levels in medaka (Oryzias latipes). Finally, the study of Cleuvers (2005) (Cleuvers, 2005), in which the ecotoxicity of three beta-blockers was tested in *Daphnia magna*, *Desmodesmus subspicatus* and *Lemna minor*, showed that PRO was the most toxic compound with EC_{50s} of 7.7 and 0.73 mg/L in the Daphnia and algal test, respectively.

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 (Bensaadi et al., 2014; Píšt'ková et al., 2015; Veloutsou et al., 2014), ozonation (Tay and Madehi, 2014; Wilde et al., 2014) or adsorption with several materials such as activated carbon or carrageenans (Mailler et al., 2014; Nanaki et al., 2015). 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 (Nanaki et al., 2015).

Graphene (Gh), a monolayer (or few layers, <10) of hexagonally arrayed sp^2-bonded carbon atoms, due to its excellent physical and chemical properties, has been studied world-wide for several purposes, since its discovery in 2004 (Liu et al., 2015a). Following this trend, graphite oxide has attracted attention from many researchers, because of its role as a precursor for the cost-effective mass production of graphene-based materials. For this reason, graphene-based materials are applied to a wide range of sciences (Chen et al., 2014; De Faria et al., 2014; Gao et al., 2013; Liu et al., 2015b; Rahmanian et al., 2014; Wang et al., 2013, 2014a, 2014b; Yang et al., 2015; Zhang et al., 2014). GhO has a layered structure similar to that of graphite, but the plane of carbon atoms in graphite oxide is heavily decorated by oxygen-containing groups, which can be exfoliated in water under moderate ultrasonication. If the exfoliated sheets contain only one or few layers of carbon atoms as in graphene, these sheets are called graphene oxide (GhO) (Travlou et al., 2013). Graphene and graphene oxide are recently used as adsorbents to remove different groups of pollutants such as methyl green dye molecules (Sharma et al., 2014), aniline (Fakhri, in press), methyl orange (Li et al., 2011a, 2011b), naphthalene and 1-naphthol (Zhao et al., 2011a, 2011b) and heavy metals (Li et al., 2014; Luo et al., 2014) from aqueous solutions, showing high adsorption amount and fast adsorption rates (Chandra and Kim, 2011; Deng et al., 2010; Yang et al., 2010). 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 (Al-Khateeb et al., 2014; Liu et al., 2014; Nam et al., 2015).

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 (Owen et al., 2007). For example, PRO has a relatively high log K_{ow} of 3.48, whereas ATL has a considerably lower log K_{ow} of 0.16 (Betageri and Rogers, 1987; Pauletti and Wunderli-Allenspach, 1994). In addition, structural differences (Fig. 1) 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.

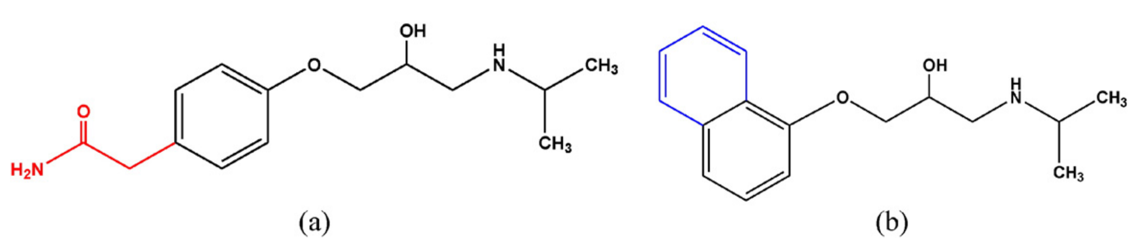

Fig. 1. Chemical structures of (a) atenolol (ATL) and (b) propranolol (PRO).