Bioresource Technology 152 (2014) 399–406

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Removal of dorzolamide from biomedical wastewaters with adsorption onto graphite oxide/poly(acrylic acid) grafted chitosan nanocomposite

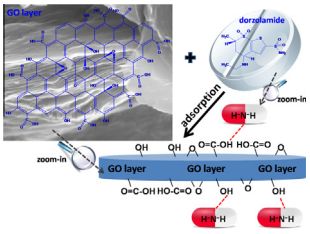
George Z. Kyzas [a,*], Dimitrios N. Bikiaris [a], Mykola Seredych [b], Teresa J. Bandosz [b], Eleni A. Deliyanni [a,*]

[a] Division of Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR–541 24 Thessaloniki, Greece
[b] Department of Chemistry, The City College of New York, 160 Convent Avenue, New York, NY 100 31, USA

HIGHLIGHTS

- The treatment of synthetic biomedical wastewaters was achieved using biosorbents.
- Graphite oxide and (acrylic acid) grafted chitosan form the nanocomposite (GO/CSA).
- Adsorption mechanism is proposed revealing interactions between chitosan and dorzo.
- Adsorbents were characterized using techniques as XRD, SEM, FTIR.
- Adsorption evaluation was achieved with equilibrium, kinetic and reuse experiments.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 September 2013
Received in revised form 17 November 2013
Accepted 20 November 2013
Available online 27 November 2013

Keywords:
Biomedical wastewater
Chitosan
Graphite oxide
Biosorbents
Dorzolamide

ABSTRACT

A novel graphite oxide/poly(acrylic acid) grafted chitosan nanocomposite (GO/CSA) was prepared and used as biosorbent for the removal of pharmaceutical compound (dorzolamide) from biomedical synthetic wastewaters. The performance was evaluated taking into account pH, kinetics and thermodynamics of adsorption. GO/CSA presented higher adsorption capacity in comparison with the parent materials (graphite oxide and poly(acrylic acid) grafted chitosan). All adsorbents prepared were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and potentiometric titration. The surface features were also evaluated after the dorzolamide adsorption in order to derive the adsorption mechanism. It was suggested that the reactive groups of GO and CSA can interact with the amino groups of dorzolamide and mainly the abundance of carboxyl groups of GO/CSA composite was the main reason for its enhanced adsorption capacity.

1. Introduction

Pharmaceuticals represent a class of health care products that are intensively used worldwide mainly to promote human health and they mostly enter water sources through discharge from pharmaceutical industries and from municipal wastewater effluent (Moussavi et al., 2013), as well as from hospital effluents (Homem and Santos, 2011). Many of these pharmaceutical compounds are not completely removed by wastewater treatment plants (WWTPs) and consequently they have been detected in WWTP effluents, surface waters and, less frequently, in ground and drinking water all over the world (Rivas et al., 2012). Several methods have been investigated to remove pharmaceuticals from contaminated water as biodegradation, photocatalysis, ozonation, Fenton process, adsorption on chitosan beads (Adriano et al., 2005), adsorption on activated carbon (Moussavi et al., 2013) or elimination by micro- and nano-scale iron particles.

Physical techniques remain the most appropriate treatment option. Among them, adsorption is the most promising one since

* Corresponding authors. Tel.: +30 2310 997807; fax: +30 2310 997859 (G.Z. Kyzas). Tel.: +30 2310 997808; fax: +30 2310 997859 (E.A. Deliyanni).
E-mail addresses: georgekyzas@gmail.com (G.Z. Kyzas), lenadj@chem.auth.gr (E.A. Deliyanni).

0960-8524/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2013.11.046

it is efficient, simple to design, unaffected by toxicity, and inexpensive (Han et al., 2008). Activated carbons are one of the most commonly used effective adsorptive materials tested for the treatment of wastewaters (Han et al., 2008). Another group of materials includes inorganic solids such as zeolites (Martucci et al., 2012). Despite their high efficiency, the application of these adsorbents is associated with the problems of materials' stability and costly regeneration procedures. To overcome these limitations, efforts have been devoted to synthesize novel and effective adsorbents that can achieve higher efficiency and better selectivity in the removal of pharmaceuticals from aqueous systems or use appropriate natural occurring compounds. Chitosan (poly-β-(1 → 4)-2-amino-2-deoxy-D-glucose) is the second most plentiful natural biopolymer, which is the deacetylated derivative of chitin (the natural polymer extracted from shrimp or crab shells). Chitosan has been proved as a promising biosorbent material and has been extensively used for the removal of dyes (Crini, 2006) and heavy metals (Laus and De Fávere, 2011; Popuri et al., 2009; Yang et al., 2011) from aqueous solutions. Owing to its biocompatibility, high biodegradability, non-toxicity it can be considered as an environmental friendly adsorbent. Modified chitosan (grafting with sulfonate or N-(2-carboxybenzyl) groups) was also tested as adsorbent for pharmaceutical compounds (pramipexole) from wastewaters revealing important adsorption properties (Kyzas et al., 2013).

Graphite oxide has been extensively studied and characterized by many researchers in last decade and a brief report in literature revealed various treatments in its structure containing multiple functional groups as carboxyl, hydroxyl, epoxide are covalently attached to its layers (Fan et al., 2012; Szabó et al., 2010). GO has been recently studied as an adsorbent (Wang et al., 2013), a component in composite materials with enhanced properties (Fang et al., 2010), or as a precursor in the formation of graphene layers (Stoller et al., 2008). Recently, the combinations of the aforementioned materials (GO and chitosan (Travlou et al., 2013b) or GO and magnetic chitosan (Huang et al., 2012) were examined in novel composite materials from an adsorption point of view and improved separation performances have been demonstrated.

The objective of this paper is to apply an environmental-friendly technique, with which pharmaceutical compounds can be effectively removed from biomedical wastewaters. Therefore, the evaluation of the performance of chitosan grafted with acrylic acid groups and its composite with graphite oxide (GO) as adsorbents of Dorzolamide (dorzo) was achieved, which was chosen as a target pharmaceutical for removal from contaminated water. Dorzo is a carbonic anhydrase inhibitor used for decreasing aqueous humor secretion in the ciliary processes of the eye. The topical administration of dorzo in the front part of the eye with conventional pharmaceutical preparations (e.g., eye drops) is inefficient since, after application are diluted rapidly with tears and are discharged through the lachrymal duct. Dorzo was not previously studied in literature as under-removal pharmaceutical compound. Given its extremely wide use as described above, it is obviously discharged in some quantities to (biomedical) wastewater streams and therefore it was selected as model pharmaceutical compound. From a chemical point of view, each drug/pharmaceutical pollutant is a chemical compound. So, in any case there would be adsorption capacity (either high or low) of any material synthesized. Then, in order to investigate and explain (suggesting various adsorption interactions) how adsorptively selective was dorzo, a further adsorption evaluation was done (equilibrium, kinetics, thermodynamics, reuse, etc.,).

Given the cationic nature of dorzo, chitosan was grafted with anionic groups (carboxyl groups) to enhance its adsorption capacity and cross-linked with glutaraldehyde to improve its resistance at extreme pH conditions. A novel nanocomposite containing GO and carboxyl grafted chitosan was characterized using swelling tests, XRD, FTIR, SEM, BET analysis and potentiometric titrations. The adsorption behavior is linked to the specific surface features of GO/polymer nanocomposite. Based on the results obtained, an adsorption mechanism is elucidated. The following variables are taken into consideration: pH of the solution, dorzo initial concentration, contact time, solution temperature and regeneration ability (desorption pH, cycles reuse). The relationship between the equilibrium, kinetic, mechanism and thermodynamics of dorzo adsorption and the surface features of the materials studied is also discussed.

2. Methods

2.1. Materials

Commercial chitosan of high molecular weight (CS) was purchased from Sigma–Aldrich and purified by extraction with acetone in a Soxhlet apparatus for 24 h. Then, its drying was carried out under vacuum at 20 °C. Its average molecular weight was estimated at 3.55×10^5 g/mol and the degree of deacetylation was 82 wt% (Rinaudo, 2006). The cross-linking agent used was glutaraldehyde (GLA) and obtained from Sigma–Aldrich (50 wt% in water). All solvents were of analytical grade. The grafting agent used was acrylic acid (AA) and the initiator for the polymerization was potassium persulfate (KPS), which were received from Merck. Dorzolamide ($C_{10}H_{16}N_2O_4S_3$; M.W. = 324.44 g/mol; abbreviated as dorzo) was purchased from Regactives (Boecielo Valladolid, Spain) (assay 99.3%). Its chemical structure is illustrated in Fig. SI1 (Supporting information section).

2.2. Synthesis of adsorbents

GO was synthesized according to the modified Hummers method (Hummers Jr. and Offeman, 1958). Commercial graphite powder (10 g) was stirred in concentrated solution of sulfuric acid (230 mL, 0 °C). Then, 30 g of potassium permanganate was slowly added to the suspension. The rate of addition was controlled in order to prevent the rapid rise of suspension's temperature, which should be less than 20 °C. The reaction mixture was then cooled to 2 °C. After the removal of ice-bath, the mixture was then stirred at room temperature for 30 min. 230 mL of distilled water were slowly added to the reaction vessel, keeping the temperature less than 98 °C. The diluted suspension was stirred for additional 15 min. Further dilution with 1.4 L of distilled water was realized and then 100 mL of solution of hydrogen peroxide (30 wt%) was added. The mixture was left overnight. The GO particles settled at the bottom were separated from the excess liquid by decantation. The remaining suspension was transferred to dialysis tubes. Dialysis was carried out until no precipitate of barium sulfate was detected by addition of aqueous solution of barium chloride. Then, the wet form of graphite oxide was separated by centrifugation. The gel-like material was freeze-dried and the fine dark brown powders of the initial GO were obtained.

CSA was synthesized according to the method described by Lazaridis et al. (2007). 0.3 g of CS was initially dissolved in 2% v/v aqueous solution of acetic acid and followed by the addition of solution of AA. Then, 0.005 g of the initiator (KPS) was added, while the final solution (50 mL) was poured into a 100 mL flask, and then placed in a water bath at the desired reaction temperature (60 °C) for 45 min in the presence of argon. After the completion of grafting reaction, the polymerization mixture was rapidly cooled down to ambient temperature and neutralized to pH 8 with the addition of NaOH (1 N). While stirring, the gelled chitosan was poured into a large amount of acetone. After 24 h, satisfactory dewatering was achieved and the hardened gel particles were filtered and