



Short Communication

Effect of humic acid on pharmaceuticals adsorption using sulfonic acid grafted chitosan

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ABSTRACT

A modified polymer (chitosan grafted with sulfonic acid and cross-linked with glutaraldehyde) was synthesized in order to examine the effect of humic acid (HA) on the adsorption equilibrium of a model pharmaceutical compound (pramipexole). The presence of humic acid in water intended for potable or industrial use can have a significant impact on the treatability of that water and the success of chemical disinfection processes. Therefore, industrial effluents are even mis-treatable. The results showed that increasing the concentration of HA (0, 2.5, 5.0, and 20 mg/L), the maximum adsorption capacity decreases. However, in both materials, it seems that there is a crucial concentration of humic acid (5.0 mg/L), which results the higher reduction of adsorption capacity (Q_m , found after fitting to Langmuir and Langmuir-Freundlich models). The presence of 5 mg/L of HA in solution causes slightly different Q_m than that of 20 mg/L. Also, techniques as BET analysis, SEM images and swelling experiments were applied for the characterization of the material.

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1. Introduction

The increasing occurrence of pharmaceuticals in the environment has raised a number of critical concerns, including their removal, fate and elimination in wastewater treatment plants (WWTPs). Hence, several advanced technologies have been evaluated as options to treat these contaminants in wastewaters, including adsorption, advanced oxidation, biological treatment and so on. Among these methods, adsorption offers a number of advantages such as low cost, easy operation and no sludge formation, and therefore is widely applied in not only lab-scale fundamental studies but also large scale industrial applications [1–25].

Commonly used adsorbents which have been successfully applied for removal of different organic pollutants are activated carbon and synthetic polymer resins etc. Despite these, alternative biopolymer based adsorbents (i.e. chitosan and cellulose) have been received recently considerable attention. The adsorption of pharmaceuticals by biopolymers is dependent on their surface morphology, physical and chemical properties of pharmaceuticals, and environmental conditions. Although adsorption assays targeting pharmaceuticals are steadily increased in recent years, not much data is currently available on the adsorption interferences from environmental conditions such as the effect and mechanisms of natural organic matter (NOM) on the removal of

pharmaceuticals from waters and wastewaters. NOM is ubiquitous in aquatic environment and plays a predominant role in the sorption of pharmaceuticals onto sorbent particles. Humic acid (HA) is a common model compound of NOM and widely exist in the aquatic environment. It is a principal component of humic substances, which are the major organic constituents of soil (humus), peat, coal, many upland streams, dystrophic lakes, and ocean water. It is produced by biodegradation of dead organic matter. It is not a single acid; rather, it is a complex mixture of many different acids containing carboxyl and phenolic groups so that the mixture behaves functionally as a dibasic acid or, occasionally, as a tribasic acid. The ubiquitous occurrence of HA in waters and wastewaters greatly affects the pharmaceutical adsorption process and thus have a significant impact on the success of both, treatment and chemical disinfection processes. In this regard, a better understanding of the interactions of pharmaceuticals with HA is of great importance and may provide guidance for a more distinctive selection of polymer materials to be applied in water/wastewater treatment systems.

In the present study, chitosan derivative (poly-β-(1 → 4)-2-amino-2-deoxy-D-glucose) grafted with sulfonic groups was synthesized and tested as adsorbent for the removal of a particular pharmaceutical compound. Chitosan is a widely used polymer which has repeatedly applied from our team in past as super-adsorbent for dyes, heavy metals, ions, pharmaceuticals, giving impressively high adsorption capacities for the removal of various pollutants from aqueous media [5,6,26–33]. As model pharmaceutical pollutant, pramipexole dihydrochloride ((6S)-

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N6-propyl-4,5,6,7-tetrahydro-1,3-benzothiazole-2,6-diamine, denoted as PRM) was used. It is widely all over the world for its unique pharmaceutical activity and on the basis of recent drug usage trends [34]; therefore, treatment of wastewater by high polluted levels of PRM is required and urgent needed.

The novelty of this study is based on the co-existence of humic acids on the adsorbate (PRM) in various concentrations and the first approach in that type of studies. Which is the effect of humic acids on the adsorbent use of chitosan derivatives? How did humic acids influence the crucial parameters of adsorption (isotherm etc.)? The latter are some of crucial questions replied with this study.

2. Materials and methods

2.1. Materials

Pramipexole dihydrochloride (C₁₀H₂₁Cl₂N₃OS, MW = 302.26 g/mol) was purchased from Amino Chemicals Ltd. (Malta) (assay 99.2%). Stock solutions of PRM (1000 mg/L) were prepared by weighing and dissolving the suitable amount of the corresponding substance in water; stock solutions were stored at -20 °C and were stable for at least 1 week, as assessed by spectrophotometric assays. Working solutions of PRM were prepared daily by diluting the corresponding stock solutions in water.

High molecular weight chitosan was purchased by Sigma-Aldrich (purification in Soxhlet apparatus by extraction overnight with acetone). Then, the drying of chitosan particles was carried out under vacuum at 20 °C. Its average molecular weight was estimated at 3.55 × 10⁵ g/mol and the degree of deacetylation was 85 wt%, according to the FTIR method described in literature [35,36]. Glutaraldehyde (GLA, 50 wt% in water), formamide (≥99.5%), sodium carbonate (≥99%), and chlorosulfonic acid (≥99%) were purchased from Sigma-Aldrich. Dichloroacetic acid (≥98.5%) was obtained from Fluka.

2.2. Methods

For the synthesis of sulfonic acid-grafted chitosan adsorbent (CsSLA) [37,38], a mixture of dichloroacetic acid (5 mL) and formamide (50 mL) was added into chitosan (4.0 g) and stirred to be an homogenized solution. This was then mixed with a complex of chlorosulfonic acid-dimethylformamide and stirred for 1 h in a water bath at 50 °C. The reaction mixture was then diluted by a small quantity of deionized water, filtered, and precipitated by pouring into ethanol 95% (400 mL). The precipitate was dissolved in deionized water, neutralized by a saturated Na₂CO₃ solution, and dialyzed against deionized water. After dialysis, the product was dried and stored in a desiccator. Then, a cross-linking procedure was realized with GLA as reagent (0.5 wt%) at 60 °C for 1.5 h and the final product is obtained (Fig. 1). The final grafting degree (GD) was determined on the basis of the percentage weight increase of the final product relative to the initial weight of chitosan GD = (W₂ - W₁) / W₁ (where W₁ and W₂ denote the weight of chitosan before and after grafting reaction, respectively). So, the grafting degree was found 2.2.

The water retention into materials caused their swelling. To calculate it, experiments were carried out using phosphate buffer pH 7.4 as immersion medium (n = 3). Firstly, each material was carefully weighed (W_{sw,1}) and then immersed in phosphate buffer pH 7.4. The sponge remnants were wiped off excess surface water using filter paper and weighed (W_{sw,2}) at different time intervals. Swelling percentage (SP) was calculated using Eq. (1):

$$SP (\%) = \left(\frac{W_{sw,1} - W_{sw,2}}{W_{sw,2}} \right) \cdot 100\% \tag{1}$$

Adsorption/desorption experiments were conducted in 20-mL amber vials using a batch approach. All experiments were run in duplicate. The residual concentration of PRM was measured

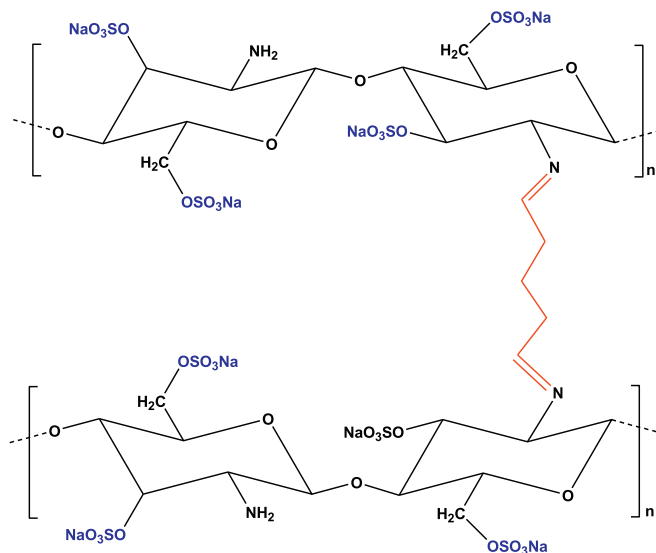


Fig. 1. Chemical structure of CsSLA.

spectrophotometrically by monitoring its UV absorbance at 263 nm (model U-2000, Hitachi). A detailed description of experimental procedure is given below, where C₀ (mg/L) is the initial PRM concentration, pH is the pH of the aqueous solutions (fixed with micro-additions of HCl or NaOH), T (°C) is the temperature, m (g) is the mass of the adsorbent used, V (mL) is the volume of adsorbate, N (revolutions or full rotations per minute, abbreviated as rpm) is the agitation rate of the shaking machine and t (h) is the contact time. For all experiments three different values of HA concentrations (2.5, 5.0, 20 mg/L) were selected to investigate their influence to adsorption of PRM onto CsSLA.

The selection of the lower tested HA concentrations (0.0, 2.5, and 5.0 mg/L) was due to the fact that HA exists in waters in relatively low concentration (~5 mg/L). Having checked the aforementioned low HA concentration (0.0, 2.5, and 5.0 mg/L), another value should be selected (by far higher than the others) in order to check the adsorption behavior of CsSLA under those HA conditions. So, the extreme value of 20 mg/L HA was then selected.

The adsorption experiments had the following conditions: C_{0,PRM} = 0–500 mg/L; C_{HA} = 0.0, 2.5, 5.0, 20.0 mg/L; pH = 10; m = 0.02 g; V = 20 mL; T = 25 °C; N = 160 rpm; t = 24 h. The equilibrium data were fitted to the Langmuir [39] (Eq. (2)) and Langmuir-Freundlich (L-F) (Eq. (3)) isotherm model [40]:

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

$$Q_e = \frac{Q_m K_{LF} C_e^{1/n}}{1 + K_{LF} C_e^{1/n}} \tag{3}$$

where Q_e (adsorbed PRM weight/adsorbent weight) is the equilibrium concentration in the solid phase; Q_m is the maximum amount of adsorption (adsorbed PRM weight/adsorbent weight); K_L (L/mg) is the Langmuir adsorption equilibrium constant; n (dimensionless) is the constant depicting the adsorption intensity; K_{LF} (L/mg)^{1/n} is the Langmuir-Freundlich constant; n (dimensionless) is the Langmuir-Freundlich heterogeneity constant.

The adsorption capacity in equilibrium (Q_e) was calculated using the mass balance equation:

$$Q_e = \frac{(C_0 - C_e)V}{m} \tag{4}$$

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