



Swelling–adsorption interactions during mercury and nickel ions removal by chitosan derivatives



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ARTICLE INFO

Article history:

Received 15 December 2014
Received in revised form 12 May 2015
Accepted 22 May 2015
Available online 22 May 2015

Keywords:

Swelling dynamics
Modeling
Heavy metals
Mercury
Nickel
Adsorption
Chitosan adsorbents

ABSTRACT

Chitosan derivatives are extensively used as adsorbents for dyes and metal ions. These materials undergo swelling after their immersion in water. The maximum adsorption potential corresponds to completely swollen material. The process rates of swelling and adsorption are comparable leading to a dependence of the apparent adsorption rate on immersion history of the material. The way of performing the adsorption experiments for this type of materials is not clear in literature raising questions on the validity of the results. To clarify the situation a total of six adsorbate–adsorbent systems is studied here with respect to the effect of the swelling degree on the adsorption kinetics. Mercury (Hg(II)) and nickel (Ni(II)) ions were selected to be the model pollutants of this work and cross-linked chitosan microspheres grafted with chlorosulfonic acid (CSSULF) or ethylenimine (CSPEI) as adsorbent materials. It is shown that the adsorption kinetics is sensitive to the time of the adsorbent immersion in water. An attempt for development of a combined swelling–adsorption model is made. It is shown that the interaction between swelling and adsorption is more complex than a single water content dependence of diffusion coefficient. The evolution of diffusion coefficient that reproduces the experimental data is derived. Differences to the behavior between the three material used, are indicated and discussed.

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1. Introduction

Adsorption is one of the most applied processes of recent years for the decontamination of wastewaters [1–7]. But when a material is used as adsorbent for the removal of some pollutant from aqueous solutions, preliminary experiments need to be performed for the investigation of swelling ability. This is crucial in adsorption technology, because if a material presents high swelling degree (e.g. >50%), its applicability as adsorbent becomes difficult. The explanation arises from the ultimate application of each adsorbent material not only in lab scale experiments (usually done in batch mode) but mainly also in industrial size columns (i.e., fixed-bed). Materials with high swelling degree can adsorb large quantity of water molecules, resulting in a gradual increase of their volume (adsorbent's volume) and consequently after fixed time in fouling and sudden stop of the wastewater flow into the column. All above can explain why swelling is a crucial factor in adsorption technology and needs further investigation.

A previous work of this research team successfully studied the effect of pre-swelling on dye adsorption dynamics [8]. The majority

of published adsorption works does not clearly report if the adsorbents are (or need to be) pre-immersed (and subsequently pre-swollen) in the adsorption media (usually water) before coming in contact with adsorbate solution. For this reason, we have carried out a series of experiments indicating that the pre-immersion (pre-swelling) caused the acceleration of dye adsorption, achieving higher kinetic rates and smaller equilibrium times [8]. In general, the “nature” of under-removal-pollutant plays important role on this phenomenon. For example, the diameter of many dye molecules is approximately 10 nm, while the radius of heavy metal ions is about 100 pm (=0.1 nm). Apart from dyes (studied in the aforementioned work), heavy metal ions are another significant class of pollutants existed in wastewaters. Therefore, it is equally important to investigate the pre-swelling effect on the adsorption of some ions. Heavy metal ions selected to be the model pollutants of this work are mercury (Hg(II)) and nickel (Ni(II)). The selection of those heavy metal ions was based on their toxic impacts to environment (in order to obtain an environmental interest this work), but mainly their different ionic radius (133 and 83 pm for Hg(II) and Ni(II), respectively), which can cause different (or not) swelling–adsorption behavior during experimental procedure.

Effluent wastewaters from processes such as electroplating, metal finishing, metallurgical, chemical manufacturing and battery

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manufacturing industries contain toxic substances, metal acids, alkalis, and other substances. Removal of heavy metals such as nickel and mercury from aqueous solutions is necessary because of the frequent appearance of these metals in waste streams. This problem has received considerable attention in recent years due primarily to concern that those heavy metals in the waste streams can be readily adsorbed by marine animals and directly enter the human food chains, thus presenting a high health risk to consumers [9]. Mercury is one of the most toxic heavy metals since it is not biodegradable and causes a lot of toxic effects in the human body [10]. Its presence is due to a combination of natural processes (volcanic action, erosion of mercury-containing sediments) and anthropogenic activities (mining operations, tanneries, metal plating facilities) as well [11]. On the other hand, nickel is a naturally occurring element widely used in many industrial applications for the shipbuilding, automobile, electrical, oil, food and chemical industries. Although it is not harmful in low quantities, nickel is toxic to humans and animals when in high concentrations. Nickel can be present in wastewater as a result of human activities. Sources of nickel in wastewater include ship cruise effluents, industrial applications and the chemical industry.

The adsorbent selected for the present study is chitosan, which has been repeatedly used as material for heavy metals removal [12–19]. Furthermore, the same adsorbents were synthesized in the current work (cross-linked chitosan microspheres grafted with chlorosulfonic acid or ethylenimine) as those of our previous one [8] in order to be more comparative. Despite the use of chitosan as materials for the removal of various heavy metal ions (Cu(II), Cd(II), Pb(II), Ni(II), Hg(II), Cr(VI), U(VI), Mo(V), V(V), Pd(II), Pt(IV), Au(III), As(V), Se(V)) [18,20], and especially for mercury [21–24] and nickel [25–30], it has not been bibliographically reported until now the study of the combination of the selected chitosan adsorbents (grafted with chlorosulfonic acid and ethylenimine) for Hg(II) and Ni(II) removal.

The focus of the present work is on the interaction between polymer swelling and adsorption processes by performing experiments for polymeric particles having undergone several levels of swelling at the start of the adsorption process. The structure of the present work is the following: at first, the experimental procedure and the corresponding results are presented in detail. Then a simple model for the simultaneous swelling–adsorption process is developed. Finally the experimental results are analyzed based on the model and the findings are discussed extensively.

2. Materials and methods

2.1. Materials

High molecular weight chitosan was obtained from Sigma–Aldrich and purified by extraction with acetone in a Soxhlet apparatus for 24 h, followed by drying under vacuum at room temperature (25 °C). The average molecular weight was estimated at 3.55×10^5 g/mol and the degree of deacetylation was 82 wt.% [31]. Glutaraldehyde (50 wt.% in water), isopropyl alcohol (99.7%), epichlorohydrin (99%), and formamide were received by Sigma–Aldrich. Polyethylenimine (50% w/v in water), chlorosulfonic acid ($\geq 98\%$), dichloroacetic acid ($\geq 98.5\%$), and sodium tripolyphosphate ($\geq 98\%$) were obtained by Fluka. Chlorosulfonic acid ($\geq 99\%$), sodium carbonate ($\geq 99\%$), and potassium persulfate obtained from Merck. All solvents were of analytical grade.

2.2. Model heavy metals

Two heavy metals were selected as model ion pollutants; mercury (Hg(II)) and nickel (Ni(II)). A crucial difference of those ions is

their different ionic radius (133 and 83 pm for Hg(II) and Ni(II), respectively). After the end of experiment, the measurement and analysis of ion residual concentration in the liquid phase was carried out. In particular, samples were collected from the supernatant and filtered in fixed pore-sized membranes (0.4 μm) purchased by Schleicher & Schuell-MicroScience. Hg(II) and Ni(II) were measured using flame atomic absorption spectrophotometer (Perkin-Elmer 1100 B) at 254 and 232 nm, respectively. The detection limit of FAAS was 300 and 6 $\mu\text{g/L}$ for Hg(II) and Ni(II), respectively, which is much lower to the studied metals residual concentrations. The detection limits are based on 98% confidence level (3 standard deviations). The absorbance was converted to concentration using calibration curve.

2.3. Adsorbents

The adsorbents used in this study are (i) cross-linked chitosan microspheres (without grafting) (CS), which were used as reference in all experiments; (ii) chitosan microspheres grafted with polyethylenimine (CSPEI), and (iii) cross-linked chitosan microspheres grafted with chlorosulfuric acid (CSSULF). The selection for the above materials was done due to (i) the desire to add/graft groups of different charge (negative (sulfonate) or positive (imino) groups). The preparation conditions were described in details in previously published works [8,32].

2.4. Swelling experiments

The swelling behavior as a function of time and hydrogel composition was studied by immersing 1 g of each adsorbent in deionized water. At fixed time intervals the hydrogel was separated from water by filtration and the swollen samples were weighed. The swelling percentage S_m (%) was calculated by Eq. (1):

$$S_m = \left(\frac{M_t - M_0}{M_0} \right) \cdot 100\% \quad (1)$$

where M_t (g) is the mass of the swollen sample at time t , and M_0 (g) is the initial mass of the sample before swelling.

2.5. Adsorption experiments

In order to run kinetic experiments, the optimum pH of the adsorption was needed. Therefore, preliminary experiments for the effect of pH were carried out. In these tests, the solution pH was adjusted at values 2–6 with micro-additions of acid or alkali (HCl or NaOH). Experiments were not carried out at pH > 6, in order to avoid precipitation phenomena of metals. In this pH-zone, the metal ions get out of the solution due to formation of colloidal precipitate of $\text{Hg}(\text{OH})_2$ or $\text{Ni}(\text{OH})_2$ and not due to the adsorption of free Hg(II) or Ni(II) ions [33]. In general the uptake of those metals at pH > 6 is attributed to the formation of metal hydroxide species such as soluble $\text{M}(\text{OH})^+$ and/or insoluble precipitate of $\text{M}(\text{OH})_2$ (in the present case M is Hg or Ni). The mass of adsorbents used was 0.05 g and added to the adsorbate solution of metals with $V = 50$ mL and $C_0 = 100$ mg/L. The conical flasks used for these batch experiments were placed to temperature-controlled shaking water bath (model Julabo SW-21C, Seelbach, Germany) adjusting the temperature and agitation speed at 25 °C and 160 rpm, respectively. The flasks were agitated for 24 h and then the residual metal concentration was analyzed as described in Section 2.2.

The experiments for isotherms (effect of initial ion concentration) were carried out at the optimum pH value found from pH-effect experiments (pH 6) and keeping constant all other parameters ($m = 0.05$ g; $V = 50$ mL; $N = 160$ rpm; $T = 25$ °C; $t = 24$ h). The only varying factor was the initial ion concentration

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