



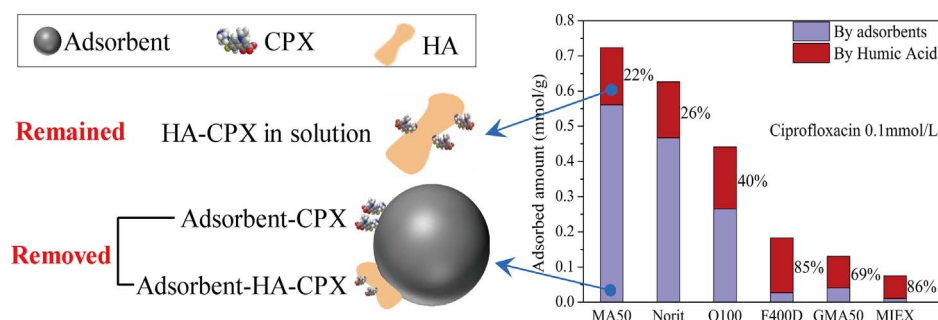
Ultrahigh selective adsorption of zwitterionic PPCPs both in the absence and presence of humic acid: Performance and mechanism

Jing Jin^a, Tianyu Feng^a, Rui Gao^a, Yan Ma^a, Wei Wang^b, Qing Zhou^{a,*}, Aimin Li^a

^a State Key Laboratory of Pollution Control and Resources Reuse, School of the Environment, Nanjing University, No. 163 Xianlin Avenue, Nanjing 210023, PR China

^b Jiangsu Province Key Laboratory of Environmental Engineering, Jiangsu Provincial Academy of Environmental Science, Nanjing 210036, PR China

GRAPHICAL ABSTRACT



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ABSTRACT

Since zwitterionic PPCPs could be combined with humic acid (HA) leading to certain contaminants residue in aqueous solution, adsorbents with much stronger binding with zwitterionic PPCPs were needed to avoid this phenomenon. Through comparison of serial magnetic carboxyl modified hypercrosslinked resins including MA10, MA30, MA40 and MA70, MA50 was found to exhibit ultrahigh selective adsorption of zwitterionic PPCPs including tetracycline and quinolone antibiotics due to the remarkable synergistic effects generated from cation exchange interaction and non-ion exchange interaction. To figure out the effect of HA, other five adsorbents including hypercrosslinked resin Q100, aminated hypercrosslinked resin GMA50, anion exchange resin MIEX, wood-based activated carbon F400D and coal-based activated carbon Norit were chosen as comparison to MA50 in adsorption performance of tetracycline (TC) and ciprofloxacin (CPX). It turned out that the percentage of CPX or TC combined with HA in aqueous solution varied greatly for studied adsorbents. There existed serious false-positive adsorption during the adsorption process by some commercial adsorbents such as MIEX and F400D, while MA50 exhibited relatively lower false-positive adsorption, ensuring the maximum safety of effluents. Breakthrough tests showed that MA50 had significant advantages in PPCPs removal at environment concentration, indicating its potential in application for real water.

1. Introduction

In recent years, pharmaceuticals and personal care products (PPCPs) have been frequently detected in aquatic environment with

concentrations varying from ng/L to µg/L due to their widespread usage [1–6]. Most PPCPs such as antibiotics, antiepileptics, analgesics exhibit false persistence [7], biological activity and chronic toxicity [8,9], thus posing potential harmful effects to both aquatic organisms

* Corresponding author.

E-mail address: zhouqing@nju.edu.cn (Q. Zhou).

and human beings [10]. Hence, many researchers have continuously focused on multifarious techniques for effective elimination of PPCPs. Thereinto, removal of PPCPs by adsorption is one of the most promising techniques due to its relatively mild operating conditions, cost efficiency and low energy consumption [11–13]. Various adsorbents including activated carbon [14], carbon nanotubes [15,16] and resins [17] have been reported to be effective for the adsorption of different PPCPs.

However, in real water environment, natural organic matter (NOM) with much higher concentrations compared to trace PPCPs is ubiquitous, which can significantly affect the adsorption performance of PPCPs [18]. Liu et al. [19] pointed out that humic acid (HA) suppressed the adsorption of ketoprofen, carbamazepine and bisphenol A to graphenes and carbon nanotubes due to competition and pore blockage. In Zhu's research, it was revealed that the adsorption amounts of various PPCPs with diverse properties including hydrophobicity, hydrophilicity and amphotericity decreased to different degrees in the presence of HA because HA captured by adsorbents through hydrophobic or electrostatic interaction can affect the adsorption of contaminants mainly through competing for adsorption sites and pore blockage [20]. In general, current researches mainly considered the interaction between HA and adsorbents, while neglecting the reaction between the negatively charged HA and ionic PPCPs. Aristilde et al. [21] found that there existed complex interactions between HA and PPCPs, especially for zwitterionic molecules like ciprofloxacin (CPX).

Wang et al. [22] investigated the effect of HA on CPX removal by magnetic multifunctional resins and disclosed that HA could impact CPX adsorption not only as a competitive adsorbate but also as an additional adsorbent. In other words, CPX could be combined with HA in aqueous solution, leading to certain contaminants residue in water environment. However, the magnetic resins Wang et al. proposed exhibited poor removal efficiency of zwitterionic CPX and the form of HA-CPX occupied a large proportion in aqueous solution as well. Therefore, adsorbents with much stronger binding with zwitterionic PPCPs were in need for the minimum combination of PPCPs and HA in aqueous solution to achieve safer effluents.

Based on our team's previous research [23], the magnetic resin MA50 was found to be fairly efficient for the adsorption of zwitterionic tetracycline (TC). Therefore, in this work, the adsorption performance and mechanism of zwitterionic PPCPs including tetracycline and quinolone antibiotics onto MA50 were further investigated in comparison with other serial resins including MA10, MA30, MA40 and MA70. What is more, the effect of HA on the adsorption of zwitterionic PPCPs onto MA50 was studied by comparison with a hypercrosslinked resin Q100, a multifunctional resin GMA50, an anion exchange resin MIEX, a wood-based activated carbon F400D and a coal-based activated carbon Norit. TC and CPX were chosen as the target zwitterionic PPCPs. Breakthrough tests were conducted to better study the adsorption performance of zwitterionic PPCPs including TC and CPX at low concentrations onto MA50.

2. Materials and methods

2.1. Materials

Tetracycline (TC), oxytetracycline (OTC), chlortetracycline (CTC), ciprofloxacin (CPX), norfloxacin (NFX) and humic acid (HA) were obtained from J&K Chemical Co. Ltd. (China). Sodium hydroxide (NaOH) and hydrogen chloride (HCl) were purchased from Sinopharm Chemical Reagent Co. Ltd. (China). Methanol and acetonitrile of chromatographic grade were bought from Merck KGaA. Deionized water was provided by Southeast Distilled Water Factory (China). The novel magnetic resin MA50 was synthesized via a sequence of suspension polymerization, hydrolysis and post-crosslinking reactions. Detailed procedures are described in the Supplementary Material. Other resins including GMA50 [22] and Q100 [24] were provided by Nanjing

University. The resin MIEX was obtained from the China Agent of Orica Watercare of Victoria. Activated carbon F400D and Norit were purchased from Sigma-Aldrich Co. LLC. (USA).

2.2. Adsorption mechanism investigation

For the adsorption thermodynamics study, 0.015 g of each resin was introduced into a series of 250 mL glass conical flasks containing 150 mL of TC at different initial concentrations (0, 0.05, 0.10, 0.15, 0.20 mmol/L) under the temperature of 278, 293 and 308 K, respectively. With regard to the study of TC adsorption onto different microspheres during the synthesis procedure, 0.015 g of the microspheres obtained after each step, namely the copolymerization, hydrolysis and post-crosslinking reactions, were added respectively to 150 mL of TC solutions of 0.1 mmol/L at 293 K. As to the Na⁺ dissolving experiment, the stock solution of TC was prepared using ultrapure water and the experiment process was the same as thermodynamics study at the temperature of 293 K. For the shielding experiment of carboxyl group, the copolymers of the five resins obtained after suspension polymerization directly underwent the post-crosslinking reaction without the hydrolysis process and the obtained hypercrosslinked resins were experimented for the adsorption of TC as above. To investigate the adsorption effect of different zwitterionic adsorbates, 150 mL of TC, OTC, CTC, CPX and NFX solutions with initial concentration of 0.1 mmol/L were prepared using deionized water, respectively and 0.015 g of revived serial resins were used for the adsorption experiment at 293 K. Initial solution pH was all adjusted to 6.5–7 using 0.1 mol/L HCl and 0.1 mol/L NaOH. All the experiments were repeated three times to obtain the average values.

2.3. The effect of HA

For single adsorbate adsorption experiments, 0.015 g of each adsorbent was introduced into a series of 250 mL glass conical flasks containing 150 mL of TC or CPX with initial concentrations of 0.1 mmol/L, respectively. The mixtures were shaken at 150 rpm under temperature of 293 K. Initial solution pH was adjusted to 6.5–7 using 0.1 mol/L HCl and 0.1 mol/L NaOH. As to the competitive adsorption experiments, 0.015 g of each adsorbent was added into 150 mL of mixed solutions composed of 0.1 mmol/L TC or CPX and 50 mg/L HA. All the experiments were repeated three times to obtain the average values. Adsorption capacity Q_t (mmol/g) was calculated using the following equation:

$$Q_t = \frac{V(C_0 - C_t)}{W} \quad (1)$$

Where V (L) is the volume of the solution, C_0 (mmol/L) and C_t (mmol/L) represent the initial concentration and the concentration at time t (min), respectively, and W (g) is the mass of the adsorbent used.

2.4. Breakthrough tests

For the breakthrough tests, mixed solution containing TC and CPX with respective concentration of 50 µg/L (1.1E-4 mmol/L and 1.5E-4 mmol/L respectively) was prepared. 0.05 g of MA50 and F400D were added into 200 mL of mixed solution respectively and the mixtures were shaken at 150 rpm for 2 h, decanted and sampled. Next, a new batch of the mixed solution was mixed with the remaining adsorbents and the above experiments were repeated. The volume of mixed solution increased to 500 mL and 1500 mL after several batches. In addition, 5 mg/L of HA was used to study the effect of NOM on adsorption and the experiments were conducted in the same processes as above. Initial solution pH was adjusted to 6.5–7 using 0.1 mol/L HCl and 0.1 mol/L NaOH. All the experiments were repeated three times to obtain the average values at 293 K. After reaction, the solutions were pretreated by solid phase extraction with Oasis HLB before HPLC

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