



Contrastive study for coadsorption of copper and two dihydroxybenzene isomers by a multi-amine modified resin

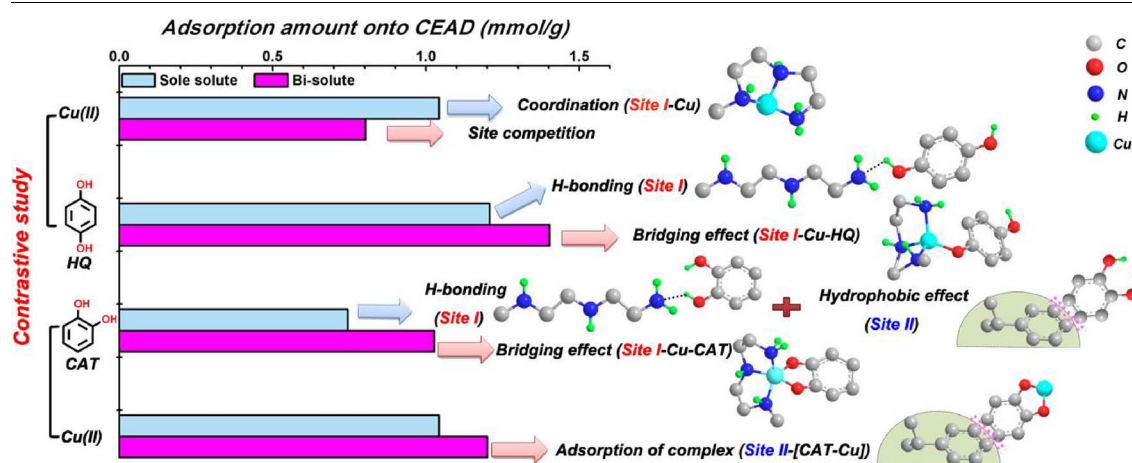
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GRAPHICAL ABSTRACT



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ABSTRACT

Coadsorption of Cu(II) and two dihydroxybenzene isomers (hydroquinone, HQ and catechol, CAT) onto a multi-amine modified resin (CEAD) were comparatively studied. The presence of Cu(II) promoted adsorption of both HQ and CAT by a maximum of 25.8% and 41.6%, respectively. However, two diphenols exerted a very different influence on Cu(II) uptake. Higher concentrations of HQ consistently suppressed Cu(II) adsorption while the co-existence of CAT facilitated it, especially at lower CAT concentrations. The interactions among solutes and adsorbents were revealed by means of kinetic tracking, sequential adsorption experiments, and characterizations/calculations (FTIR, XPS, MINTEQA2 and DFT). Cu(II) and HQ/CAT competed for amine sites with the order of adsorption affinity as HQ > Cu(II) > CAT. The bridging effect of Cu(II) forming ternary complexes (amine-Cu-CAT/HQ) on the resin phase was the dominant mechanism for the enhanced adsorption of diphenols. The [Cu-CAT] complex species showed a lower affinity to bind directly to amine sites compared with free Cu²⁺. Instead, the complex could be attracted by the polyphenyl matrix of CEAD, contributing to the increase of Cu(II) adsorption. Additionally, Cu(II) and diphenols were successively recovered, and CEAD could be stably reused. The findings will guide adsorbent applications and the environmental fate of concurrent heavy metals and phenolic compounds.

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1. Introduction

Heavy metals (HMs) and phenolic compounds (PCs) often coexist in industrial wastewaters (e.g. plating effluent) and surface waters. Due to their individual and combined toxic effects to both the ecosystem and human beings, the resulting combined pollution has attracted considerable attention [1–4]. Thus, the efficient treatment of both HMs and PCs is necessary and urgent. Traditionally, HMs and PCs are often separately treated by physic-chemical and biochemical methods [5,6]. Alternatively, it is more attractive to perform the coadsorption of HMs and PCs using one kind of adsorbent as a relatively simple and clean method. However, most reported adsorbents such as minerals [3,7], biomass [1] and polymer materials [8] faced many application bottlenecks: relatively low adsorption capacities, difficult separation/reuse and strong inhibition during the coadsorption. Therefore, it still requires a significant effort to seek new attractive adsorbents and to study their behaviors during the co-removal of HMs and PCs from water.

Recently, multi-amine modified materials (MAMs) have exhibited multifunctional adsorption to many kinds of HMs and polar organic pollutants (like PCs) [9–14]. The surface amine groups ($-\text{NH}_2$, $-\text{NH}-$) tend to coordinate with HMs and also interacted with PCs through hydrogen bonding (H-bonding) or electrostatic attraction. In addition, the polyphenyl skeletons could also contribute to PCs adsorption through hydrophobic and $\pi-\pi$ interactions [15]. Thus, it is promising to efficiently co-remove HMs and phenols by MAMs, which has rarely been addressed. In our previous work, a multi-amine modified resin (CEAD) showed greater adsorption capacities for both HMs and monophenols (*p*-nitrophenol, chlorophenol etc.) in a bi-solute system than other commercial resins under the same conditions [9]. Competitive and cooperative effects simultaneously occurred and controlled the coadsorption behaviors of HMs and monophenols. For example, the part of the *p*-nitrophenol (PNP) pre-adsorbed onto the skeleton of CEAD was proven to offer $-\text{OH}$ groups to bridge Cu(II) adsorption, while the part of PNP bonded (H-bond) with amines tended to be replaced by Cu (II) due to the strong coordination between Cu(II) and amines. The work has advanced the understanding of coadsorption interaction of HMs and PCs onto MAMs, and to some extent, confirmed the excellent potential of MAMs in co-removal of HMs and PCs.

However, more conditions should be studied as the mutual interactions may change with different PCs due to their varied chemical structures (including functional groups and $-\text{OH}$ positions). Their structures influence their hydrophobicity, hydrogen donor ability, and complexation affinities with HMs [16–18]. The former two directly affect the preference of adsorption sites (amines or skeletons) for PCs [19,20], while the latter is closely related to the extent of mutual interaction occurring between HMs and PCs in aqueous/ solid phases [21]. Moreover, the preferred adsorbate species (free forms or HM–PC complex) and their interactions during coadsorption are of concern since these mechanisms fundamentally decide coadsorption behaviors.

It is apparent that the coadsorption of HMs and PCs onto MAMs has not been fully understood. The aim of this study was to further investigate the coadsorption behaviors of HMs and diphenols onto MAMs, and also to determine how the molecular geometry of diphenols

influences their adsorption behaviors onto MAMs. Two dihydroxybenzene isomers (hydroquinone, HQ and catechol, CAT) were set as model diphenols since they are widely applied in the chemical industry and are also metabolites of various macromolecular organics [22]. These isomers exhibit different properties (see Table S1, in the Supplementary material). Cu(II) was set as the HM model due to its high prevalence and activity [23]. CEAD was used as a model of MAMs because of its relative clear and stable structure [9,10]. Specifically, we hypothesize that the coadsorption behaviors of Cu(II) and the two isomers onto CEAD are driven by different multi-form interactions including replacement and bridging effects. Also, the bridging effect for Cu(II)-CAT will be greater than that of Cu(II)-HQ, similar to the stronger complexation affinity between Cu(II) and CAT in the aqueous phase. The results of this study will provide new information for the coadsorption of HMs and PCs onto MAMs and other similar colloid interfaces, which may give guidance on adsorbent designs for water treatment and the environmental fate of concurrently occurring HMs and PCs.

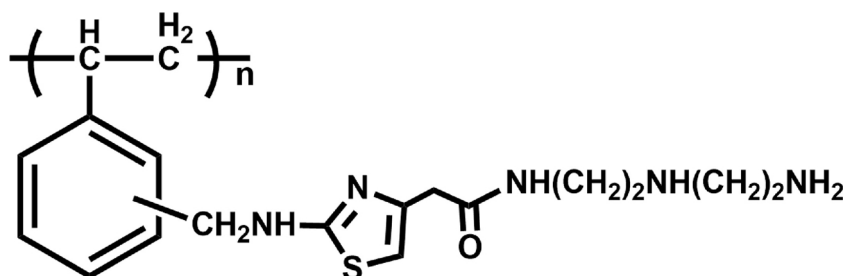
2. Materials and methods

2.1. Materials

CEAD was synthesized as reported in our previous works [9,10]. Briefly, it was derived from the chloromethyl polystyrene resin (CMPS, Cl content was 18%). CMPS was first reacted with ethyl 2-amino-4-thiazoleacetate at 85 °C in *N,N*-Dimethylformamide (DMF) for 24 h. Then the obtained resin (CEA) underwent the aminolysis reaction with diethylenetriamine at 125 °C for 24 h, resulting in the resin CEAD. The general structure of CEAD was shown in Scheme 1. The typical properties of all tested adsorbents are listed in Table S2. $\text{Cu}(\text{NO}_3)_2$, HQ and CAT and other reagents were all analytical grade purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, P. R. China) and were used directly without further purification. All solutions were prepared using ultrapure water produced by a Millipore-Q system (Millipore Synergy, USA).

2.2. Static adsorption studies

0.050 g of fresh dry resins were mixed with 50 mL solutions containing sole solute (Cu(II), HQ, or CAT) and two kinds of solutes (Cu(II) and HQ/CAT) in 150 mL conical flasks. The initial concentrations and pH values were set as desired and are shown below each figure. The solution pH was adjusted with 1.0 M HCl and NaOH. The flasks were sealed and continuously agitated at 160 rpm for 36 h at 30 °C in an incubation shaker. For the kinetic study, the adsorption scale was enlarged with the same dosage, while the aqueous solution was sampled at pre-set time intervals. In the sequential adsorption tests, fresh CEAD resin was first mixed with dihydroxybenzene or Cu(II), filtered after equilibrium, and then the Cu(II) or dihydroxybenzene solutions were added to the preloaded resins again and were allowed to reach equilibrium.



Scheme 1. General structure of CEAD.

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