An innovative zinc oxide-coated zeolite adsorbent for removal of humic acid

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ABSTRACT

Zinc oxide (ZnO)-coated zeolite adsorbents were developed by both nitric acid modification and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ functionalization of zeolite 4A. The developed adsorbents were used for the removal of humic acid (HA) from aqueous solutions. The synthesized materials were characterized by porosimetry analysis, scanning electron microscopy, X-Ray diffraction analysis, and high resolution transmission electron microscopy. The maximum adsorption capacity of the adsorbents at 21 ± 1 °C was about $60 \text{ mgC} \cdot \text{g}^{-1}$. The results showed that the positive charge density of ZnO-coated zeolite adsorbents was proportional to the amount of ZnO coated on zeolite and thus, ZnO-coated zeolite adsorbents exhibited a greater affinity for negatively charged ions. Furthermore, the adsorption capacity of ZnO-coated zeolite adsorbents increased markedly after acid modification. Adsorption experiments demonstrated ZnO-coated zeolite adsorbents possessed high adsorption capacity to remove HA from aqueous solutions mainly due to strong electrostatic interactions between negative functional groups of HA and the positive charges of ZnO-coated zeolite adsorbents.

Keywords: *electrostatic interaction, humic acid, water treatment, zeolite, zinc oxide, natural organic matter*

1. Introduction

Humic acids (HA) and fulvic acids are ubiquitous in surface water. They are also found in ground water and sources of drinking water supply. Humic and fulvic acids could bring undesirable color and odor to drinking water [1] and react with chlorine to produce potential carcinogens such as trihalomethanes and haloacetic acids during drinking water treatment [2-5]. Therefore, it is of great importance to remove HA from sources of drinking water supply.

Adsorption has gained much attention to remove HA from water due to its ease of operation and high efficiency. Furthermore, the adsorption process can remove a large number of toxic substances from the treated water, and has no side effects or secondary pollution [6-15]. However, one process, granular activated carbon (GAC), is generally effective, but not cost effective, thus new adsorbents are being sought. Since the amount of adsorbent required in the adsorption process and the required frequency of regeneration are important parameters for processes to determine operational costs, there is a need to develop a highly efficient adsorbent for the maximum removal of HA from water.

HA is a coiled, long-chain molecule that can contain negatively charged functional groups under typical environmental pH values. The functional groups are mainly derived from the ionization of carboxyl groups, leading to mutual repulsion and expansion of the coil of HA [16]. Therefore, it is important to develop positively charged adsorbents to improve the efficiency of HA removal for adsorption processes [17].

In view of their unique external and internal surface reactivity, zeolites have attracted much attention in the scientific community. Extensive research effort has been undertaken to improve further their physicochemical properties, which are directly associated with the efficiency of zeolites for the removal of HA and other pollutants from water [11-15]. Furthermore, since ZnO could dissociate hydrogen in a heterogeneous manner [18-20], an appropriate matrix tailored by ZnO will increase the amount of positively charged groups on the matrix. As a result, we chose zeolite 4A as a matrix and developed ZnO-coated zeolite adsorbents. Herein, zeolite 4A was modified by nitric acid (HNO_3) treatment and then was functionalized by $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. In addition, we have demonstrated that ZnO-coated zeolite adsorbents could efficiently remove HA from aqueous solution. The adsorption of HA onto ZnO-coated zeolite adsorbent was investigated in batch adsorption experiments in order to determine 1) the optimal amount of ZnO coated on zeolite, 2) the role of ZnO on the effectiveness of HA adsorption onto ZnO-coated zeolite adsorbents, and 3) the effect of initial HA solution pH and ionic strength on the adsorption capacity. We focused on the evaluation of the effect of nitric acid modification on the HA adsorption capacity. ZnO-30-zeolite was produced without nitric acid modification for comparison. Since the evaluation of selective adsorption of ZnO-coated zeolite adsorbents is crucial for their future practical applications in the field of environmental remediation, we investigated the surface properties of ZnO-coated zeolite adsorbents by surface characterization techniques. Finally, the effect of contact time was examined to provide important information on the adsorption mechanism.

2. Experimental

2.1. Adsorbates

HA was the target contaminant in this study to assess the adsorption capacity of the prepared adsorbent materials. HA was purchased from Sigma-Aldrich (Milwaukee, WI). A stock solution of HA ($140 \text{ mgC}\cdot\text{L}^{-1}$) was prepared by dissolving HA in autoclaved de-ionized water for 48 h and filtered with a membrane filter (pore size: $0.45 \text{ }\mu\text{m}$, EMD Millipore, Germany). The stock solution of HA was stored in the dark at $4 \text{ }^{\circ}\text{C}$ before use.

2.2. Preparation and Characterization of ZnO-coated zeolite adsorbents

2.2.1. Preparation of ZnO-coated zeolite adsorbents

A portion of commercial zeolite 4A was modified by HNO_3 with an optimal concentration and then a $\text{Zn}(\text{NO}_3)_2$ solution, which would result in 10, 20, and 30 wt% loading of ZnO on zeolite, was physically mixed with HNO_3 treated zeolite under vigorous stirring. Then, the mixtures were heated to dry and annealed for 2 h at $300 \text{ }^{\circ}\text{C}$ to convert zinc nitrate to zinc oxide. Finally, the samples were finely powdered in an agate mortar and referred to as ZnO-10N-zeolite, ZnO-20N-zeolite, and ZnO-30N-zeolite, respectively, which were stored in a desiccator until use. To investigate the effect of nitric acid modification on the HA adsorption capacity, ZnO-30-zeolite was produced without nitric acid modification for comparison.

2.2.2. Characterization of ZnO-coated zeolite adsorbents

To determine the crystal structure of zeolite, ZnO-10N-zeolite, ZnO-20N-zeolite, and ZnO-30N-zeolite, X-ray diffraction (XRD) spectra were obtained using an X'Pert PRO (Philips) XRD diffractometer with Cu K α ($\lambda=1.5406$ Å) radiation. To characterize the morphology of zeolite, ZnO-10N-zeolite, ZnO-20N-zeolite and ZnO-30N-zeolite, an environmental scanning electron microscope (ESEM, Philips XL 30ESEM-FEG) was employed. To investigate the crystal structure and crystal size of ZnO-30N-zeolite, a high resolution transmission electron microscope (HR-TEM, Philips FEI Tecnai F30) with a field emission gun at 200 kV was used. Furthermore, Brunauer, Emmett and Teller (BET) surface area and pore size distribution of zeolite, ZnO-10N-zeolite, ZnO-20N-zeolite and ZnO-30N-zeolite were measured using a TriStar 3000 Surface area and Porosimetry analyzer (Micromeritics). For the analysis, adsorbents were pre-treated at 100 °C in vacuum for 1 hr, and then nitrogen adsorption-desorption isotherms were determined in the whole partial pressure range at 77 K. Finally, the zeta potential values of ZnO-30N-zeolite were determined with a Malvern Zetasizer 3000 HS_A. 0.1 g ZnO-30N-zeolite was suspended in 10 mL autoclaved de-ionized water at different initial solution pH ranging from 4 to 12. The zeta potential of each initial solution pH was measured three times.

2.3. Adsorption experiments

An amount of 50 mg of ZnO-coated zeolite adsorbent was added into 40 mL vial followed by 25 mL HA stock solution (140 mgC·L⁻¹). In order to reach the adsorption equilibrium, vials were placed on a Rotamix Mixer and mixed for 15 min with 50 rpm at 21±1 °C. Then, the vials were kept at 21±1 °C for 5 days. Finally, the solid was

separated by filtration using a syringe filter (pore size: 0.20 μm , PVDF Filter Media, Whatman, USA). The collected solutions were immediately analyzed to quantify the adsorption capacity of HA using Shimadzu TOC (total organic carbon)-V CSH/CSN analyzer (Columbia, MD, USA). The amount of adsorbed HA was calculated from the difference between the concentration of HA in the solution before and after the adsorption experiment. In the case of TOC measurement, samples were diluted to a final volume of 20 mL. The experiments were carried out in triplicates for each TOC point.

3. Results and discussion

3.1. Characterization

Mechanisms contributing to the adsorption of HA on ZnO-coated zeolite adsorbents were explored by surface characterization techniques and adsorption tests. Figure 1 shows the X-ray diffraction patterns of (a) zeolite, (b) ZnO-10N-zeolite, (c) ZnO-20N-zeolite, and (d) ZnO-30N-zeolite, compared to the standard patterns of zeolite A (PDF#38-0241) and ZnO (PDF # 89-0511). Compared with that of the zeolite 4A, ZnO-10N-zeolite, ZnO-20N-zeolite, and ZnO-30N-zeolite exhibited similar characteristic diffraction peaks to those of parent zeolite, indicating that the modification did not affect the mineralogy of zeolite. However, there was a slight decrease of the intensity of the diffraction peaks with the loading of ZnO on zeolite. Furthermore, ZnO-coated zeolite adsorbents exhibited similar characteristic diffraction peaks to those of ZnO, while there was a slight increase of the intensity of

the diffraction peaks of ZnO with increase in the amount of ZnO coated on zeolite 4A. These results indicate that ZnO was successfully coated on the zeolite 4A by the preparation method.

Figure 1. X-ray diffraction spectra of zeolite 4A, ZnO-10N-zeolite, ZnO-20N-zeolite, and ZnO-30N-zeolite.

SEM was used to examine the size and morphology of zeolite 4A and ZnO-coated zeolite adsorbents (Fig. 2). According to the SEM images, zeolite 4A appears in cubic crystals with uniform particle size while the surfaces of the other samples were much rougher than that of zeolite 4A and formed non-uniform particle size. The amorphous ZnO is distributed disorderly and formed randomly shaped aggregates of variable size. Namely, the particles of zeolite partially and non-uniformly are coated with amorphous zinc oxides, which do not have distinct morphology, and the surface roughness of zeolite increased with the amount of ZnO coated on zeolite 4A. Figure 3a shows an HR-TEM image of ZnO-30N-zeolite demonstrating that the modification did not change the mineralogy of the zeolite 4A, which is in fairly good agreement with XRD analysis. Moreover, the image shows that a small amount of subnanometric

ZnO crystallites formed inside the zeolite. The crystalline structure of the ZnO particles inside the zeolite was further studied by the HR-TEM analysis; (100) plane of ZnO with an interplanar spacing of approximately 0.28 nm is observed in Figure 3b, which clearly demonstrates a small amount of ZnO particles deposited in the pores of zeolite 4A.

Figure 2. SEM images of (a) zeolite, (b) ZnO-10N-zeolite, (c) ZnO-20N-zeolite and (d) ZnO-30N-zeolite. The images have a magnification of 3500 while the inset pictures have a magnification of 50000.

Figure 3. HR-TEM images of ZnO-30N-zeolite.

Surface area and porosity of porous materials are important characteristics for their applications as adsorbents since they determine the accessibility of target compounds to the active surface sites of the adsorbents, which is directly associated with their adsorption capacity. The BET surface area and porosity of zeolite 4A, ZnO-10N-zeolite, ZnO-20N-zeolite, and ZnO-30N-zeolite were investigated based on

nitrogen adsorption–desorption isotherms at 77 K (Figures 4 (a) and (b)). The BET surface areas of zeolite, ZnO-10N-zeolite, ZnO-20N-zeolite and ZnO-30N-zeolite were respectively 0.431, 1.595, 3.719 and 6.199 m² g⁻¹ and pore volumes were respectively 0.006, 0.024, 0.028 and 0.035 cm³ g⁻¹. The surface areas and pore volumes of ZnO-coated zeolite adsorbents increased by the modification of zeolite with HNO₃ and functionalization with Zn(NO₃)₂·6H₂O. This is related to its agglomerative morphology (Fig. 2), where more void space is built among the stacked ZnO cluster and causes profound external surface roughness. The N₂ adsorption–desorption isotherms of ZnO-coated zeolite adsorbents showed an isotherm shape with an evident hysteresis loop at relative pressure range of 0.2-0.9 (Fig. 4(a)). The isotherm presents a wide and asymmetrical hysteresis loop of type H2, suggesting the distribution of pore sizes and the pore shape is not well-defined or is irregular, while there exists the interconnectivity of pores [21]. The Barrett-Joyner-Halenda (BJH) pore diameter distribution of zeolite, ZnO-10N-zeolite, ZnO-20N-zeolite and ZnO-30N-zeolite are shown in Figure 4b. A peak centered at 3.6-4.6 nm size can be observed for all samples. The results demonstrated that all samples had similar textural properties; this is consistent with the XRD results. The average pore diameter and pore volume increased with the increase of the quantity of ZnO coated on zeolite. Furthermore, ZnO-coated zeolite adsorbents had a wide pore diameter distribution since the differential pore volumes (dV/dD) are above zero at diameters larger than 100 nm which is different from the pore diameter distribution of the parent zeolite.

Figure 4. Nitrogen adsorption isotherms of zeolite 4A, ZnO-10N-zeolite, ZnO-20N-zeolite and ZnO-30N-zeolite (a) and the corresponding pore size distribution (b) at 77 K.

3.2. Effect of the amount of ZnO coated on zeolite

In order to increase efficiency, the optimal amount of ZnO coated on the zeolite had to be determined. Adsorption equilibrium experiments with different ZnO-coated zeolite adsorbents at a constant concentration of HA ($140 \text{ mgC} \cdot \text{L}^{-1}$) were performed. Figure 5 illustrates the HA adsorption of zeolite 4A and ZnO-coated zeolite adsorbents. The order of efficiency of HA adsorption was $\text{ZnO-30N-zeolite} > \text{ZnO-20N-zeolite} > \text{ZnO-10N-zeolite} > \text{zeolite}$. Since the amount of ZnO coated on 4A zeolite is directly associated with positive charges on the surface of ZnO-coated zeolite adsorbents, the adsorption capacities of ZnO-coated zeolite adsorbents were proportional to the amount of ZnO coated on zeolite 4A, which likely resulted from enhanced electrostatic-driven interactions due to ZnO coating on zeolite 4A. However, above 30 wt% ZnO, the mixture agglomerated while drying and would not easily turn into a fine powder. The surplus addition of ZnO tremendously decreased the surface area of the composite, which in turn led to a drastic decrease of positively charged sites,

namely, a drastic decrease of adsorption capacity.

Figure 5. HA adsorption capacities of zeolite, ZnO-10N-zeolite, ZnO-20N-zeolite and ZnO-30N-zeolite with lines depicting error ranges on the top of each bar.

3.3. Effect of nitric acid modification

The texture and surface chemistry of zeolite were modified by means of liquid phase oxidation with HNO_3 to optimize HNO_3 's ability of dispersing active ZnO particles [22]. Based on the results of the effect of the amount of ZnO coated on zeolite 4A on the efficiency of HA adsorption, ZnO-30-zeolite (without HNO_3 modification) and ZnO-30N-zeolite were chosen for this study.

The maximum adsorption capacity of ZnO-30N-zeolite adsorbent ($60 \text{ mgC}\cdot\text{g}^{-1}$) is much larger than that of ZnO-30-zeolite ($39 \text{ mgC}\cdot\text{g}^{-1}$) (Fig. 6). The results indicate that acid modification can significantly affect HA adsorption since a part of acidic functional groups on the external surface of the adsorbent may contribute to an increase of sites that are positively charged. It is difficult to determine the type of

cations present in ZnO-coated zeolite adsorbents, while they were added into the HA solution. Since the literature [23] concluded that there were three kinds of zinc species, small ZnO crystals, ZnO clusters, and Zn ions (Zn^{2+} and $\text{Zn}(\text{OH})^+$) in Zn/HZM-5 prepared by impregnation, we speculated the type of cations present in ZnO-coated zeolite adsorbents may be formed through Eqs. (1) and (2).

Figure 6. HA adsorption capacities of ZnO-30-zeolite and ZnO-30N-zeolite with error lines included.

3.4. Effect of ionic strength

The effect of ionic strength on the adsorption capacity of ZnO-30N-zeolite was evaluated at different concentrations of potassium nitrate (KNO_3) and calcium nitrate ($\text{Ca}(\text{NO}_3)_2$): 0.001, 0.01 and 0.1 M. The increase of solution ionic strength from

0.001 to 0.1 M KNO_3 resulted in a notable decrease of HA adsorption capacity of the ZnO-30N-zeolite (Fig. 7). Consequently, electrostatic interactions are believed to be a major factor at the first stage of adsorption, which is in good agreement with previous studies reporting that an increased electrolyte concentration could reduce electrostatic attraction [24, 25]. In contrast, increasing the concentrations of $\text{Ca}(\text{NO}_3)_2$, the adsorption of HA on the ZnO-30N-zeolite resulted in slightly increased (Fig.7). This can be explained by the charge reduction of HA since metal ions bind to the negatively charged carboxylic groups [26-28]. Calcium ion bridging could reduce the electrostatic repulsion between free HA in aqueous solution and HA adsorbed on the adsorbents [29], which results in the enhancement of HA adsorption onto ZnO-30N-zeolite. However, when the concentration of $\text{Ca}(\text{NO}_3)_2$ surpassed 0.01 M, though subtle, the HA adsorption capacity of the ZnO-30N-zeolite decreased due to weak electrostatic attractions.

Figure 7. Effect of ionic strength on HA absorption of ZnO-30N-zeolite.

3.5. Effect of initial pH of HA solution

The point of zero charge (pH_{pzc}) plays an important role in determining the charge of the surface and the adsorption capacity of the adsorbent. A batch equilibrium method was applied to determine the pH_{pzc} according to the method of Smičiklas et al. [30].

The equilibrium solution pH was plotted against the initial solution pH for ZnO-30N-zeolite to obtain pH_{pzc} by increasing the initial pH (Fig. 8a), which is a pH_{pzc} of about 6.2 for ZnO-30N-zeolite. ZnO-30N-zeolite exhibits amphoteric properties and acts as a buffer in a wide pH range from 4 to 9.5. It means that the pH_{final} is the same and equal to pH_{pzc} for all values of $\text{pH}_{\text{initial}}$ from 4 to 9.5. The stability of the final pH of the solution at this wide range of initial pH from 4 to 9.5 supports the use of this ZnO-30N-zeolite as a good adsorbent. Correspondingly, the effect of initial solution pH on humic acid adsorption onto ZnO-30N-zeolite was studied by varying the initial pH of HA solution between 3 and 11 (Fig. 8b). The HA adsorption capacities of ZnO-30N-zeolite were almost the same when the initial pH of HA was varied from 3 to 9.5, and reached a maximum value of $60 \text{ mgC} \cdot \text{g}^{-1}$. This was attributed mainly to the Coulombic attraction between the positive surface of ZnO-30N-zeolite and the negatively charged HA. At lower pH from 4 to 6.2, the surface of ZnO-30N-zeolite becomes more positive, while there is a lower degree of deprotonation of the acidic functional groups of HA and the charge overall of a macromolecule HA becomes less negative. Conversely, at higher pH from 6.2 to 9, the surface of ZnO-30N-zeolite becomes less positive, while the hydrophilic functional groups of HA deprotonate to a higher degree and the charge overall of a

macromolecule HA becomes more negative. Furthermore, the zeta potential of ZnO-30N-zeolite as a function of pH was successfully measured (Fig. 9). The isoelectric point of ZnO-30N-zeolite was 11.2. When the solution pH is below 11.2, the surface of ZnO-30N-zeolite had positive charges which resulted in the electrostatic attraction between the positively charged surface sites of ZnO-30N-zeolite and negatively charged HA. This was in agreement with the above mentioned conclusion obtained from the effect of initial solution pH on HA adsorption.

Figure 8. (a) The pH_{final} as a function of pH_{initial} for ZnO-30N-zeolite after 48 h of equilibrium and (b) The effect of initial solution pH on humic acid adsorption onto ZnO-30N-zeolite.

Figure 9. The effect of pH on the zeta potential of ZnO-30N-zeolite.

3.6. Effects of contact time and initial HA concentrations

The effects of contact time on the adsorption capacity of HA onto ZnO-30N-zeolite at various initial concentrations (70, 100, and 140 mg/L) was thoroughly explored at 21 ± 1 °C (Fig. 10), as they can provide important information on the adsorption mechanism. Figure 10 showed that rapid initial adsorption is followed by a slow adsorption which continues for 7 days, and the equilibrium adsorption capacities of HA increased with the initial HA concentrations. The result proved that electrostatic interaction plays a main role in the initial adsorption of HA on ZnO-30N-zeolite, and initial HA concentrations can increase the electrostatic attraction to overcome the mass transfer resistance. Since the adsorption rate decreased greatly after 1h, it is hypothesized that after the first step of HA adsorption, HA self-aggregated by π - π stacking interactions, which played an important role in the second step of HA adsorption, as there are abundant aromatic rings on HA. Hence, the adsorption mechanism of HA on ZnO-30N-zeolite could be depicted as Fig. 11.

Figure 10. Effects of contact time on the adsorption capacity of HA on ZnO-30N-zeolite at various

initial concentrations.

Figure 11. Sketch of the adsorption mechanism of HA on ZnO-30N-zeolite.

In order to further investigate the mechanism of the HA adsorption of ZnO-30N-zeolite, the pseudo-first-order and pseudo-second-order kinetic models were used. The linear form of the pseudo-first-order (3) and the pseudo-second-order (4) equation could be expressed as follows [31,32]:

$$\lg(q_e - q_t) = \lg q_e - k_1 t / 2.303 \quad (3)$$

$$t/q_t = 1/(k_2 \cdot q_e^2) + t/q_e \quad (4)$$

where q_e and q_t ($\text{mg} \cdot \text{g}^{-1}$) represent the amounts of HA adsorbed at equilibrium and any time (h), respectively. k_1 (h^{-1}) is the rate constant of the pseudo-first-order model and k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{h}^{-1}$) is the pseudo-second-order rate constant.

As shown in Figure 12, $\lg(q_e - q_t)$ and t/q_t were plotted against time (h) at different initial HA concentrations respectively. From the slopes and intercepts of plots, first-order rate constant (k_1), second-order rate constant (k_2) and q_e values were determined and listed in Table 1. The pseudo-second-order model is very suitable for describing the equilibrium of HA adsorption on ZnO-30N-zeolite in the whole range of contact time, as very high regression correlation coefficients (>0.99) were found for all fitting lines, and the calculated q_e values from the slopes of plots which were determined from pseudo-second-order model agreed very well with the experimental

q_e values. However, the pseudo-first-order equation does not fit well for the whole range of contact time.

Figure 12. (a) $\log(q_e - q_t)$ vs. t plot for the adsorption of HA on ZnO-30N-zeolite and (b) t/q_t vs. t plot for the adsorption of HA on ZnO-30N-zeolite.

Table. 1 Kinetic parameters for the adsorption of HA on ZnO-30N-zeolite

$C_0(\text{mg} \cdot \text{L}^{-1})$	$q_e(\text{mg} \cdot \text{g}^{-1})$	$k_1(\text{h}^{-1})$	R^2	$q_e(\text{mg} \cdot \text{g}^{-1})$	$k_2(\text{g} \cdot \text{mg}^{-1} \cdot \text{h}^{-1})$	R^2
70	18.6	0.021	0.9699	40.8	0.0082	0.9963
100	21.3	0.020	0.9619	50.5	0.0078	0.9972
140	24.4	0.019	0.9816	60.3	0.0064	0.9966

It is evident that the maximum adsorption capacity at equilibrium of ZnO-coated zeolite adsorbents at 21 ± 1 °C was about $60 \text{ mgC} \cdot \text{g}^{-1}$, which was larger than that of the reported adsorbents in previous literature studies (Table 2).

Table 2 The comparison of maximum HA adsorption capacities of various adsorbents

Adsorbent	$Q_m(\text{mg} \cdot \text{g}^{-1})$	Reference
CPB-modified zeolite	92.0	[11]
chitosan modified zeolite	31.32	[14]
activated carbon	6.9	[33]
Chitosan treated granular activated carbon	71.4	[34]
ZnO-30N-zeolite	109-120	this study

Note: The carbon content of humic acids range from 50% to 55% [35].

4. Conclusions

ZnO-coated zeolite adsorbents were developed with high adsorption capacity for the removal of HA from aqueous solutions. The highest adsorption capacity was achieved

with 30 wt% loading of ZnO on the zeolite. Modification of the ZnO-coated zeolite adsorbents with HNO₃ significantly improved their HA adsorption capacity. Structural characterization proved that ZnO particles coated on zeolite and ZnO-coated zeolite adsorbents have higher BET surface area and porosity. This helped to increase adsorption capacity and accessibility of HA to the active surface sites of the sorbents. Studies on the effects of ionic strength and initial solution pH proved that electrostatic interaction is the potential mechanism contributing to the enhanced HA adsorption on ZnO-coated zeolite adsorbents. The effects of contact time and initial HA concentrations further proved that electrostatic interaction was the most important parameter at the first step of HA adsorption on ZnO-coated zeolite adsorbents, and this first step probably acts as a trigger of the process of adsorption. As the adsorption rate decreased greatly after 1h, we speculated that π - π stacking interactions between HA molecules played an important role in the second step of HA adsorption on the ZnO-coated zeolite adsorbents. Furthermore, a kinetic model has been developed and indicated that pseudo-second-order model is very suitable for describing the equilibrium of the HA adsorption on ZnO-30N-zeolite. In general, ZnO-30N-zeolite adsorbent exhibited enhanced adsorptive properties for HA in a wide pH range from 4 to 9.5, which will make it more competitive than other adsorbents to remove HA, and have the possibility to be widely used in water treatment.

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Graphical Abstract

GRAPHICAL ABSTRACT

25mL, 140mg/L
humic acid solution

50mg ZnO-30-zeolite

after adsorption