

Adsorption of 2,4-dichlorophenol on metal-nitrate modified activated carbon

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Abstract—To remove 2,4-dichlorophenol (2,4-DCP) from aqueous solution, the surface of the activated carbon was first treated with HCl and then the surface was modified by using various metal ions (Cu, Co, Fe, Ni, Zn, and Mg). Metal doping significantly enhanced the adsorption efficiency of activated carbon, an effect that was further increased by HCl treatment of the modified activated carbons. Of all the preparations, the zinc(II)-modified activated carbon with HCl treatment showed the highest adsorption capacity for 2,4-DCP. Analysis of the zinc(II)-modified activated carbon by SEM and BET showed a surface area and micropore volume of around 1,154.69 m²/g and 0.291 cm³/g, respectively, values about 20% higher than in the starting material. In the pH range of 2.0-11.0, the maximum uptake of 2,4-DCP from an initial concentration of 1,000 mg/L was 508 mg/g at pH 4.0.

Key words: Activated Carbon Modification, 2,4-Dichlorophenol, Adsorption, Metal Ions, Metal-doped Activated Carbon

INTRODUCTION

Chlorophenols constitute an important category of organic water pollutants that are not readily biodegradable [1], and chlorophenolic compounds are listed as priority pollutants by the US Environmental Protection Agency (EPA) [2]. The compounds are produced in plastics, pharmaceuticals, and dye industries, steel plants, petroleum refineries, etc. [3-6]. These mutagenic, carcinogenic, and persistent chemicals must be decomposed before discharge into receiving waters to avoid toxic bioaccumulation in aquatic food chains.

Adsorption technology can efficiently remove toxic materials from the liquid phase, and chemical surface treatments of adsorbents can significantly enhance the selectivity and capacity of substrates [7,8]. Advantages of activated carbons for this purpose include a high adsorption capacity for organic pollutants due to their high specific surface area, adequate pore size distribution, and relatively high mechanical strength [3]. These properties have encouraged the use of activated carbons to remove phenolic compounds in past decades [9-14].

Importantly, activated carbons are also hydrophobic, with strong affinity for organic molecules such as phenols that have limited solubility in water [15]. The hydrophobic effect forces these molecules against the adsorbent surface to the exclusion of more hydrophilic compounds. The surface modification of activated carbon is of interest because it can substantially improve adsorption selectivity and capacity. Both activated carbons [16] and modified activated carbons [17-20] have therefore been tested for use in adsorptive removal or sequestration of organic pollutants. Surface-modified activated carbons are especially useful to treat refractory or hazardous (e.g., halogenated) compounds because alternative, decomposition processes, including combustion, incineration, and supercritical water oxidation for halogenated compounds produce corrosive re-

sidues under acidic conditions [21].

We tested the removal of 2,4-DCP from water by activated carbon treated or not treated with HCl, and modified with various metal ions. We compared the adsorption performance of the modified activated carbons, and noted the effects of the modifications on the carbon pore structure and surface properties.

MATERIALS AND METHODS

1. Preparation and Characterization of Modified Carbon

Powdered activated carbon (PAC) was purchased from Hanil Green Tech, South Korea, and hydrated metal nitrates (Cu, Co, Fe, Ni, Zn, and Mg), analytical grade, were purchased from Sigma Aldrich Ltd., South Korea. Powdered activated carbon (10 g) was treated with 0.1 M metal solution for 24 hr, then oven-dried at 120 °C for 24 hr to produce metal nitrate-impregnated activated carbon (MAC1). To improve pore development, carbons were first treated with 18% HCl solutions for 24 hr, oven-dried at 120 °C for 24 hr, and then treated with metal nitrates as described above. These were the MAC2 preparations. HCl treated PAC is denoted as PAC2.

The amount of metal ion adsorbed was calculated from the difference between the quantity of metal ions added to the modified activated carbon and the metal ion content of the supernatant by using the following equation:

$$Q = \frac{V(C_0 - C_f)}{M} \quad (1)$$

where Q is the amount adsorbed (mg/g); C₀ and C_f are the initial and equilibrium metal concentrations in the solution (mg/L), respectively; V is the volume of solution (L); and M is the mass of activated carbon (g).

Scanning electron microscopy (SEM, S-4200 Hitech, Japan) and nitrogen adsorption and desorption measurements (Micromeritics ASAP 2020) were used to compare surface textures and porosities of the activated carbons.

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2. Batch Equilibrium Studies

Batch adsorption studies were conducted to determine the time needed to reach saturation and maximum adsorption capacity (i.e., equilibrium time). Adsorption equilibria were determined using 10 ml samples of 2,4-DCP at desired concentrations, initial pH 4.0, with 500 mg of adsorbent, in 10 ml vials. Samples were stirred continuously at an agitation speed of 185 rpm. At predetermined time intervals, samples were withdrawn and separated by centrifugation at 15,000 rpm for 15 min. A UV spectrophotometer (1601 PC, Shimadzu) was used to determine 2,4-DCP content in the supernatant. The pH of aqueous solutions was adjusted by using 0.1 M HCl or 0.1 M NaOH.

RESULTS AND DISCUSSION

1. Characterization of Modified Activated Carbons

The isotherms of adsorption and desorption of N_2 at 77 K for PAC, ZnAC1, and ZnAC2 are shown in Fig. 1. The curves for PAC and ZnAC1 have almost the same hysteresis loop. In the case of HCl-treated carbon (ZnAC2), the increment of N_2 adsorption is clearly observed in the hysteresis loop. These findings reveal a high portion of pores with indefinite pore size and shape in the carbon particles. Results of the BET analysis are shown in Table 1. Compared to the PAC, the surface area and pore volume of HCl-untreated activated

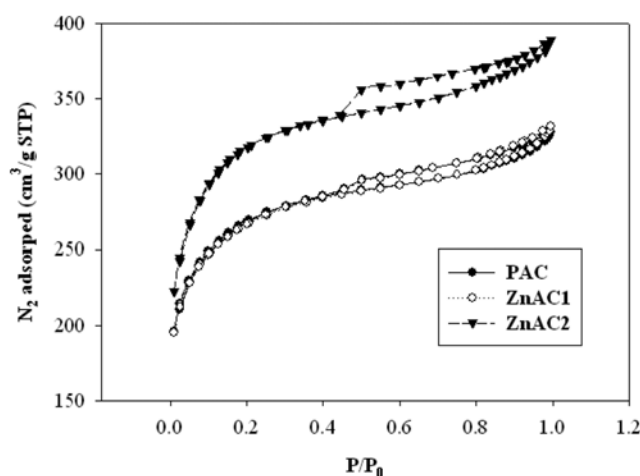


Fig. 1. Nitrogen adsorption-desorption isotherms of activated carbons.

carbon (ZnAC1) decreased slightly after modification with metal nitrate, while its external surface area increased. These results have come from blockage of the pore entrance by oxygenated functional groups and metal ions at the surface [22]. Zinc nitrate impregnation is a chemical activation process. During this step, a chemical reaction such as hydrolysis occurs with the surface of the carbon and cleans the impurity of the surface. Thus wide pore size distribution was observed [23,24]. In the case of HCl-treated activated carbon, however, the acid opened new micropores and broadened existing micropores as both surface area and pore volume increased [25]. The HCl induced these changes even though the activated carbon was treated with a metal nitrate.

The surface morphology of the activated carbon and modified activated carbon was observed by scanning electron microscopy (SEM). Fig. 2 shows the SEM images of PAC, ZnAC1, and ZnAC2. It can be seen from the micrographs that HCl treatment of ZnAC2 (Inset Fig. 2(c)) made the interior of the pores expand uniformly. The HCl treatment effectively developed pores on the surface of the precursor, which greatly enlarged the surface area and porous structure of the activated carbon. As shown in Table 1, the external surface areas of the activated carbons modified by the metal nitrate were greater than that of the PAC, regardless of the increase or decrease of surface area and pore volume after the modification. The salt particles scattered on the surface of the activated carbon in Figs. 2(b) and (c) are probably due to the presence of metal compounds on the activated carbon.

2. 2,4-DCP Removal

Activated carbons modified with various metal nitrates (Cu, Co, Fe, Ni, Zn, and Mg ions) at different initial concentrations were tested for their adsorption capacity to remove 2,4-DCP (Fig. 3 and Table 2). The amount of 2,4-DCP adsorbed on the various HCl-untreated

Table 1. BET analysis for carbon

Physical parameters:	PAC	ZnAC1 ^a	ZnAC2 ^b
Specific surface area (m ² /g)	968.57	961.77	1154.69
Langmuir surface area (m ² /g)	1214.02	1207.74	1459.95
Micropore volume (cm ³ /g)	0.2460	0.2274	0.2912
Micropore area (m ² /g)	583.79	540.48	699.83
External surface area (m ² /g)	384.78	421.29	454.87
Average pore diameter (Å)	25.96	26.65	27.68

^aWithout HCl treatment

^bWith HCl treatment

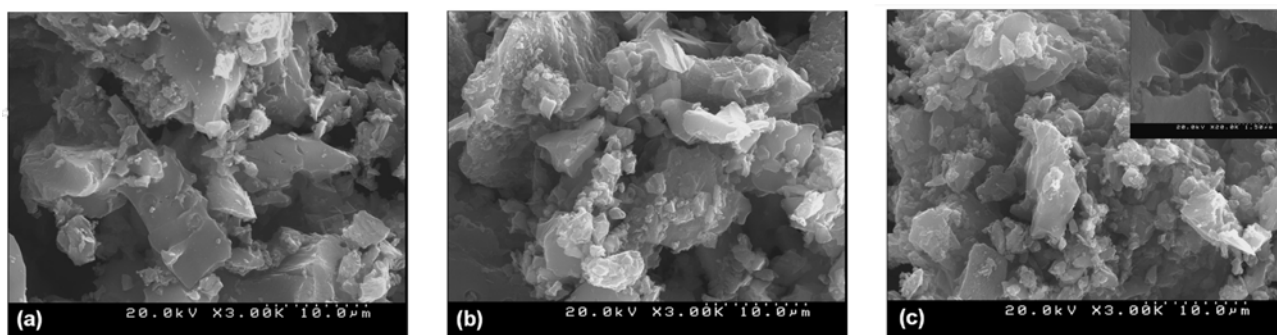


Fig. 2. SEM images of the surface of the carbons: (A) PAC (B) ZnAC1 (C) ZnAC2 with scan of 10 μ m and (C) an inset scan of 1.5 μ m.

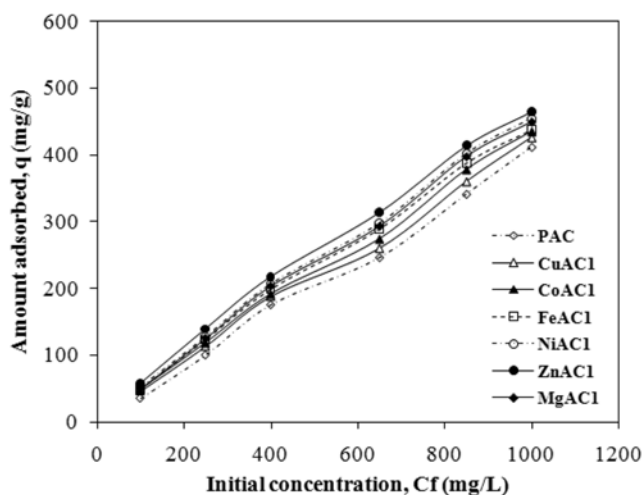


Fig. 3. Adsorption of 2,4-DCP by metal nitrate-modified carbon without HCl treatment at an adsorbent dosage of 500 mg/L at pH 4.

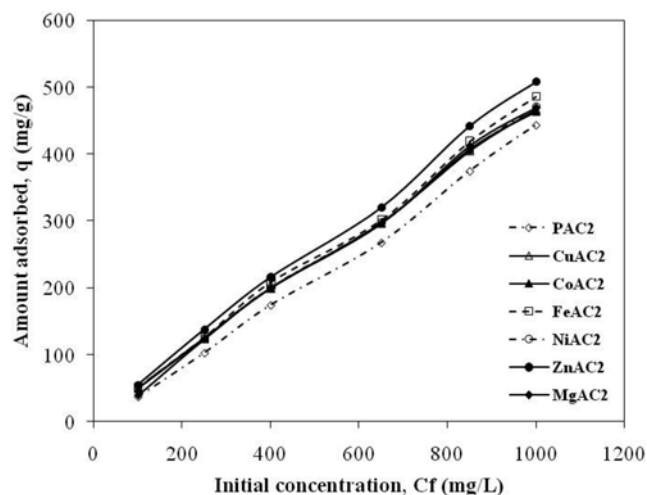


Fig. 4. Adsorption of 2,4-DCP by HCl-treated, metal-nitrate modified carbon at an adsorbent dosage of 500 mg/L and a pH of 4.

activated carbons increased almost linearly with initial concentration. The adsorption capacity of the Zn(II) ion-modified activated carbon was higher than that of the other metal-impregnated activated carbons. The adsorption capacities varied as follows: ZnAC1>NiAC1≥MgAC1>FeAC1≥CoAC1>CuAC1>PAC.

For the HCl-treated activated carbons, the linear increase in adsorption amount with initial concentration was the same as in Fig. 3. The adsorption capacities varied as follows: ZnAC2>FeAC2≥NiAC2≥MgAC2≥CuAC2>CoAC2>PAC2.

The adsorption capacities of all the modified activated carbons were improved compared to those not treated with HCl (Fig. 4 and Table 2) because the HCl treatment increased the surface area and porosity of the carbons. Moreover, the adsorption capacity of HCl-treated PAC was even higher than that of some metal-impregnated activated carbons not treated with HCl. The modified activated carbons differed little in adsorption capacity, except for ZnAC2 and PAC2. The absolute improvement in removal capacity between ZnAC and PAC, however, was greater for the HCl-treated preparations than for the untreated ones, as shown in Table 2.

2-1. The Effect of pH on Removal of 2,4-DCP

We studied the adsorption of 2,4-DCP on ZnAC2 across a range of pH values, with an initial concentration of 1,000 ppm (Fig. 5). As the pH increased from 2 to 4, the amount of 2,4-DCP adsorbed

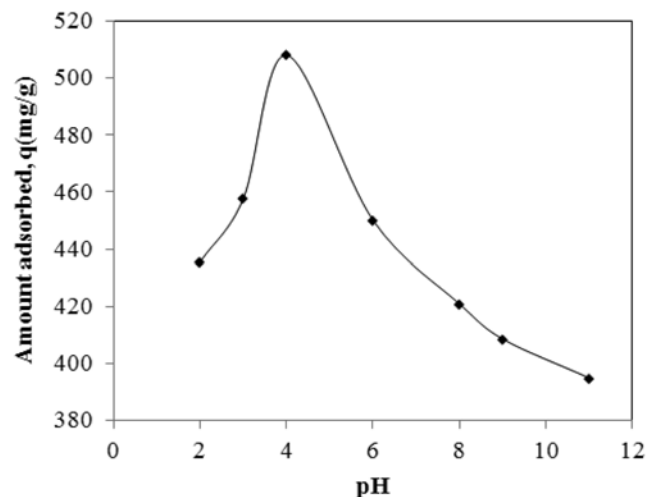


Fig. 5. Effect of pH on 2,4-DCP (1,000 mg/L) adsorption by HCl-treated activated carbon with Zn(II) (ZnAC2).

increased, and decreased thereafter. The pH influences the adsorbent for adsorption capacity because the surface of the activated carbon has a large number of negatively charged functional groups. At pH 4, the phenol group is positively charged as $C_6H_5OH_2^+$, which

Table 2. Adsorption of 2,4-DCP (1,000 mg/L) by metal-nitrate modified activated carbon (500 mg/L) at pH 4

Metal-nitrate modified activated carbon (MAC)	Amount adsorbed (%) without HCl treatment (MAC1)	Amount adsorbed (%) with HCl treatment (MAC2)
PAC	41.1	44.3
CuAC	42.6	46.7
CoAC	43.5	46.4
FeAC	43.8	48.6
NiAC	45.5	47.1
ZnAC	46.5	50.8
MgAC	45.1	46.9

increases the electrostatic attraction (and the adsorption) of 2,4 DCP to the carbon. At pH 2, hydrogen ions surround negative charges on the surface of the activated carbon, which prevents interaction with $\text{C}_6\text{H}_5\text{OH}_2^+$ and decreases adsorption. As pH increases above 4, the amount adsorbed again declines significantly, as both $\text{C}_6\text{H}_5\text{OH}_2^+$ and $\text{C}_6\text{H}_5\text{O}^-$ interact on the surface of the carbon. The negatively charged phenol group and negatively charged carbon surface repel each other, which reduces the removal of phenolic compounds. Above pH 4, the physical adsorption of phenol may predominate over the exchange mechanism at the carbon surface [4,26].

CONCLUSIONS

We studied the removal of 2,4-DCP from solution by various activated carbons. The HCl treatment improved the adsorption capacity of activated carbon for 2,4-DCP by increasing both the surface area and pore volume, and enhancing impregnation with metal ions. Although the metal impregnation decreased surface area and pore volume in the HCl-untreated activated carbon, the metal-impregnated activated carbon showed better adsorption capacity than the original activated carbon. With or without HCl treatment, the Zn(II) ion modification increased the efficiency of 2,4-DCP removal. The solution pH strongly influenced the adsorbent capacity of the activated carbon for 2,4-DCP, with an optimum effect between pH 2 and pH 4. Hence, HCl-treated activated carbon with Zn(II) ion can be applied efficiently to increase the removal of 2,4-DCP and facilitate the treatment of wastewaters enriched in phenolic compounds.

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