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# Adsorption behaviors of atrazine and Cr(III) onto different activated carbons in single and co-solute systems

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ABSTRACT

Three kinds of activated carbons (ACs) from apricot shells (AS), wood (W), and walnut shells (WS) were used for the adsorption of atrazine and Cr(III) in single and co-solutions. The elemental composition, Brunauer–Emmett–Teller (BET) surface area, pore volume, and surface functional groups of the used ACs were characterized by elemental analysis, surface area analyzer, and X-ray photoelectron spectroscopy. The adsorption kinetics of atrazine and Cr(III) are consistent with the pseudo-second-order model. The adsorption isotherms of atrazine follow the Freundlich model, whereas those of Cr(III) follow the Langmuir model. The maximum adsorption capacities for Cr(III) are found to be of the order: WAC > ASAC > WSAC. The adsorption capacities for atrazine and Cr(III) onto ASAC, WAC, and WSAC conform to the results of activation energy. The adsorption of atrazine and Cr(III) onto samples is an endothermic and spontaneous process. The pH value of solution minimally affects the adsorption of atrazine, while the adsorption amount of Cr(III) significantly increases with increasing pH value up to around 6. When Cr(III) and atrazine coexisted in the aqueous solution, the competitive adsorption was observed due to the different porosities and specific surface areas, affinities and active sites.

## 1. Introduction

Atrazine (2-chloro-4-(ethylamino)-6-isopropylamino-striazine) is globally applied in agricultural production to control broadleaf weeds and annual weeds, and thus improve crop yields and farming efficiency [1]. Atrazine is an endocrine disrupting chemical. It is durable and highly mobile herbicide that contaminates surface water and groundwater and affects the central nervous, endocrine, and immune systems, causing serious damage to frogs, fish, and other wildlife and potential harm to human health [2]. Therefore, this chemical is subjected to strict water regulations worldwide, and its pollution urgently requires a solution [3]. Cr(III) is widely used as an anti-corrosive in industries such as metal finishing, wood preservation, and leather tanning; however, it was discovered as a contaminant in industrial wastewaters [4]. Excessive Cr(III) can cause skin allergies and cancer [5]. The Environmental Protection Agency set the permissible limit for Cr(III) to 0.1 mg/L in drinking water [6].

Adsorption process is widely applied as an effective and promising method in waste water treatment [7,8]. New, cheap, effective, low-cost, and readily available adsorbents should be explored due to the difficulties in regenerating adsorbents and the substantial demand for water purification on large-scale [7,9]. Activated carbon (AC) is an adsorbent that can be easily produced at huge amounts from different agricultural by-products, such as nut, coconut and apricot shells, wheat and rice straws, soybeans and corn stalks, peach kernels, poultry manure and wood [10–14]. In previous works, some kinds of ACs have been used to remove atrazine by adsorption process, i.e., a biochar derived from wheat straw, which can form the π bond with atrazine [11]. And Liu et al. also reported the functional groups also play the critical roles for promoting the adsorptive removal of atrazine using biochars with the small specific surface area produced from soybeans and corn stalks, rice straws, poultry, cattle and pig manures [12]. In addition, some nanomaterials synthesized as excellent adsorbents were used for adsorption metal ions, such as hierarchical porous MgO microrods used as effective adsorbents for removing Pb (II) and Cr (VI) [15], hierarchical mesoporous $SrCO_3$ microspheres showed excellent adsorption for removing $Fe^{3+}$, $Pb^{2+}$ and other metal ions [16], and hierarchical porous $Ca(BO_2)_2$ microspheres used for adsorption of $Pb^{2+}$ and $Cd^{2+}$ [17]. What's more, Cr(III) has also been removed by using different adsorbents, such as silica forming the electrostatic attraction with Cr(III) [18], zirconium-pillared montmorillonite porous ceramic adsorption of Cr(III) influenced by electrostatic attraction and the coordination, and

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*Abbreviations:* ACs, activated carbons; AS, apricot shells; W, wood; WS, walnut shells; ASAC, activated carbons prepared from apricot shells; WAC, activated carbons prepared from wood; WSAC, activated carbons prepared from walnut shells; BET, Brunauer–Emmett–Teller; XPS, X-ray photoelectron spectroscopy.

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the micropore structure lead to the tight binding [19]. The difference in nature of the adsorbents, such as elemental content, porosity and functional groups, may influence their adsorption performance toward pollutants. In addition, a single adsorbent with adsorbates can have different adsorption mechanisms due to their varying characteristics. However, the real water environment can be polluted by both atrazine and Cr(III) because these two substances are widely used. Therefore, the research on adsorption of atrazine and chromium is meaningful.

In this study the adsorption processes of single and mixed components of atrazine and Cr(III) onto ACs from apricot shells (AS), wood (W), and walnut shells (WS) and the effect of ACs properties in aqueous solutions were investigated due to as the cheap, effective, low-cost, and readily available adsorbents. ASAC, WAC and WSAC were characterized by Brunauer–Emmett–Teller (BET), elemental analysis, and X-ray photoelectron spectroscopy (XPS). The pH influence, adsorption kinetics, activation energy, adsorption isotherm, and thermodynamics of atrazine and Cr(III) on samples in a single solution were studied to identify the governing adsorption properties and mechanisms. We also investigated the adsorption of atrazine and Cr(III) onto the adsorbents in a co-solution system and explored the mechanism underlying the competitive adsorption of atrazine and Cr(III) by using various carbon adsorbents.

## 2. Materials and methods

### 2.1. Adsorbents

Three types of ACs derived from wood, walnut and apricot shells were provided by Henan Zhongbang Environmental Technology Co., Ltd., China. All chemical reagents and chemicals were of analytic grade.

### 2.2. Characterization of activated carbons

The samples were dried at 80 °C for 24 h before analysis. The carbon, hydrogen, nitrogen, and sulfur contents of ASAC, WAC, and WSAC were measured using an elemental analyzer (Vario EL cube, Germany). The surface and pore properties of the adsorbents were measured by using a surface area analyzer (ASAP2020, Micromeritics, America) through the nitrogen adsorption–desorption method at 77 K. The specific surface areas of the samples were obtained based on the BET equation. The micropore volume and external surface area were calculated using the Horvath–Kawazoe method. The samples were tested with an XPS device (Thermo ESCALAB 250XI, America) that uses an Al Ka X-ray source (1486.6 eV). The graphite peak at 284.6 eV was obtained to calibrate the XPS spectrum of the samples.

### 2.3. Adsorption of atrazine and Cr(III) onto the AC samples

#### 2.3.1. Adsorption of single atrazine

In consideration of the low solubility of atrazine in water, the atrazine solution was prepared by dissolving atrazine in 5% (v/v) ethanol solution. The adsorption experiments were performed by batch mode with 50 mL of atrazine solution and 20.0 mg of adsorbents in a 100 mL conical flask with cover. All conical flasks were sealed and agitated at 160 rpm in a water bath shaker. The adsorption kinetics of atrazine (90 mg/L) onto the samples were evaluated at different adsorption times (1 s to 12 h) and temperatures (20, 35 and 50 °C). The adsorption isotherms of atrazine were evaluated at different initial concentrations (60, 70, 80, 90, and 100 mg/L) and temperatures (20, 35 and 50 °C) and were filtered thereafter. The concentration of residual atrazine was determined on a UV-75 N spectrophotometer at a wavelength of 222.5 nm.

#### 2.3.2. Adsorption of single Cr(III)

The adsorption experiments were performed by batch mode with 50 mL of 80 mg/L of Cr(III) solution and 20.0 mg of adsorbents in a 100 mL conical flask with cover. The adsorption kinetics investigation was the same as the above-described in Section 2.3.1. The adsorption isotherms of Cr(III) were evaluated at different initial concentrations (20, 40, 60, 80, and 100 mg/L) and temperatures (20, 35 and 50 °C). The residual concentrations of Cr(III) were quantified on an inductively coupled plasma emission spectrometer (HG-AFS, AI3300, Aurora Instruments Ltd., Vancouver, BC, America).

The adsorption amount ($q_t$, mg/g) of the adsorbates onto the samples at different times was calculated based on the mass balance by using the following equation (1):

$$q_t = (C_0 - C_t)V/M \tag{1}$$

where $C_0$ and $C_t$ (mg/L) are the concentrations of the adsorbate at the initial and given time t, respectively. $V$ (mL) is the volume of the aqueous solution, and $M$ (mg) is the mass of the adsorbent added to the flask.

#### 2.3.3. Competitive adsorption of atrazine and Cr(III)

In brief, 80 mg/L of Cr(III) was additionally spiked in a 100 mL conical flask with cover to evaluate the influences of Cr(III) on atrazine adsorption. All conical flasks were sealed and agitated at 160 rpm in a water bath shaker at 20 °C for 5 h. All experiments were conducted in duplicate, and the results were calculated as the mean values. The pollutant removal in the control experiments was negligible.

### 2.4. Model analysis

The experimental data of adsorption kinetics were fitted to pseudo-first-order (Eq. (2)) and pseudo-second-order (Eq. (3)) rate equations to use for the adsorption equilibrium time [17].

$$q_t = q_e\left(1 - e^{-k_1{}^{t}}\right) \tag{2}$$

$$t/q_t = 1/(k_2 q_e{}^2) + t/q_e \tag{3}$$

where $q_e$ and $q_t$ (mg/g) are the adsorption amounts of the adsorbate onto the adsorbents at the equilibrium and any time t (h), respectively. $k_1$ ($h^{-1}$) and $k_2$ (g/(mg h)) are the kinetic constants.

The diffusion mechanism of adsorption can be identified by using an intraparticle diffusion model (Eq. (4)), and film diffusion model (Eq. (5)) as follows [20].

$$q_t = k_p \cdot t^{1/2} + C \tag{4}$$

$$-\ln(1 - q_t/q_e) = k_{bf} t \tag{5}$$

where $k_p$ mg/(g $h^{1/2}$) and $k_{bf}$ ($h^{-1}$) are rate constants for intraparticle diffusion and liquid film diffusion, respectively.

The experimental data of the equilibrium research were fitted to Langmuir (Eq. (6)), Freundlich (Eq. (7)), Temkin (Eq. (8)), and Dubinin–Radushkevich (D–R) (Eq. (9)) isotherm models [21]. The

**Table 1**
Elemental composition of adsorbents.

| Adsorbent | N% | C% | H% | S% | O,diff% | N/C atomic ratio | H/C atomic ratio | O/C atomic ratio | (O + N)/C atomic ratio |
|---|---|---|---|---|---|---|---|---|---|
| ASAC | 0.31 | 47.98 | 0.58 | 0.66 | 50.47 | 0.006 | 0.012 | 1.052 | 1.058 |
| WAC | 0.30 | 72.86 | 0.52 | 1.32 | 25.00 | 0.004 | 0.007 | 0.341 | 0.345 |
| WSAC | 0.58 | 67.88 | 0.89 | 0.91 | 29.74 | 0.009 | 0.013 | 0.438 | 0.447 |