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Removal of atrazine as an organic micro-pollutant from aqueous solutions: a comparative study

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ABSTRACT

In the present study, different adsorbents were prepared: activated carbon (AC), MgO and ZnO nanoparticles, and the composite of AC/MgO/ZnO. The AC was prepared from oak charcoals, as low-cost and abundantly available materials in Iran, by chemical activation. MgO and ZnO nanoparticles were synthesized using a sol–gel method. The adsorbents were characterized using Powder X-ray diffraction (XRD), Field Emission-Scanning Electron Microscope (FESEM), and Energy Dispersive X-ray Spectroscopy (EDS). Then, the adsorption behavior of the adsorbents was tested for the removal of atrazine (ATZ) herbicide as a model of organic micro-pollutant. The average crystallite size of MgO and ZnO nanoparticles was calculated from their XRD data using the Scherrer equation. The results showed that the MgO and ZnO nanoparticles had a size in nano scale, which was supported by FESEM images. The experimental data showed that the pH of solution had no considerable effect on the adsorption of ATZ herbicide. The experimental data obtained for the AC and AC/MgO/ZnO composite were fitted to nonlinear pseudo first-order, pseudo-second order, and general order kinetic models. The general order kinetic model provided the best fit to experimental data compared with the other models. The adsorption isotherm data of these two adsorbents at different temperatures fitted well to the Langmuir and Liu models, but followed the Liu isotherm model most precisely, based on the lowest SD value provided by this model. The results of this study indicate that the chemically prepared AC has excellent

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adsorptive capacity and can be used as an effective adsorbent for the removal of ATZ from aqueous solutions. However, MgO and ZnO nanoparticles exhibited low adsorptive capacity for ATZ and could not be suitable adsorbents for the removal of this pollutant.

1. Introduction

Micro-pollutants, which are also termed as emerging contaminants, consist of a wide variety of anthropogenic as well as natural substances, including pesticides, personal care products, pharmaceuticals, steroid hormones, and industrial chemicals (Luo et al., 2014). Over the last few decades, with the development of analytical techniques with lower detection limits, the occurrence of micro-pollutants is increasingly being identified in the environment. Although, they are typically present at trace concentrations (a few $ng\,L^{-1}$ to several $\mu g\,L^{-1}$) in the environment, especially in aquatic environment, their low concentrations raise considerable ecological and public health concerns almost worldwide (Luo et al., 2014; Maeng et al., 2010). In addition, the low concentrations as well as diversity of micro-pollutants create challenges for water and wastewater treatment processes because current available water and wastewater treatment processes are not specifically designed for the removal of micro-pollutants (Luo et al., 2014). Atrazine is a selective herbicide, which is used for weeds control in various agricultural crops. This herbicide is also used in non-agricultural areas. Atrazine was introduced into the market in the 1950s, and since then has become the most widely used herbicide in agricultural and forestry applications, with an estimated annual worldwide usage amount of 70,000–90,000 tons (Graymore et al., 2001; Premazzi and Stecchi, 1990; Royal Society of Chemistry, 1991; WHO, 2011). Due to its long half time, high chemical stability in soils and aquifers, apparent mobility, moderate solubility in water, and great leaching potential, atrazine is frequently detected in surface, ground, and even drinking waters at levels exceeding the permissible limits (Chen et al., 2011; Liu et al., 2014). It has been reported in some studies that atrazine is toxic to human and animals; therefore, due to this fact, the USEPA has classified it as a potential human carcinogenic compound (Belluck et al., 1991; Premazzi and Stecchi, 1990; U.S. EPA, 2006). Although the use of atrazine has been banned in European Union countries since 2003, most countries including USA, China, and Iran continue its use on large scales (U.S. EPA, 2006). The USEPA has set a maximum contaminant level for atrazine at $3\,\mu g\,L^{-1}$, while the recommended level of atrazine in drinking water in European Union countries is $0.1\,\mu g\,L^{-1}$ (Bethsass and Colangelo, 2006; U.S. EPA, 2006). By considering the above-mentioned facts, the development of a useful and cost-effective method to remove atrazine from water bodies has become an important global environmental issue because conventional water and wastewater treatment techniques are not sufficient for its removal and have low removal efficiency (Liao et al., 2013). Therefore, advanced removal technologies are required for its complete removal.

Despite the availability of numerous treatment techniques, adsorption technology has been widely applied for the removal of recalcitrant organic micro-pollutants, due to its low capital cost, simplicity of design, high removal efficiency, insensitivity to toxic substances, and simple operation (Shirmardi et al., 2013a; Shirmardi et al., 2013b; Singh, 2009; Vosoughi Niri et al., 2014). Among various adsorbents investigated for the removal of atrazine, AC has a special place because it has been known for a long time that it can adsorb and exhibits high adsorptive capacity for the adsorption of various organic compounds, such as dyes and colored contaminants, odorous substances and pesticides (Ayranci and Hoda, 2004; Khalfaoui et al., 2015; Rojas et al., 2014; Zhou et al., 2014). Therefore, there is necessity of obtaining activated carbons from different organic precursors such as low-cost agricultural residues, wood charcoals and other cheaper materials, which can be used for industrial-scale production of activated carbon, following either physical or chemical activation (Amin, 2008; Pastor-Villegas et al., 2006; Rojas et al., 2014). In addition to the preparation of AC from low-cost available materials as alternative adsorbent, in recent years, the application of nanotechnology such as the use of nanomaterials, nanoparticles, or nano-adsorbents has been considered as a new and fascinating area of interest for the removal of various contaminants from water, wastewater, and polluted air streams (Sharma et al., 2009). For instance, during the last decade, nano-crystalline metal oxides have been applied as potential adsorbent for the treatment and remediation of pollutants from the environment (Venkatesha et al., 2013). The present study focuses on the preparation of activated carbon from oak charcoal, as a low-cost and abundant available precursor in Iran, by chemical activation. Furthermore, since atrazine adsorption studies have been mainly limited to activated carbon as adsorbent, we also synthesized MgO and ZnO nanoparticles as well as the composite of AC/MgO/ZnO. Then, the efficacy of these adsorbents for the removal of atrazine from aqueous solutions was compared to each another. The effects of most important parameters on the adsorption of ATZ were evaluated. The experimental data were also fitted to nonlinear kinetic and isotherm models.

2. Materials and methods

2.1. *Reagents, materials, and solutions*

Magnesium nitrate hexa-hydrate ($Mg(NO_3)_2{\cdot}6H_2O$), polyvinyl pyrrolidone (PVP), sodium hydroxide pellets (NaOH), zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) were all analytical grade with the purity ≥98% and were used without further purification. These materials were purchased from Samchun Pure Chemical Co., Ltd., South Korea. HPLC grade methanol and water were purchased from Merck Company, Germany. A technical grade atrazine herbicide, as a model of organic micro-pollutant, was purchased from Meshkfam Company, Fars Province, Iran. This technical grade herbicide had a purity of ≥95% and was used without any further purification to prepare atrazine solutions. All other chemicals used in this work were analytical or HPLC grade. A stock solution of atrazine with the concentration of $30\,mg\,L^{-1}$ was initially prepared. It should be noted that since it has been reported in some literature (Chen et al., 2009; Flora et al., 2013; Lemić et al., 2006; U.S. EPA, 2015) that the maximum solubility of atrazine in water at ambient conditions (20–25 °C and 1 atm) is in the range of $28–33\,mg\,L^{-1}$, the stock solution