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Modification of zeolite 4A for use as an adsorbent for glyphosate and as an antibacterial agent for water

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ABSTRACT

The aim of this work was to design a low cost adsorbent for efficient and selective removal of glyphosate from water at neutral pH conditions. For this purpose, zeolite 4A, a locally abundant and cheap mineral material, was ion-exchanged with Cu^{2+} to produce Cu-zeolite 4A. The FTIR results revealed that the modification has no important effect on chemical structure of zeolite 4A. After modification, highly crystalline zeolite 4A was converted to amorphous Cu-zeolite 4A according to XRD studies. The SEM images showed spherical-like particles with porous surfaces for Cu-zeolite 4A compared to cubic particles with smooth surfaces for zeolite 4A. Adsorption equilibrium data were well fitted with non-linear forms of Langmuir, Freundlich and Temkin isotherms. The maximum adsorption capacity for Cu-zeolite 4A was calculated to be 112.7 mg g^{-1} based on the Langmuir model. The adsorption of glyphosate by the modified adsorbent had fast kinetics fitted both pseudo-first-order and pseudo-second-order models. A mechanism based on chemical adsorption was proposed for the removal process. The modified adsorbent had a good selectivity to glyphosate over natural waters common cations and anions. It also showed desired regeneration ability as an important feature for practical uses. The potential use of the developed material as antibacterial agent for water disinfection filters was also investigated by MIC method. Relatively strong antibacterial activity was observed for Cu-zeolite 4A against Gram-positive and Gram-negative model bacteria while zeolite 4A had no antibacterial properties. No release of Cu^{2+} to aqueous solutions was detected as unique feature of the developed material.

1. Introduction

Organophosphorus pesticides are known as a class of synthetic compounds with potent effectiveness against pests of agricultural products. Glyphosate is one of the most extensively applied herbicides of this class. It is considered as non-selective, post-emergence and highly effective herbicide. A large volume of glyphosate is commercially produced and consumed annually (Duke and Powles, 2008). There is an increasing demand for glyphosate due to the development of genetically resistant crops and application of excessive amount of the herbicide to ensure effective and long lasting control of weeds and grasses (Bonny, 2008; Domingo and Bordonaba, 2011). Additionally, glyphosate is moderately persistent and it can be transferred to the environment by run-off or leaching, as several reports have indicated the presence of glyphosate in soil and water resources (Aronsson et al., 2011; Kjær et al., 2011; Laitinen et al., 2009). The toxicity of glyphosate is a well-known issue on the presence of this herbicide in the environment (dos Santos and Martinez, 2014; Mikó et al., 2017; Vera-Candioti et al., 2013). From some reports, it has been suggested that glyphosate interferes with the function of nervous and endocrine systems (Cattani et al., 2014; Mesnage et al., 2015; Roy et al., 2016). Furthermore, glyphosate has been placed in the category of likely carcinogenic to human by the World Health Organization (WHO) (Myers et al., 2016).

Various techniques such as chemical and photochemical degradation (Assalin et al., 2009; Jönsson et al., 2013; Manassero et al., 2010), membrane filtration (Samuel et al., 2017; Yuan et al., 2017), biodegradation (Fu et al., 2016; Rott et al., 2018) and adsorption have been studied and developed for treatment of glyphosate containing water and wastewater. Among these, adsorption has been widely studied due to its simple and low cost process. Many adsorbents such as montmorillonite (Khoury et al., 2010; Ren et al., 2014), activated carbon (Mailler et al., 2016) and goethite (Sheals et al., 2002) have been employed for removal of glyphosate from water. Many efforts have been conducted to promote efficiency of adsorbents for glyphosate removal. Modification of the existing low-cost adsorbents has been known as one of the most significant strategies to improve their performance. For instance, amine-functionalized iron oxide/SBA-15 (Fiorilli et al., 2017; Rivoira et al., 2016), polyaniline/ZSM-5 composite (Milojević-Rakić

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et al., 2013) and magnetic $MnFe_2O_4$–graphene (Yamaguchi et al., 2016b) have been prepared and employed successfully for efficient removal of glyphosate. However, the main challenge with the use of adsorbents is their low selectivity against co-existing compounds in real water samples. Therefore, design of an adsorbent with enhanced both capacity and selectivity can be considered as one of the important research objectives for adsorptive removal of glyphosate.

The main goal of this work was to develop a modified adsorbent for effective and selective removal of glyphosate from natural waters. A low-cost and locally abundant material, zeolite 4A was considered for our studies and modified by cation exchange with cupric ion. The modified adsorbent, Cu-zeolie 4A, was characterized and employed for adsorption studies. The development of an insoluble antibacterial material without producing of hazardous byproducts is of great importance in drinking water disinfection. Hence, the performance of the modified zeolite as a solid antibacterial agent for water filters was also investigated and considered as another aim of this work.

2. Experimental

2.1. Materials

A commercially available zeolite 4A with purity of 98% was purchased from a local supplier (Poshtiban Salamat Co). Glyphosate (41% aqueous solution) was obtained from Moshkfam company. All of other chemicals were of analytical grade and purchased from Sigma-Aldrich.

2.2. Modification of adsorbent

For preparation of Cu-zeolite 4A, 5 g zeolite 4A was mixed with 200 mL $CuSO_4$ solution (5%) for 1 h. Then, the suspension was filtered and the solid was washed thoroughly with distilled water to remove all impurities and it was dried in an oven at 120 °C for 3 h. The Conditions of modification process including concentration of $CuSO_4$ solution, zeolite dosage and time were selected according to a series of optimization experiments to reach maximum saturation capacity for Cu^{2+} adsorption by the zeolite.

2.3. Characterization

Scanning electron microscopy (SEM) was employed to study morphological properties of zeolite 4A and Cu-zeolite 4A. The SEM images of samples were obtained using a Vega Tescan SEM (Czech Republic). The surface of all samples was sputter-coated with gold before observation. Elemental analysis of samples surface was performed using Energy-dispersive X-ray (EDX) spectroscopy simultaneously with SEM imaging.

The surface area of neat and modified zeolite 4A was determined using Brunauer-Emmett-Teller (BET) isotherm for adsorption/desorption of nitrogen gas at 77 K. A Quantachrome ChemBET-3000 instrument was employed to perform BET experiments.

Fourier transform infrared (FTIR) spectra of samples were recorded on a Bruker Tensor 27 spectrometer (Germany).

The crystalline characteristics of samples were investigated using wide angle X-ray diffraction (XRD). The diffraction patterns were obtained by using a Siemens D-500 X-ray diffractometer (Germany).

2.4. Determination of pH_{pzc}

The batch equilibrium method (Babić et al., 1999) was employed to determine the pH at the point of zero charge (pH_{pzc}) for samples. A series of KNO_3 solutions (0.1 M) was selected and their pH was adjusted in different values of the range between 2 and 11 by adding 0.1 M HCl or NaOH solutions and the exact value of the initial pH (pH_i) for KNO_3 solutions was recorded. Then, a weighted amount of the sample (0.2 g) was added to a certain volume (100 mL) of the KNO_3 solutions. The constant ionic strength for all solutions was provided by using KNO_3 as background electrolyte. The suspensions were shaken for 48 h at room temperature to ensure complete equilibration. Afterwards, the suspensions were filtered to separate solid adsorbents and the pH of the solutions was measured and recorded as the final pH value (pH_f). The plot of ΔpH ($pH_i - pH_f$) versus pH_i intersects pH_i-axis at a value which is considered as pH_{pzc}.

2.5. Adsorption studies

The adsorption experiments were performed in batch mode at room temperature. The pH of all solutions was adjusted in the range of 7–8. To study adsorption rate, a 100 mg L^{-1} glyphosate solution was brought into contact with the adsorbent (2 g L^{-1}) by stirring at 100 rpm and then the concentration of glyphosate was determined at certain time intervals.

For equilibrium studies, the adsorption experiments were performed using a series of glyphosate solutions with varying initial concentrations (50–150 mg L^{-1}), adsorbent dose of 2 g L^{-1} and contact time of 2 h. After equilibration, the adsorbent was separated and the filtrate solution was analyzed for glyphosate. The equilibrium concentration of glyphosate on the adsorbent surface (solid phase), q_e (mg g^{-1}), was obtained using the following equation:

$$q_e = (C_i - C_e)V/m \quad (1)$$

where C_i and C_e are initial and equilibrium concentrations of glyphosate in mg L^{-1}, m is dry mass of adsorbent in grams and V is volume of solution in liters.

2.6. Regeneration of adsorbent

The regeneration of the used adsorbent was performed simply by mixing 2 g of the sample with 100 mL of $CuSO_4$ solution (5%) for 2 h at room temperature followed by filtration, washing and drying at 120 °C. To assess the regeneration ability of the adsorbent, the adsorption capacity of the adsorbent was determined during five repeated adsorption-regeneration cycles.

2.7. Interfering effect

The interfering effects of natural water common anions (nitrate, chloride, sulfate and phosphate) and cations (calcium, magnesium and sodium) on glyphosate adsorption were studied by performing adsorption experiments in the presence of each interfering agent in the concentration 5 times higher than glyphosate. The initial concentration of glyphosate (100 mg L^{-1}) and adsorbent dosage (2 g L^{-1}) were kept constant in all experiments.

2.8. Antibacterial activity

Antibacterial activity of zeolite 4A and Cu-zeolite 4A was evaluated by their minimum inhibitory concentrations (MIC) against bacteria strains. The MIC value of test samples was determined using broth dilution method according to National Committee of Clinical Laboratory Standard (NCCLS) protocol (Espinel-Ingroff et al., 2002). A log-phase culture of *Escherichia coli* and *Staphylococcus aureus* in Meuller-Hinton broth was employed as bacterial strains. The mixtures containing different concentrations of the test samples and bacterial suspension (0.5 McFarland standard) were introduced into the wells of a microtiter plate and then it was incubated while shaking for 24 h at 37 °C. The minimum concentration of the test sample causing irreversible inhibition of bacteria growth is considered as its MIC value.