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Removal of carbamazepine from municipal wastewater effluent using optimally synthesized magnetic activated carbon: Adsorption and sedimentation kinetic studies

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ABSTRACT

This study investigated adsorption of the carbamazepine (CBZ) from wastewater effluent to optimally synthesized magnetic nanocomposite of activated carbon (AC). The adsorbent was characterized by SEM, XRD, VSM, BET and FTIR analysis. Increase in the magnetite content up to mass ratio of 1:8 (Fe_3O_4: AC) had no adverse effect on the porous structure of adsorbent and decrease in adsorption capacity was only due to increase in inactive mass fraction of adsorbent. However, at higher contents of magnetite, decrease in adsorption capacity may be due to blockage of porous structure of AC. Sedimentation data of MAC 1:8 were well predicted by second order kinetic model with the rate constant of 8.9×10^{-3} NTU^{-1} min^{-1}. Response surface methodology was applied to optimize the treatment process. A significant quadratic model was achieved with the maximum removal efficiency of 93% within investigated intervals. By increasing of total dissolved solids (TDS); adsorption performance decreased slightly due to increase in water cluster formation on carboxylic groups which can block adsorption on the carbonyl sites. The equilibrium adsorption data were in agreement with the results predicted using Radke-Prausnitz, Redlich-Peterson and Temkin models. The maximum capacity was found to be 182.9 mg g^{-1}. The adsorption kinetic data were closely fitted to Elovich, intraparticle diffusion and pseudo-second-order models. According to thermodynamic parameters, the adsorption process was found to be spontaneous and exothermic in nature. The error functions were used to evaluate the agreement between the experimental data and predictions using models.

1. Introduction

Over the last decades, the occurrence of pharmaceuticals in aquatic environments has recognized as one of the environmental issues. Carbamazepine (CBZ) as an antiepileptic drug is among the most frequently reported micropollutants in surface waters [1]. CBZ was observed at a concentration more than 10 times higher than that of other micropollutants due to its high persistency [2]. The main source of pharmaceuticals in the aquatic environments was found to be effluents of urban wastewater treatment plants (WWTPs) [3], because the urban WWTPs have not been designed for micropollutants removal. CBZ was reported to be the most persistent pharmaceutical which can be removed through biological wastewater treatment on average by only 32.7%. The highest removal of CBZ in WWTPs was reported as high as 64.5% [4]. Therefore, discharge of effluents of urban WWTPs to environment can lead to occurrence of micropollutants in the aquatic environments, and subsequently in drinking water [5]. Therefore, finding the efficient post treatment is required to reduce the release of micropollutants into surface waters.

In recent years, various treatment technologies have been presented for removal of micropollutants from effluents of WWTPs, including, coagulation-flocculation [6,7], chemical oxidation [8,9] and adsorption [10–12]. Coagulation–flocculation process is ineffective in removal of most micropollutants with the removal efficiencies ranged from nil to 50%. The removal efficiency of micropollutants with high octanol-water partition coefficient (K_{OW}) is as high as 50% [1]. The removal efficiency of 2% was reported for CBZ (K_{OW}: 2.54) using coagulation–flocculation

Abbreviations: CBZ, carbamazepine; AC, activated carbon; GAC, granular activated carbon; PAC, powder activated carbon; MAC, magnetic activated carbon; NAT-AC, Nitric acid treated- activated carbon; RSM, response surface methodology; CCD, central composite design; RMSE, residual root-mean-square error; AARE, average absolute relative error.

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process [6]. The formation of by-products is the main disadvantage of chemical oxidation processes [13], which may increase the toxicity of treated wastewater. In order to remove the oxidation by-products, sand filtration or activated carbon (AC) filtration are required. The adsorption process is more effective in micro-pollutants removal in comparison with coagulation–flocculation process [14]. Several adsorbents have been recently reported for removal of micropollutants from wastewaters, including carbon nanotube [15], graphene oxide [16] and functionalized materials [17]. However, theses adsorbents have a low potential for large-scale applications. Activated carbon is one of the well-known adsorbent which has great specific surface area and pore structure. Adsorption by granular activated carbon (GAC) is the most commonly used process which can be operated in large-scale for water and wastewater treatment. However, powder activated carbon (PAC) has been considered as a more efficient adsorbent compared to GAC for removal of persistent organic micropollutants [18] and inorganic pollutants [19]. However, the large scale application of PAC has been limited in wastewater treatment due to small particle size and subsequently difficulty in separation of its particles from effluent after adsorption process [20,21]. In order to overcome the mentioned disadvantage, magnetic nanocomposite of AC has been proposed instead of AC which can be separated easily after treatment by a magnetic separator. Magnetic activated carbon (MAC) is mainly prepared by a two-step method in which activated carbon is combined with magnetic nanoparticles. Chemical co-precipitation iron salts at the presence of AC has also been reported [22]. The loading of nanoparticles on the AC can affect the porous structure of AC and subsequently its adsorption capacity.

In this research, optimally synthesized magnetic nanocomposite of AC was used in order to overcome the limitation of large scale application of PAC in micropollutants removal from effluent of WWTPs. The effect of magnetite content of nanocomposite on its adsorption capacity was investigated. The sedimentation kinetic of magnetic nanocomposite was compared with that of AC. Central composite design (CCD) was applied to optimize the CBZ removal from effluent of urban wastewater. The effect of adsorbent dosage, CBZ concentration, contact time and TDS were studied. The thermodynamics, equilibrium and kinetics of adsorption process were comprehensively investigated using several models. The error functions were used to evaluate the extent of agreement between the experimental data and predictions using models.

2. Materials and methods

2.1. Materials

Commercial powder activated carbon was supplied from Loba Chemie (India). Nitric acid (65% wt), ammonia solution (25% wt) and iron salts ($FeCl_2{\cdot}4H_2O$ and $FeCl_3{\cdot}6H_2O$) were purchased from Merck (Darmstadt, Germany) and used for preparation of the adsorbent. Initial pH of solutions was adjusted using NaOH and HCl which were also purchased from Merck. CBZ with a purity of 99.9% was obtained from Sigma-Aldrich (St. Louis, MO). Stock solution of CBZ was prepared at a concentration of 4000 mg L^{-1} in acetonitrile and was stored in dark at 10 °C and used within 1 month. All obtained reagents were of extra pure grade and were used without further purification. Deionized water was used throughout the whole experiments.

2.2. Wastewater effluent sample

Treated wastewater samples were taken from the effluent of secondary sedimentation tank of Ekbatan wastewater treatment plant (Tehran, Iran). The analysis of obtained sample is presented in Table 1. Although the CBZ can only be found in municipal wastewater in the range from a few ng L^{-1} to tens of μg L^{-1}, in this study to investigate the performance of prepared adsorbent, the concentration of CBZ in the wastewater was kept higher than 2 mg L^{-1}.

2.3. Preparation of MAC

In this work, magnetite nanoparticles were first synthesized and then mixed with nitric acid treated activated carbon (NAT-AC). Nitric acid treatment can decrease the point of zero charge of AC (pHpzc = 2). Magnetite nanoparticles have a high enough point of zero charge (pHpzc = 6) to support a positively charged surface in acidic medium. Therefore, magnetite nanoparticles and NAT-AC attract each other at pH range of 2–6 due to the opposite charges. Nitric acid treatment was performed using the method reported by Jafari et al. [23]. Briefly, 40 g of AC was slowly added to 200 mL of HNO_3 (65% wt). The mixture was constantly stirred for 3 h at 80 °C. NAT-AC was filtered, rinsed several times with deionized water and finally dried in an oven at 50 °C for 24 h. Magnetite nanoparticles were synthesized by co-precipitation of Fe^{2+} and Fe^{3+} ions in the absence of atmospheric oxygen. For this purpose, 2.92 g of $FeCl_3{\cdot}6H_2O$ and 1.05 g of $FeCl_2{\cdot}4H_2O$ were dissolved in 300-mL deoxygenated water and then vigorously mixed at 80 °C under the nitrogen flow, followed by adding the 80 mL of ammonia (25% wt) dropwise to the solution within 30 min. The colloidal magnetite nanoparticles were separated by a neodymium magnet (4 × 4 × 6 cm) and rinsed with 100 mL of deoxygenized water. Magnetite nanoparticles (0.3 g) and NAT-AC were dispersed in 500 mL of deoxygenated water in different mass ratios of magnetite to AC (1:2, 1:4 and 1:8), followed by pH adjustment to 4 and stirring under N_2 flow at room temperature for 1 h. The magnetic nanocomposite was easily separated by a magnet, dried at 50 °C overnight, and finally, dried at 110 °C for 4 h. In order to remove the iron ions adsorbed on the surface of nanocomposite, the MAC was washed with 500 mL of 0.2 mol L^{-1} HCl, followed by washing with deionized water and drying at room temperature.

2.4. Analytical methods

CBZ concentration was determined by HPLC (Agilent 1100) equipped with a C-18 column (5 μm, 4.6 × 250 mm) and a UV detector at the wavelength of 286 nm in the isocratic mode. A mixture of acetonitrile/water (60:40 v/v) was used as the mobile phase and was delivered at 1.0 mL min^{-1}. Samples were filtered on the PTEF filter (0.2 μm) and then were injected through a 20 μL-injector loop. Chemical oxygen demand (COD) was determined using a UV/VIS spectrophotometer (HACH, DR 5000, USA) according to standard method 5220 D (Closed Reflux, Colorimetric Method) [24]. Total suspended solids (TDS) were measured according to standard methods 2540 D [24]. pH measurements were performed using a pH meter (Metrohm 691, Switzerland).

Table 1
The analysis of wastewater effluent*.

Parameter	Unit	Quantity
pH	–	6.65
TDS	mg L^{-1}	693
EC	mg L^{-1}	989
COD	mg L^{-1}	29

*Taken from the effluent of secondary sedimentation tank of Ekbatan wastewater treatment plant (Tehran, Iran).