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A novel approach to adsorption kinetics calculation

Miroslav Kukučka [a,*], Nikoleta Kukučka [a], Andrej Kukučka [b]

[a] EnviroTech d.o.o., Sterije Popovića 42, Kikinda, Serbia
[b] Faculty of Sciences, Department for Chemistry, Biochemistry and Environmental Protection, University of Novi Sad, Trg Dositeja Obradovića, Novi Sad, Serbia

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ABSTRACT

A new model for synthetic zeolite adsorption kinetics calculation was developed. Investigations were carried out using dynamic fixed-bed pilot plant on natural groundwater with ammonia concentration of 2.24 mgNH_4^+-N/L. The new approach for computing the pseudo-equilibrium adsorption capacity of zeolite toward ammonia was applied and specific adsorption rate was theoretically defined and empirically putted to use. Three-stage adsorption kinetic process was cognized on the base of experimental data. The first stage characterized slow decrease and then slow rise of effluent ammonia concentrations until 20 h of experimental time and 200 BV. Subsequently, fast ammonia increase across the breakthrough point comprised the second stage. After 530 BV and 50 h of overall experimental time slow rise of effluent concentrations toward the inlet ammonia concentration value was observed until 96.5 h and 1017 BV and characterized as the third stage. Applied pseudo-first and pseudo-second kinetic modeling showed that all experiments data can be explained by the pseudo-first kinetic model with $Q_e = 112.31$ mgNH_4^+-N/g and $k_1 = 0.068\ h^{-1}$ while the third stage better fits to the pseudo-second model where obtained values for Q_e and k_2 were 125 mgNH_4^+-N/g and $7.5 \cdot 10^{-4}$ g mgNH_4^+-$N^{-1}\ h^{-1}$, respectively. It was found that investigated adsorption process was non-equilibrium in all stages with the exception of the final part of the third stage. Pseudo-equilibrium occurred at the end of the third stage with adsorption capacity of 109.60 mgNH_4^+-N/g.

1. Introduction

Adsorption is a rapid process with a low cost of construction, maintenance and operation, and it is considered the best and most universal technique as it is used for the removal of a wide variety of organic and inorganic pollutants [1].

Zeolites are natural or synthetic crystalline hydrated aluminosilicates porous minerals. Alkali or alkaline-earth cations reversible fixed in the cavities inside the zeolite framework structure can easily be exchanged by surrounding positive ions [2]. The most often application of zeolites is removal of ammonia from natural [3] and wastewaters [4–6]. It is known that synthetic zeolites show superiority in adsorption and ion-exchange capacity when compared to the natural zeolite form [7]. Gruett found that natural zeolites can handle only one-fourth of the capacity of synthetic zeolites [8]. Other investigators have found that synthetic zeolite NaY synthesized by ash from rice husks had three times higher adsorption capacity toward ammonia than mordenite [9].

Different natural zeolites show diverse adsorption properties and ion-exchange capacities toward ammonia [10]. During the investigations of ammonium removal efficiency it was found that natural zeolite shows good performance of more than 97%, depending of contact time, ammonia concentrations and pH [11]. Transformations of two types of natural zeolites to sodium form enhanced ion-exchange capacities to more than 30 mgNH_4^+-N/g [3]. Zeolite tuffs were suitable for removal of ammonia and other contaminants specific for landfill leachates as a barriers proposed for protection of groundwater environment in vicinity of old landfills [12]. Also, Hedström and Amofah successfully applied zeolite for ammonia removal from primary treated municipal wastewater [13]. Investigations of ammonia adsorption at synthetic zeolite based on natural mineral resulted with maximal adsorption capacity of 44.3 mgNH_4^+-N/g [14]. Experimental results of Zhang and the group of authors showed that synthetic zeolites are promising materials for ammonia removal from wastewater [15].

* Corresponding author.
E-mail addresses: miroslav@envirotech.rs (M. Kukučka), nikol@envirotech.rs (N. Kukučka), kukucka.rio@gmail.com (A. Kukučka).

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The previous studies on zeolite ion-exchange were batch adsorber experiments [16–21] but many investigations were also conducted in the continuous flow system by zeolite fixed-bed [22–26]. Column adsorption processes on different adsorbents such as activated carbon [27], bagasse fly ash [28,29], waste adsorbents [30–32], cellulose/chitin beads [33] and alumina-coated carbon nanotubes [34] were wide investigated. In most water flowing systems, it is required to perform equilibrium studies using columns. Manganese dioxide-coated multiwall carbon nanotube was utilized as a fixed bed for removal of Pb(II) from water [35], as well as, successful media for removal of arsenic from wastewater [36]. In experiments where fixed-bed was used, column studies were based on calculation of maximum zeolite capacity for a settled feed concentration and flow rate [37,38]. Previous articles included kinetic studies according to pseudo-first and pseudo-second models and determination of equilibrium adsorption capacities under various adsorption isotherm models [38–41] as a main topic, with the aim to define complex mechanism of ion-exchange and adsorption processes coming up at active zeolite sites. Maximum adsorption capacities were achieved according to different adsorption isotherms [28,42–46]. The loading behavior of different sorbates that need to be removed from solution in a fixed-bed column was usually expressed in terms of effluent and influent sorbate ions concentrations as a function of time or adsorbent's bed volume. The fixed-bed adsorption process was found to be more advantageous over batch technique as in fixed-bed operations adsorbent continuously remains in contact with fresh sorbate solution. Accordingly, the concentration of sorbate solution remains constant throughout lasting time of the experiment [47]. Thereby, the breakthrough curves were examined [34,48,49]. Ji and associates supposed that the maximum column capacity was equal to the area under the plot of the adsorbed sorbate concentration vs. time [37], whence the equilibrium adsorption capacity using the value of adsorbent mass was computed. During the investigation of ammonia adsorption kinetic, results obtained from different zeolites were presented as a one stage process in all cited studies. Runping et al. found the different way of breakthrough description for all experimental data and initial region [38]. Gupta and associates studied heterogeneous photo-catalytic degradation process and the effects of catalyst dose, initial dye concentration, pH, electron aceptor, ilumination intensity and temperature [50]. Also, the effects of adsorbents amount, particle sizes, concentration and contact time during adsorption process of “Congo red” from wastewater on bottom ash and deoiled soya were investigated to determine kinetic adsorption data [31].

The task of this study was to examine the behavior of synthetic zeolite in a fixed-bed system using continuous flow of natural well water rich with ammonia. The primary aim was to associate measured ammonia concentrations and water flow rate in experiment's time to obtain specific adsorption rate data as a feature of the flow and continual adsorption process.

Also the goal of this work was to calculate adsorbent mass in mass transfer zone and zeolite adsorption capacity at every sampling point in time, as well as equilibrium adsorption capacity using novel mathematical expressions.

2. Experimental

2.1. Water source

The groundwater used in this study originated from the waterworks of the City of Kikinda (Latitude: 45.8283, Longitude 20.4653) in the Vojvodina Province, Northern Serbia. The groundwater from the City of Kikinda waterworks, which is in use as drinking water, is a sodium bicarbonate type with pH of 8.3 and an intense yellow color due to the presence of dissolved natural organic matter. Ammonia content in this water always exceed 2 mgNH_4^+-N/L. Average value of 2.24 mgNH_4^+-N/L of ammonia (C_0) in investigated water is considerably greater than standard maximum allowed concentration (MAC) of ammonium ion 0.5 mg/L i.e. 0.39 mgNH_4^+-N/L according to Europe Council recommendations [51]. Investigated groundwater and effluents ammonia concentrations were determined by standard analytical Nessler method using spectrophotometer Hanna C-100. The instrument directly displays concentrations in mg/L of ammonia nitrogen and thus all the experimentally measured values of inlet water and effluents (C) are presented in mgNH_4^+-N/L. All presented results of groundwater and effluents are the mean values of three repetitions.

2.2. Dynamic fixed-bed pilot plant

Adsorption kinetics parameters of ammonia in dynamic flow conditions were investigated using synthetic zeolite Crystal Right, type CR-100 (CR) [52] zeolite fixed-bed.

Dynamic fixed-bed column experiments were performed in a professional scale composite column (Structural composite pressure vessel Q-0844). Volume of the vessel with top opening was 38 L. Column also contained a central tube with down distributor of 200 μm fineness as well as a manually controlled three position valve (model 2750, made by company Fleck), with up distributor of 200 μm fineness. During the investigations control valve enabled three operations: service flow rate, backwash and fast rinsing. Regeneration of exhausted zeolite was not the scope of this article and therefore will not be commented.

Experimental column was filled with 23.8 kg of CR originated from producer's package. Moisture content of CR, as average value of measurements at 130 °C i 180 °C was 42.14%. Thus, mass of dry CR used in experiments was 13,771 g (M). CR particle size ranged from 0.3 to 2.4 mm. The volume of the CR (V_{CR}) was constant in all experiments and amounted 28 L.

The continuous flow rate meter and total effluent quantity meter were installed at the effluent outlet pipeline. Schematic presentation of the experimental apparatus is shown in Fig. 1.

Waterworks water was fed into the pilot downstream, previously passing through suspended solids particle protective 5 μm polypropylene filter cartridge. The effluent samples were collected randomly, and analyzed for ammonia concentration. Time, water flow and total passed effluent volume were recorded during the samplings. All dynamic sorption experiments were carried out at 20 ± 1 °C. Service flow rate of the column was stopped when effluent ammonia concentrations were approximately equal to influent ammonia concentration. Experimental operating data of the pilot plant are shown in Table 1.

3. Adsorption kinetics

Effects of ammonia adsorption presented via measured effluent ammonia concentrations during the experiments were shown in the dependence of cumulative time ($\Sigma\tau$) expressed in hours i.e. number of effluent's bed volumes (BV). Shapes of these curves present primary overview of adsorption process kinetics following start, breakpoint and pseudo-equilibrium stages.

The overall volume of water that passed through the CR bed was expressed as bed volume (BV). This parameter is a dimensionless quantity which expresses the water volume as a multiple of the volume of the resin bed, as calculated using expression [53]: