ZEOLITE A IN A FLUIDIZED BED REACTOR: HYDRODYNAMIC AND Cu(II) SORPTION STUDIES

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ABSTRACT

In this work, we have investigated possibilities for applications of zeolite A beads (diameter of ~2.5 mm) in a fluidized bed reactor (FBR) aimed for removal of heavy metal ions from aqueous solutions. Hydrodynamic properties of the reactor were investigated first, followed by sorption studies of Cu(II), chosen as a model heavy metal ion. Operating conditions of the experimental FBR were determined to be in the range of superficial liquid velocities between the minimum fluidization velocity amounting to 2.1 cm s^{-1} and the terminal velocity estimated as 15.5 cm s^{-1}. The FBR was used then for removal of Cu(II) from the aqueous solution (300 mg dm^{-3} Cu(II) concentration) operating at the superficial velocity of 3.0 cm s^{-1}, at which the bed height and porosity were 4.3 cm and 0.71, respectively. At these conditions, intra-particle diffusion was shown to be the rate limiting step for Cu(II) sorption in zeolite A beads with the diffusivity determined as $(1.50 \pm 0.15) \times 10^{-8}$ cm^2 s^{-1}. Results of these studies imply that granulated zeolite A in conjunction FBR systems could be potentially utilized in wastewater treatment processes.

Keywords: fluidized bed reactor, zeolite A, heavy metal sorption, intra-particle diffusion.

INTRODUCTION

Zeolite A finds widespread applications as an ion exchanger, adsorbent and catalyst. It has been well reported that zeolite A has a great capacity and selectivity with respect to removal of different heavy metal ions present in industrial wastewaters [1-4]. Moreover, in wastewater treatment processes, one of attractive reactor systems is based on fluidization of particulates due to simple control and automation of this reactor type, efficient mixing, low shears, high heat and mass transfer coefficients and simple scale-up. Accordingly, zeolite A granules could be a suitable material for the use in fluidized bed reactors as intermediate density particles with relatively good mechanical stability.

The aim of this work was to experimentally investigate hydrodynamic properties of a fluidized bed reactor (FBR) with zeolite A beads and possibilities for application of this system for heavy metal removal from aqueous solutions using Cu(II) as a model heavy metal ion.

EXPERIMENTAL

In this work, zeolite A (Silkem doo, Slovenia) was utilized in the form of beads (2.4±0.4 mm in diameter, density of 1555±14 kg m^{-3}). The salt $CuSO_4 \cdot 5H_2O$ (Zorka Šabac, Serbia) was used to prepare Cu(II) solutions in deionized water. The fluidized bed reactor was a polycarbonate column (2.4 cm inner diameter, 16.7 cm height) with a layer of glass pellets at the bottom, serving as a liquid distributor. The column was equipped with two piezometers for measurements of the pressure drop. The reactor was connected to a recirculation loop consisting of a glass reservoir, a peristaltic pump (Cole-Parmer Instruments, USA), and an electromagnetic flowmeter (Yamatake-Honeywell, Tokyo, Japan) for measurements of the liquid flow rate (Fig. 1).

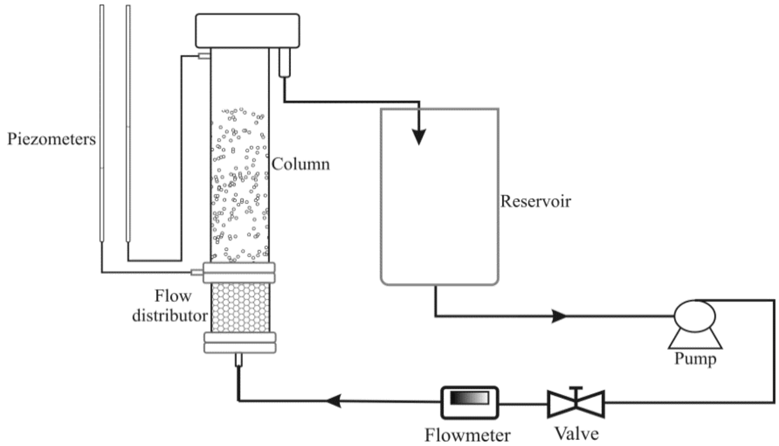

Figure 1.Experimental set up: a column with a fluidized bed of zeolite A beads is connected to a recirculation loop consisting of a reservoir, peristaltic pump, a valve and a flowmeter; pressure drop is determined by two piezometers

In hydrodynamic studies, the column was filled with 17 g of beads comprising the static bed height of 6.5 cm. Water was recirculated at flow rates in the range 1.0 to 28.0 $cm^3\ s^{-1}$ and the fluidized bed height and pressure differences were measured at increasing as well as at decreasing flow rates.

In Cu(II) sorption studies, the column was filled with 10.5 g of beads comprising the static bed height of 3.7 cm. The system was filled with 2 dm^{-3} of Cu (II) solution with the initial concentration of 300 mg dm^{-3}. Recirculation of the solution was performed at the flow rate of 13.5 $cm^3 s^{-1}$ at which the fluidized bed height was 4.3 cm. Liquid samples were collected at the column outlet, at certain time intervals. Cu(II) concentrations were determined with four-digit accuracy by AAS using Varian Spectra AA 55B; at least five measurements were done for the each determination. The experiments lasted for 24 h and were carried out in duplicates.

RESULTS AND DISCUSSION

Hydrodynamic studies of the experimental FBR with zeolite A were performed with the aim to determine the minimum fluidization velocity (U_{mf}) and the terminal velocity (U_t), which set the limits for the reactor operating conditions. Figure 2 shows the bed pressure loss and the pressure drop as functions of the superficial velocity, *U*, calculated from experimental data obtained at decreasing the water flow rate.

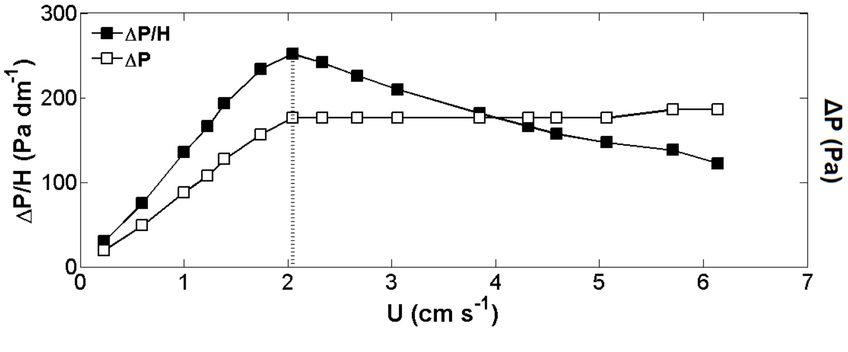

Figure 2. Bed pressure loss and pressure drop in the fluidized bed of zeolite A beads as functions of the superficial velocity at decreasing the water flow rate; dashed line presents the minimum fluidization velocity determined at the point of maximal value of the pressure drop

The minimum fluidization velocity was determined as 2.1 cm s^{-1} corresponding to the maximal value of the pressure drop. At these experimental conditions, the bed porosity was determined as 0.66.

Terminal velocity can be assessed by application of the Richardson–Zaki equation, which describes expansion of the fluidized bed as [5]:

$$U = U_t \varepsilon^n \tag{1}$$

where n is the expansion index. Therefore, a logarithmic plot of the bed porosity as a function of the superficial velocity should be constructed. Porosities for different bed heights were calculated by the equation:

$$\varepsilon = 1 - \frac{M}{\rho_p A_c H} \tag{2}$$

where M is the mass of the beads in the reactor, ρ_p is the bead density , A_c is the column cross-sectional area, and H is the bed height. The plot log(ε) *vs*. log(U) for the experimental FBR was linear (Fig. 3), so that U_t is determined as 15.5 cm s^{-1} as the extrapolated value of U at ε=1.

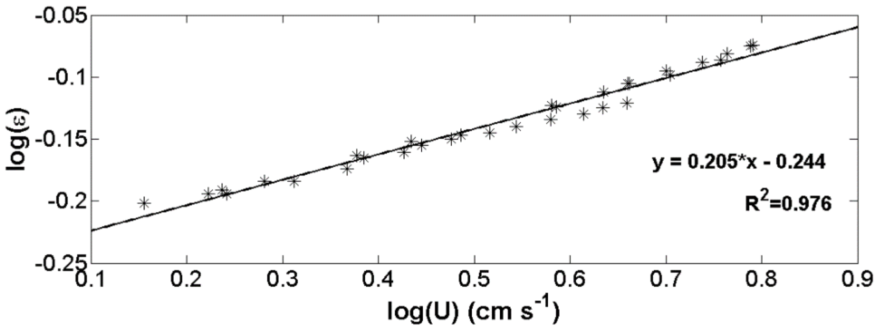

Figure 3. Porosity of the fluidized bed with zeolite A beads as a function of the superficial velocity: experimental data (symbols) and the best linear fit (line)

Operating conditions for the experimental FBR with zeolite A beads are thus in the range of superficial velocities between 2.1-15.5 cm s^{-1}. The velocity suitable for sorption studies was chosen as 3.0 cm s^{-1} corresponding to the flow rate of 13.5 cm^3 s^{-1}. At these conditions, the fluidized bed height and porosity were 4.3 cm and 0.71, respectively.

The experimental FBR was shown to successfully remove Cu(II) from the aqueous solution reaching the equilibrium concentration of sorbed ions on zeolite A beads over approximately 24 h (Fig. 4a). The sorption kinetics was modeled by intra-particle diffusion so that the amount of sorbed ions per mass of zeolite, q_t, is a function of time, t, as [6]:

$$q_t = k_d t^{0.5} \tag{3}$$

where k_d is the intra-particle diffusion rate constant related to the intra-particle diffusivity, D. For a spherical particle, this relation is expressed as [6]:

$$k_d = \frac{6q_e}{R}\sqrt{\frac{D}{\pi}} \tag{4}$$

where R is the particle radius and q_e is the equilibrium amount of sorbed Cu(II) per mass of zeolite.

According to the model, a plot of q_t *vs.* $t^{0.5}$ should produce a straight line passing through the origin with the slope being the intra-particle diffusion rate constant. Experimental data clearly showed a linear trend (Fig. 4b) and the model predictions of sorbed Cu(II) concentrations as a function of time were in close agreement with the experimental data (Fig. 4a). Thus, intra-particle diffusion was the rate limiting step in Cu(II) sorption on zeolite A beads used in this study. The intra-particle diffusivity was determined from Eq. (4) as $(1.50 \cdot \pm 0.15) x 10^{-8}$ cm^2 s^{-1}, which is in agreement with 1.83 x 10^{-8} cm^2 s^{-1} reported for Zn(II) as well as 3.35 x 10^{-8} cm^2 s^{-1} reported for Cd(II) in zeolite A [3].

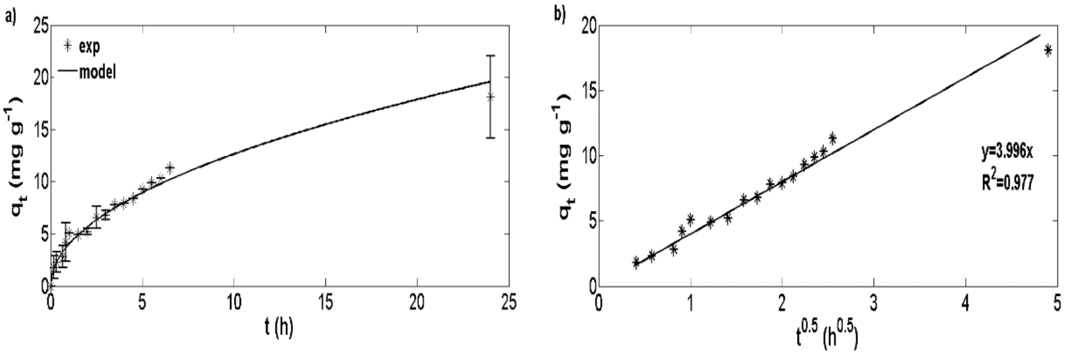

Figure 4.Sorption of Cu(II) in the FBR with zeolite A beads: experimental data (symbols) and intra-particle diffusion model predictions (lines); a) concentrations of sorbed Cu(II) as a function of time; b) determination of the intra-particle rate constant by the best linear fit

CONCLUSION

In this study, a fluidized bed reactor with zeolite A beads was characterized regarding the operating conditions and potentials for Cu(II) removal from aqueous solutions. The use of relatively large beads (~2.5 mm in diameter) ensured rather stable and ordered particulate fluidization while induced, on the other hand, intra-particle diffusion limitations for Cu(II) sorption. Results of these studies imply that the size of zeolite A beads could be optimized in application as fluidized bed reactors for industrial wastewater treatment.

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