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Adsorption of zinc and toluene by alginate complex impregnated with zeolite and activated carbon

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ABSTRACT

In this study, a novel alginate complex was developed for removal of mixed contaminants containing both organic and inorganic compounds. The alginate complex was generated by impregnating synthetic zeolite and powdered activated carbon (PAC) into alginate gel bead. The adsorption of zinc and toluene as target contaminants onto the alginate complex was investigated by performing both equilibrium and kinetic batch tests. Equilibrium tests showed that adsorption of two contaminants followed Langmuir isotherm and that the alginate complex was capable of removing zinc (maximum binding energy $\beta = 4.3$ g/kg) and toluene ($\beta = 13.0$ g/kg) best compared to other adsorbents such as granular activated carbon (GAC), zeolite, and alginate impregnated with PAC (AG–AC bead). These values were higher than those of any other adsorbents for each contaminant. It was further revealed from kinetic tests that removal efficiency of zinc and toluene was 54% and 86% for the initial solution concentrations of 250 mg/L, respectively. This indicates that the alginate complex developed in this study can be used as promising adsorbents for simultaneous removal of organic and inorganic compounds from industrial wastewater or groundwater containing mixed contaminants.

1. Introduction

Industrial wastewater often contains both organic and inorganic compounds such as aromatic hydrocarbons and heavy metals since the latter comes from industrial use of organic compounds containing metal additives in the petroleum and organic chemical industries. Heavy metal ions should be removed from wastewater before disposal since they are highly toxic even at low concentrations and therefore sources of great concern in aquatic environment. Aromatic compounds such as toluene are used as raw materials in many chemical productions and solvents in manufacturing processes. These compounds are carcinogenic and their presence in water stream even at low concentrations poses significant environmental risks. So far a considerable effort has been made for removal of these compounds. For instance, removal of heavy metals was attempted using various adsorbents such as chitosan [1,2], zeolite [3–5], and clay [6] among which zeolite was found the cost efficient adsorbent [7]. For removal of aromatic compounds, many attempts were made via adsorption process using various adsorbents. To date the most widely used adsorbent is activated carbon for removal of organic compounds such as phenol, benzene and toluene. Adsorption of phenol [8], benzene and toluene [9,10] on activated carbon was studied to investigate the structure of activated carbon. However, for simultaneous removal of both organic and inorganic compounds from industrial wastewater, complex adsorbents other than these materials are needed. Therefore in this study we attempted to develop a new adsorbent, alginate gel bead impregnated with zeolite and activated carbon for removal of mixed industrial contaminants. In order to examine the adsorption capacity of the alginate complex, both equilibrium and kinetic batch studies were performed.

2. Materials and methods

2.1. Preparation of alginate complex beads

All chemicals of sodium alginate, granular activated carbon (GAC), powdered activated carbon (PAC) and calcium chloride were obtained from Sigma Aldrich, Korea except for synthetic zeolite which was purchased from Jishim tech. Korea. The type of synthetic zeolite was zeolite A that exhibits the LTA (Linde Type A) structure. It has a three-dimensional pore structure with pores running perpendicular to each other in the *x*, *y*, and *z* planes, and is made of secondary building units 4, 6, 8, and 4–4. The pore diameter is 4.2 Å and defined by an eight member oxygen ring. This leads into a larger cavity of minimum free diameter 11.4 Å. The cavity is surrounded by eight sodalite cages (truncated octahedra)

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connected by their square faces in a cubic structure. The unit cell is cubic (a = 24.61 Å) with $Fm\bar{3}c$ symmetry. Zeolite A has a void volume fraction of 0.47, with a Si/Al ratio of 1.0. It thermally decomposes at 700 °C.

Formation of alginate complex is as follows. First, 5.0% sodium alginate solution was prepared by mixing 20 g of sodium alginate powder with 400-mL distilled water. After adding 4 g of each PAC and zeolite into 400-mL alginate solution, homogeneous mixing was performed for 20 h to yield 1% (w/v) alginate solution mixed with activated carbon and zeolite. The 1% alginate solution contained in a burette was then allowed to drop into a solution of 4% $CaCl_2$ (500 mL) solution and thus forming 200 g of 4-mm spherical alginate complex beads. In order to compare with other type of alginate bead, alginate bead impregnated with powdered activated carbon only (AG–AC bead) was also formed using the same procedure except for addition of 4 g of zeolite to alginate solution.

2.2. Equilibrium adsorption test

In order to determine the adsorption capacity of the alginate complex, and compare with those of other existing adsorbents such as granular activated carbon, zeolite and AG–AC bead, equilibrium batch tests were conducted. Twenty gram of complex beads and other adsorbents was allowed to react with each 80 mL of $Zn(SO_4)_2$ solutions (pH 6.7–6.8) with various initial zinc concentrations (50, 100, 300, 500, 700, 1000 mg/L) in 125 mL wide neck bottle using air shaker (140 rpm, 32 °C). For toluene adsorption, 280 ml solutions of five different initial concentrations (50, 100, 200, 500, 700 mg/L) were used to react with 8 g of adsorbents. At equilibrium (48 h), zinc and toluene solutions were analyzed by ICP-OES (Optima 2000 DV, Massachusetts) and HPLC (Young Lin, Seoul, Korea), respectively.

2.3. Kinetic adsorption test

Kinetic batch tests were also performed to evaluate the adsorption capacity of alginate complex for each type of contaminants. Tests were initiated by placing 42 g of complex beads in 840 ml mixed solution (250 mg/L of aqueous zinc and toluene, respectively) in 1 L glass flask and allowed to react in an air shaker. After reaction, aqueous samples were analyzed at pre-determined times.

2.4. Modeling of kinetic adsorption

In order to compare the adsorption capacity for different adsorbents (Alginate complex, zeolite, GAC, AG–AC bead), both equilibrium and kinetic adsorption models were used by introducing the Langmuir adsorption isotherm model (Eq. (1)) and three-stage kinetic model (Eq. (2)) [11] developed for adsorption of aqueous benzene as follows:

$$S = \frac{\alpha\beta C}{1+\alpha C} \tag{1}$$

where S and C are the adsorbed and aqueous concentrations, and α and β are the constants related with binding energy (L/mg) and the maximum adsorption capacity (mg/kg).

$$\frac{C(t)}{C_0} = \frac{(1-\xi_1)(1-\xi_1-\beta\xi_2)}{(1-\xi_1-\beta\xi_2\exp[-\gamma t])} \tag{2}$$

$$\xi_1 = \frac{MS_1(\infty)}{VC_0}; \quad \xi_2 = \frac{MS_2(\infty)}{VC_0}; \quad \gamma = \frac{(1-\xi_1-\beta\xi_2)\alpha}{\beta\xi_2} \tag{3}$$

where $C(t)$ and C_0 is the aqueous concentrations at time t and initial stage, V is the solution volume, M is the mass of adsorbent, $S_1(\infty)$ and $S_2(\infty)$ are the adsorbed concentrations for the Type-1 (instantaneous) and the Type-2 (kinetic), α is mass transfer rate from solution to Type-2 site, and β is defined as a limiting factor for $S_2(\infty)$ with its range $0 < \beta \leqslant 1$. The relative concentration curve (C/C_0) of the aqueous phase versus time is characterized by four parameters, ξ_1, ξ_2, γ, and β, where ξ_1 and ξ_2 are the relative fraction of mass adsorbed at Type-1 and Type-2 sites, respectively.

3. Results and discussion

3.1. Equilibrium adsorption

The adsorption isotherms of various adsorbents for zinc obtained from the equilibrium batch tests are shown in Fig. 1. All of the isotherms resulted in a nonlinear curve with an asymptotic increase and therefore was fitted with the Langmuir adsorption model. Among the curves, GAC showed the lowest adsorption capacity while AG–AC bead exhibited a higher adsorption than GAC. This would be due to the contribution of alginate for adsorption of heavy metals since as a polysaccharide biopolymer it is well known to have a significantly high affinity to divalent metal ions [12]. The adsorption isotherm of zeolite showed a sharp increase of adsorbed concentration in the lower range of equilibrium concentration but it reached maximum capacity about 200 mg/L, whereas that of alginate complex extended the maximum capacity to a much higher value. This indicates that the binding energy (α) of zeolite for zinc seems to be very high compared to others since the steepness of the curve represents the extent of the binding energy (Table 1). In general, the highest adsorption capacity of alginate complex among the adsorbents is due to the contribution from the relatively high binding energy of zeolite in the low concentration range and the relatively high adsorption capacity of alginate in the high concentration range. The maximum adsorption capacity (β) of alginate complex was found to be 4.3 g/kg which is higher than those of any other adsorbents used in this study. This value is also higher than the values of 0.50 g/kg [13] and 2.70 g/kg [14] for adsorption capacity of natural zeolite clinoptilolite but slightly lower than that of 5.50 g/kg [14] for adsorption capacity of natural zeolite chabazite reported in the literature.

The adsorption isotherm for toluene is shown in Fig. 2. Contrary to the case of zinc, zeolite showed the least adsorption capacity for toluene although its capacity was higher than that of GAC for zinc. GAC and AG–AC bead showed a similar capacity for toluene. This would be due to the role of activated carbon in adsorption of toluene. It is remarkable that the alginate complex showed the highest

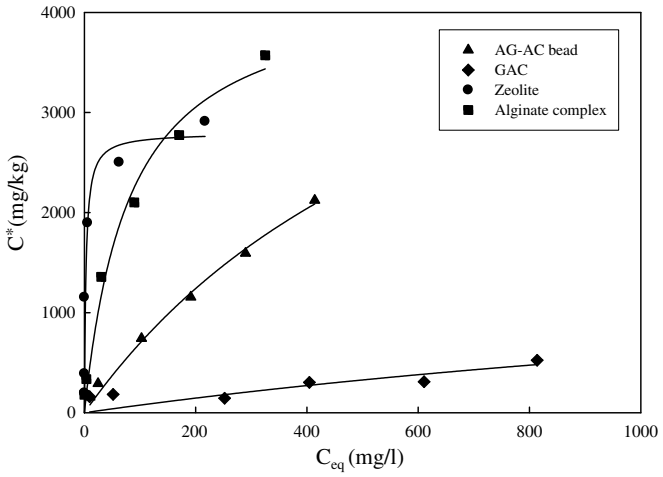

Fig. 1. Adsorption of zinc fitted with Langmuir isotherm on AG–AC beads, GAC, zeolite, alginate complex.