Journal of Water Process Engineering 25 (2018) 54–57

Contents lists available at ScienceDirect

Journal of Water Process Engineering

journal homepage: www.elsevier.com/locate/jwpe

Analysis of F^- removal from aqueous solutions using MgO

Tomohito Kameda*, Yusuke Yamamoto, Shogo Kumagai, Toshiaki Yoshioka

Graduate School of Environmental Studies, Tohoku University, 6-6-07 Aoba, Aramaki, Aoba-ku, Sendai, Japan

ARTICLE INFO

Keywords:
MgO
F^-Water treatment
Kinetics
Equilibrium

ABSTRACT

MgO was found to take up F^- from NaF aqueous solutions due to the electrostatic attractive force between the positively charged MgO and F^-. The F^- adsorption by MgO can be represented by pseudo first-order reaction kinetics, and the magnitude of the apparent activation energy (71.6 kJ mol^{-1}) confirms that this is a chemisorption process. The thermodynamic behavior of this process follows Langmuir-type adsorption, with the maximum adsorption amount of 5.6 mmol g^{-1}. The F^- can be desorbed from MgO using NaOH solution. The regenerated MgO can still take up F^- from the solution despite the lowered adsorption capacity. Therefore, it is possible to recycle the MgO for F^- adsorption.

1. Introduction

F^--containing wastewater originates from the electronics industry, the glass industry, and from etching processes in general. The effluent standard in Japan for F^- is 8 mg L^{-1}. The primary treatment involves capturing the F^- ions in the form of slightly soluble CaF_2, by adding calcium salts such as $Ca(OH)_2$ and $CaCl_2$ to the wastewater. In a second step, aluminum salts, such as polyaluminum chloride, are added to the wastewater, producing gelatinous aluminum hydroxide to capture the remaining F^- ions. However, this two-step process is very cumbersome, and a single-step treatment for F^--containing wastewater is therefore in keen demand.

We have examined several new treatment methods for F^--containing wastewater using adsorbents. For example, we studied the possibility of recycling Mg − Al layered double hydroxide (Mg − Al LDH) and its calcination product (Mg − Al oxide) for F^- treatment [1,2], and tested them in removing F^- in real wastewater [3]. Furthermore, we found that MgO could remove F^- in aqueous solutions [4]. In several subsequent studies, Li et al. examined F^- removal by porous hollow MgO microspheres [5], and Jin et al. investigated the effective removal of F^- by porous MgO nanoplates and the adsorption mechanism [6]. Recently, Lee et al. examined the synthesis of pillar- and microsphere-like MgO particles, and their F^- adsorption performance in aqueous solutions [7]. However, the desorption and recycling of these materials after they are used for F^- removal have not been considered.

In this study, we tested the reusability of MgO for removing aqueous F^-, as shown in Fig. 1. The MgO adsorbed with F^- is then treated with an aqueous solution of NaOH. After the desorption of F^-, the MgO is regenerated and reused. We systematically examined the kinetic and thermodynamic aspects of F^- removal by MgO. The effects of the amount of MgO and the temperature were investigated. Finally, the effect of ionic strength on the adsorption of F^- by MgO was examined, which helps to reveal the adsorption mechanism.

2. Experimental

All reagents were of chemical reagent grade and used without further purification. MgO is purchased from KANTO CHEMICAL CO., INC.. The average particle size is 28.5 μm, and the specific surface area is 4.8 m^2/g.

2.1. Removal of F^- from aqueous solution

NaF solutions were prepared by dissolving NaF in deionized water. For the kinetic measurements, MgO was added to 100 mg L^{-1} NaF solution (500 mL) without initial pH control, and the resultant suspension was stirred at 10, 30, and 60 °C for 100 h. Samples were withdrawn from the suspension at different time intervals and immediately filtered, and then the filtrates were analyzed for residual F^-. To study the thermodynamics of the adsorption process, MgO was added to NaF solutions with the molar ratio of Mg/F = 1, 5, 10, and 20. To determine the adsorption isotherm, 20 mL of a NaF solution (0.005–0.1 mol L^{-1}) and 0.2 g of MgO were placed in a 50-mL screw-top tube and shaken at 30 °C for 1 week.

* Corresponding author.
E-mail address: kameda@env.che.tohoku.ac.jp (T. Kameda).

https://doi.org/10.1016/j.jwpe.2018.06.009
Received 26 March 2018; Received in revised form 15 June 2018; Accepted 26 June 2018

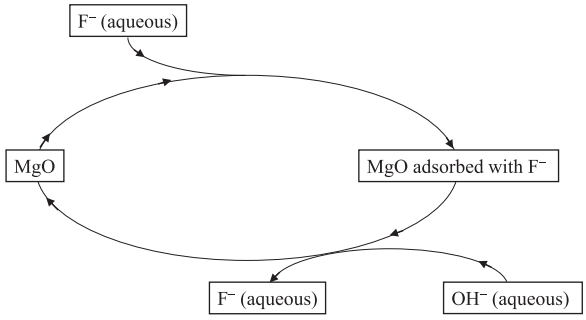

Fig. 1. Scheme of the proposed method to remove aqueous F^- by MgO. .

2.2. Desorption of F^- from MgO

The desorption of F^- from MgO was carried out using NaOH solution. After a MgO suspension in NaF (Mg/F = 10) was kept at 30 °C for 48 h, the MgO was found to contain 0.8 wt% of F^-. This MgO adsorbed with F^- (0.1 g) and 20 mL of NaOH solution (1.0 M) were placed in a 50-mL screw-top tube and shaken at 30 °C for 24 h.

2.3. Removal of F^- from aqueous solution by regenerated MgO

MgO regenerated from the MgO adsorbed with F^- in 1.0 M NaOH solution at 30 °C for 12 h was suspended in 100 mg L^{-1} NaF solution at Mg/F = 10 and 30 °C. For comparison, $Mg(OH)_2$ was suspended in 100 mg L^{-1} NaF solution at the same Mg/F molar ratio and temperature.

2.4. Effects of ionic strength on adsorption

The effect of ionic strength on the adsorption of F^- by MgO was examined in 100 mg L^{-1} NaF solutions prepared using 0, 0.001, or 0.01 M NaCl solution with initial pH of 2 − 12. MgO was suspended in this solution at Mg/F = 5 and 30 °C.

2.5. Analytical methods

MgO before and after F^- adsorption was analyzed using X-ray diffraction (XRD) measurements with Cu Kα radiation. For the adsorption experiments, the residual F^- and Mg^{2+} dissolved from MgO in the filtrates were separated using a Dionex DX-120 ion chromatograph and a Dionex model AS-12 A column (eluent: 2.7 mM Na_2CO_3 and 0.3 mM $NaHCO_3$; flow rate: 1.3 mL min^{-1}). Their concentrations were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The pH after the adsorption was also measured.

3. Results and discussion

3.1. Removal of F^- from aqueous solution

Fig. 2 shows change in the F^- concentration over time in various MgO suspensions in NaF at 30 °C. For all Mg/F molar ratios, the concentration of F^- decreased with time, and the concentration after a given time decreased with increasing Mg/F ratio. When Mg/F = 20, the concentration of F^- after 24-h treatment was less than the effluent standard in Japan (8 mg L^{-1}). Therefore, MgO was confirmed to effectively take up F^- from NaF solutions. Fig. S1 shows the change in the pH over time in the various suspension at 30 °C. For all Mg/F molar ratios, the pH value first increased rapidly and then remained constant at around 11. This is attributed to the buffer action of Mg^{2+}. Fig. S2 shows that at all Mg/F ratios and 30 °C, the Mg^{2+} concentration in the solution increased rapidly at first and then decreased with time. The maximum amount of Mg^{2+} dissolved was around 3% for Mg/F = 10, and this low value indicates that the dissolution of Mg^{2+} from MgO had little effect on the uptake of F^- from the solution. Fig. S3 shows the

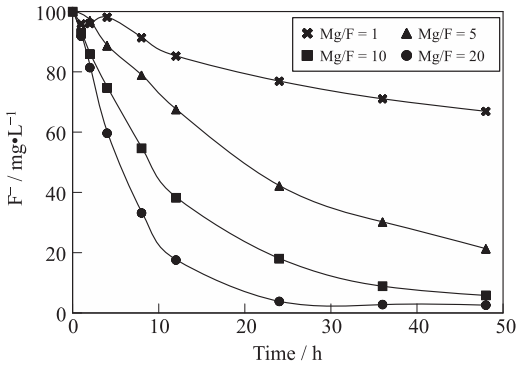

Fig. 2. Change in the F^- concentration over time in the MgO suspension in NaF solution at various Mg/F molar ratios at 30 °C.

XRD patterns for the solids from MgO suspension in NaF at Mg/F = 10 at 30 at 30 °C for 0–48 h. After 12 h, the XRD peak ascribed to $Mg(OH)_2$ was hardly observed; but its intensity increased with time, suggesting hydration on the surface of MgO particles, which caused the dissolution of Mg^{2+}. The XRD patterns (Fig. S3) did not show the peak ascribed to the products composed of Mg and F^-. The zero point of charge (ZPC) of MgO is known to be 12.4 [8]. Since the pH values in Fig. S1 are all lower than this, the surface of MgO particles should be positively charged. Therefore, the uptake of F^- is attributed to the electrostatic attractive force between the positively charged MgO and F^-, implying chemical adsorption. Fig. 3 shows the change in F^- removal at Mg/F = 10 at various temperatures. For all temperatures, the F^- adsorption increased with time, particularly at 60 °C. At any time, the F^- adsorption also increased with temperature. The kinetics of F^- removal by MgO was examined by first-order kinetics, which depend on the concentration of F^- as

$$-ln(1-x) = kt \quad (1)$$

where x is the degree of F^- adsorption, t (h) is the reaction time, and k (h^{-1}) is the rate constant. In the plots in Fig. 4 (Mg/F = 10), good linearity was obtained at each temperature, indicating that F^- adsorption can be represented by pseudo first-order reaction kinetics. The respective apparent rate constants at 10, 30, and 60 °C were 8.0×10^{-3}, 7.1×10^{-2}, and 7.8×10^{-1} h^{-1}, clearly increasing with increasing temperature. Fig. S4 shows the corresponding Arrhenius plot of the apparent rate constant, yielding an apparent activation energy of 71.6 kJ mol^{-1}. This value confirms that the uptake of F^- by MgO proceeded under chemical reaction control. Fig. 5 shows the adsorption isotherm, in which the equilibrium adsorption amount increased with increasing equilibrium concentration. These isotherms showed Langmuir-type behavior, which was confirmed by fitting to the Langmuir equation expressed as

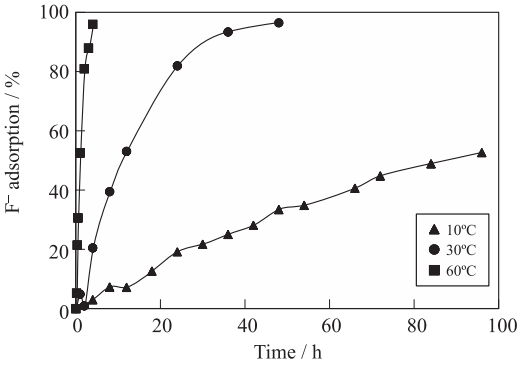

Fig. 3. Change in the F^- removal over time in the MgO suspension in NaF solution at Mg/F = 10 and various temperatures.