Effect of calcium ions on aluminum recovery by fluidized-bed homogeneous granulation process

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Abstract

Fluidized-bed homogeneous granulation process (FBHGP) is an innovative process that can synthesize solid granules in the absence of a seed material. This unique technology is highly efficient, no sludge, low moisture, saves land and capital cost. The granules are formed inside the reactor by altering the reactor designs and conditions as hydraulic parameters were varied. The effects of Ca^{2+} ions on Al (aluminum) recovery and granulation ratio (GR) were further investigated by adjusting 200-400 $mg \cdot L^{-1}$ of influent Al^{3+} concentrations, 5.5-6.5 molar ratios (MR) of $[OH^-]_{in}/[Al^{3+}]_{in}$, and 11.5-12.1 pH of precipitant with 11.8 of pH_e. Results showed that 99.2% of *Al removal* and 98.9% of *GR* were achieved at 1.15 $kg \cdot m^{-2}h^{-1}$ of cross-section loading (L), 200 $mg \cdot L^{-1}$ of influent Al^{3+}concentration, 6.0 MR of $[OH^-]_{in}/[Al^{3+}]_{in}$, and 12.1 pH of precipitant, whereas the 32.47 $m \cdot h^{-1}$ of hydraulic loading (U) was achieved at the same parameters with 99% of *Al removal* and 97.6% of *GR*, Ca^{2+} ions affect the Al granule composition, while it has no effect on the Al removal. To conclude, a useful way of recovering Al^{3+} in the form of tetra calcium dialuminum dodecahydroxide carbonate pentahydrate ($Al_2Ca_4H_{22}O_{20}$) from aqueous solution was successfully done.

Keywords: Fluidized-bed, homogeneous granulation, calcium ions, supersaturation, granules

1. Introduction

The exposure of Al to the surroundings is due to natural activities. There are several factors that affects the Al mobility and means of transport to the environment. These involves the geophysical pathways, soil-water contacts, chemical substitutes, and the structure of the fundamental environmental resources. (ATSDR, 1992; WHO, 1997). Al occurrence can be in the form of precipitates, colloidal polymeric solutions, monomeric and polymeric hydroxyl species, gels, everything based on hydroxylated aluminates or water coordinated positive ions. It can also bind with various organic compounds (fulvic or humic acids) and inorganic ligands (chloride, fluoride, and sulfate), but not all are soluble. Al has minimum solubility in pure water at pH range of 5.5-6.0. The concentration of total dissolved Al increases at alkaline and acidic medium (CCME, 1988; ISO, 1994). The hardness of tap water is due to the ions present in it. USDA National Nutrient Database stated that the tap water is composed of Ca, Cu, Fe, K, Mg, Mn, Na, P, and Zn. According to the USEPA, 150-400 $mg \cdot L^{-1}$ of $CaCO_3$ is the allowable concentration for water hardness (Chen *et al*., 2000). The (Ca^{2+}) content of water coming from drinking water supplies in Asia is about 2-80 $mg \cdot L^{-1}$ (Ong *et al*., 2009). Wastewaters from Al finishing processes contains dissolved Al as major contaminant. Removal methods of heavy metals like Al from wastewaters are biosorption, adsorption, coagulation, flocculation, cementation, chemical precipitation, ion exchange, complexation, and membrane processes (Ahn *et al*., 2009). These methods show inadequate metal recovery, high operating cost, and continuous input of chemicals as weaknesses (Goher, 2015). Chemical precipitation is commonly used method due to low cost of operation and efficiency. But, large amount of sludge with high moisture is being generated which is the major problem (Macchi *et al*., 1993). The fluidized-bed crystallization (FBC) process is a better alternative than chemical precipitation. İt uses a small amount of chemicals and produces a low moisture content crystals (Chen and Yu, 2000). Fluidized-bed reactor (FBR) process is a widely used method for treating wastewaters with heavy metals such as (Zn, Cu, As, Ni) and inorganic acids (phosphoric and boric acid) (Huang *et al*., 2007; Su *et al*., 2013). At the metastable region of the FBR, nucleation can be measured with the aquatic conditions that forms heavy crystals instead of high moisture soft slurry (Bhuiyan, 2008). This work deals with the recovery of Al by FBHGP without using a seed. The best reactor condition in terms of pH of precipitant, influent $[Al^{3+}]_{in}$, concentration and MR of $[OH^-]_{in}/[Al^{3+}]_{in}$ were identified. The effect of calcium ions on the *Al removal (%)* and *GR (%)* were also determined. The concentrations of the residual Al with and without calcium ions was analyzed by ICP-OES. The granule characteristics were analyzed by using SEM and XRD.

2. Materials and methods

Table 1. Nomenclature definition of hydraulic parameters in FBHGP.

Symbol	Definition	Unit	Remarks
Q_{Al}	Influent flow rate of aluminum ion	$mL \cdot min^{-1}$	
Q_{OH}	Influent flow rate of precipitant	$mL \cdot min^{-1}$	
Q_t	Total influent flow rate	$mL \cdot min^{-1}$	$=Q_{Al}+Q_{OH}$
Q_r	Reflux flow rate	$mL \cdot min^{-1}$	
$[Al^{3+}]_{in}$	Inlet concentration of aluminum salt	mM	
$[Al^{3+}]_t$	Total concentration of aluminum in effluent	mM	
$[Al^{3+}]_s$	Soluble aluminum concentration in effluent	mM	
$[OH^-]$	Inlet concentration of sodium hydroxide	mM	
$[OH^-]_{in}/[Al^{3+}]_{in}$	Inlet molar ratio		
A_{low}	Internal cross-section area of reaction region	m^2	
U	Upflow velocity (hydraulic loading)	$m \cdot h^{-1}$	$=(Q_t+Q_r)/A_{low}$
L	Cross-section loading	$kg \cdot m^{-2}h^{-1}$	$=Q_{Al}[Al^{3+}]_{in}/A_{low}$
V_T	Total volume of reaction solution in reactor	mL	
HRT	Hydraulic Retention Time	min	$=V_T/Q_t$
pH_e	Effluent pH		

2.1. Experimental procedure and analytical techniques

The homogeneous granulation was conducted in FBR by controlling the influent flows ($Q_t=Q_{Al}+Q_{OH}$) and the reflux flows (Q_r). An influent $[Al^{3+}]_{in}$ concentration of 200-400 $mg \cdot L^{-1}$ was prepared to achieve the supersaturation at MR of $[OH^-]_{in}/[Al^{3+}]_{in}$ at 5.5-6.5. The initial pH of precipitant is 11.5-12.1. Initially, at supersaturation condition, the nuclei was formed on top of the glass beads and moved upward with the flow that formed cloudy agglomerates. In the reaction region, the collision of grown particles caused to slow down and become fluidized. The tiny Al particles can be seen within 10-14 days. At Q_t=50 $mL \cdot min^{-1}$, the desired hydraulic retention time (HRT) was 11.0 min. After altering the hydraulic parameters and pH measurements, the whole system reached equilibrium at about 9 times the HRT (~1.65 h). Effluent samples (5mL) were taken twice on the top of the reactor. The first sample was filtered with 0.45 μm filter (GHP membrane, Pall) and the other was not. Both samples were acid digested with 0.5 mL concentrated nitric acid to reduce the supersaturation. The soluble $[Al^{3+}]_s$ concentration is the Al concentration in the filtrates and the total $[Al^{3+}]_t$ concentration is the Al concentration in acidic digestion. To evaluate the efficiency of the FBHGP, *Al removal (%)* and *GR (%)* was calculated as expressed in Eq. (1) and (2) *Al removal* (%)

$$= \left(1 - \frac{[Al^{3+}]_s xQ_t}{[Al^{3+}]_{in} xQ_{Al}}\right) x100 \quad (1)$$

$$GR\ (\%) = \left(1 - \frac{[Al^{3+}]_t xQ_t}{[Al^{3+}]_{in} xQ_{Al}}\right) x100 \quad (2)$$

The concentrations of $[Al^{3+}]_s$ and $[Al^{3+}]_t$ withdrawn on top of the reactor was analyzed using inductively coupled-plasma-optical emission spectrometer (ICP-OES, ULTIMA 2000, HORIBA Ltd., Japan). The scanning electron microscope (SEM, JSM-6700F, JEOL Ltd., Japan) was used to determine the surface morphology and the crystallographic structure patterns was analyzed using x-ray diffraction (XRD, DX III, Rigaku Co., Japan) at a scanning rate of $0.06^{\circ}\ s^{-1}$ in the incidence angle of 10 - 70° (2θ) with CuKα radiation source (λ = 1.5406Ā).

3. Results and discussion

3.1. The formation of aluminum granules

When $AlCl_3 \cdot 6H_2O$ was reacted with NaOH, precipitation of $Al(OH)_3$ occurred at room temperature as shown in Eq. (3) (Kazumichi *et al.*, 2007). Bayerite is a polymorph of $Al(OH)_3$ that consists of very fine crystals (Music *et al.*, 1998).

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \quad (3)$$

$$Al(OH)_3 \rightarrow AlOOH + H_2O \quad (4)$$

$$Al(OH)_3 \rightarrow AlOOH \rightarrow Al_2O_3 \quad (5)$$

When the pH of a solution having $[Al^{3+}]$ ions is increased with adequate supply of $[OH^-]$, dissolved species of $[Al^{3+}]$ and $[OH^-]$ are formed, and precipitation of $Al(OH)_3$ occured. $Al(OH)_3$ is stable between pH 4 to 9.5. and its solubility increases with excess NaOH. Under acidic conditions, formation of $[Al^{3+}]$ is visible, and AlOOH is formed under neutral and alkaline conditions (Hem and Robersons, 1967), and then it is converted into Al_2O_3 (Eq. (5)) (Noordin and Liew, 2010).

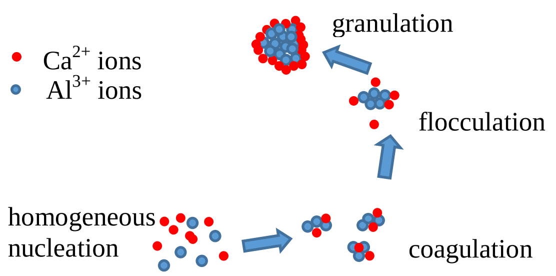

Figure 2. Proposed mechanism for the granule growth governed by calcium.

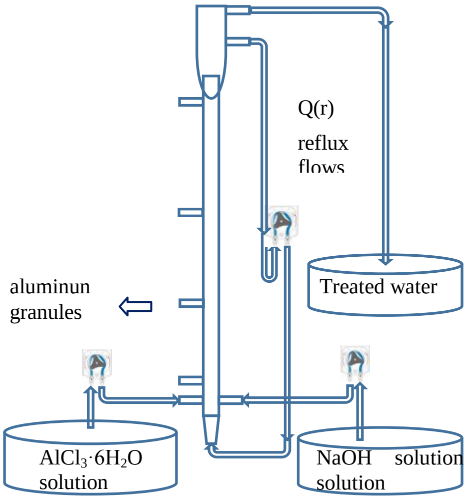

Figure 1. The fluidized-bed reactor set-up

3.2. Chemicals

The synthetic Al wastewater was prepared by using aluminum chloride ($AlCl_3 \cdot 6H_2O$, 97%, Katayama Chemicals, Co. Ltd.) at different concentrations and sodium carbonate (Na_2CO_3, AppliChem Panreac ITW Companies) as precipitant. For the pH adjustment of the precipitant solution, potassium hydroxide (KOH, 86.32%, Choneye Pure Chemicals) and nitric acid (HNO_3, 69%, Panreac, Spain) was used. All reagents used were analytical grade and used without purification. The water used was laboratory-grade reverse osmosis (RO) ultrapure water system (18.2 MΩ resistance). The source of Ca^{2+} ions came directly from tap water.

3.3. Fluidized-bed apparatus

The cylindrical Pyrex glass column reactor has a total volume of 550 mL (Figure 1). The upper part is the effluent region with diameter of 4.0 cm and a height of 20 cm. On the lower part is the reaction region with 2.0 cm diameter and 80 cm height. Three inlets at the bottom part of the reactor is connected to a peristaltic pump. Glass beads were packed at 4.0 cm height to uniformly distribute the hydraulic loading and support the granulation bed. Table 1 defined the important parameters and their corrsponding nomenclature. $CaCO_3$ precipitation happens when its solubility exceedes the Al present in the synthetic Al wastewater at high pH. At lower-pH bulk water, $CaCO_3$ maybe completely soluble, and it supersaturates at high-pH bulk water. The fluidized velocities and rough surfaces of $Al(OH)_3$ formed inside the reactor is an ideal site for crystal nucleation of $CaCO_3$. The high-pH environment supports the further precipitation and additional crystal growth of $CaCO_3$at an accelerated rate. The proposed mechanism for granule formation of Al surrounded by Ca^{2+} ions is shown in Figure 2. (GE Water & Process Technologies, 2012).

3.4 The effect of Ca^{2+} ions on the Al removal and GR

The effect of cross-section loading (L, 0.31-1.72 $kg \cdot m^{-2}$ h^{-1}) and hydraulic loading (U, 21.01-43.93 $m \cdot h^{-1}$) of Al in the presence of Ca^{2+} ions was evaluated. The cross-section loading (L, $kg \cdot m^{-2}$ h^{-1}) is the mass of Al that passed through a cross-section unit area per unit time which is being varied by the influent Al flow rate (Q_r). The best operating condition is at 200 $mg \cdot L^{-1}$ (0.83 mM) influent $[Al^{3+}]$ concentration, 11.8 of pH_e and 12.1 pH of precipitant with 6.0 MR of $[OH^-]_{in}/[Al^{3+}]_{in}$. The effect of L (1.15 $kg \cdot m^{-2}$ h^{-1}) on Al with Ca^{2+} ions generally increased the *Al removal (%)* from 96.70 (without Ca^{2+} ions) to 99.1% (with Ca^{2+} ions) (Figure 3a). The presence of Ca^{2+} ions affects the granulation of Al in the synthetic wastewater. An increase in the *GR (%)* from 96.70 (without Ca^{2+} ions) to 99.01% (with Ca^{2+} ions) (Figure 3b) in the effluent region was also observed. That increase is attributed to the presence of Ca^{2+} ions in the solutions. The amount of Ca^{2+} ions in the effluent region preferred the nucleation and growth of granules. More binding sites are available on the surface of the Al granules that increased the *GR* and *Al removal*. The hydraulic loading (U, $m \cdot h^{-1}$) was varied by adjusting the reflux flow rates (Qr=60-180 $mL \cdot min^{-1}$) while the Al inflow rate ($Q_t=Q_{Al}+Q_{OH}$=50 $mL \cdot min^{-1}$) was held constant. The adjusted reflux flow rates dilute the influent $[A^{3+}]_{in}$ concentrations that resulted to variable degree of supersaturation at the bottom region of the reactor. At low U<21.01 $m \cdot h^{-1}$, a low bed expansion is observed due to the low mixing energy that led to poor removal (Figure 4). The removal at U=21.01 $m \cdot h^{-1}$ increased in the presence of Ca^{2+} ions due to the formation of more nuclei that retained inside the reactor. The Ca^{2+} ions compete with Al ions in the formation of granules (Salcedo *et al*., 2016). At U>26.74 $m \cdot h^{-1}$, the removal increased in the presence of Ca^{2+} ions. The Ca^{2+} ions bind onto the surface of the Al granules that is supported by the high bed expansion leading to an improved FBR efficiency. But, at U>38.2 $m \cdot h^{-1}$ the removal decreased due to too high bed expansion that enable to maintain the tiny nuclei in the reactor. The K_{sp} of $CaCO_3$ (3.36 x 10^{-9}) is greater than the K_{sp} of $Al(OH)_3$ (1.1 x 10^{-33}). Formation of $CaCO_3$ crystals come first and the surface of the Al granules provide the binding sites for Ca^{2+} ions.

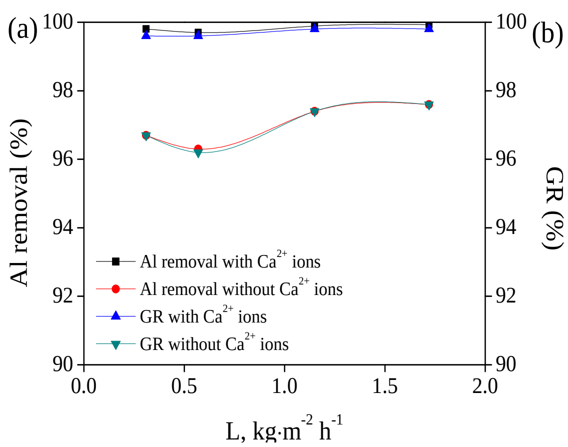

Figure 3. The effect of cross-section loading on a) Al removal (%) and b) GR (%) in the presence of Ca^{2+} ions at 200 $mg \cdot L^{-1}$ influent $[Al^{3+}]_{in}$ concentration, pH=12.1 of precipitant, and at 6 MR of $[OH^-]_{in}/[Al^{3+}]_{in}$.

interactions were considered to influence the growth, formation, and solubility of the granules. Figure 5 revealed the actual SEM image of the Al granules in the presence of Ca^{2+} ions formed in the FBR. The morphology shows the aggregation of irregular fine nuclei forming a firm and larger structures at 10, 000 magnification with granule diameter of 10 μm. The

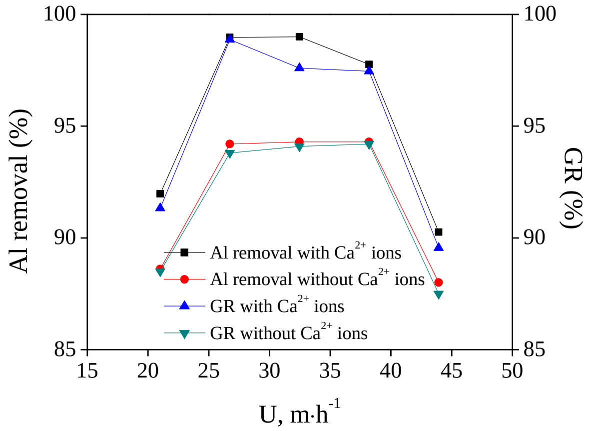

Figure 4. The effect of hydraulic loading on a) Al removal (%) and b) GR (%) in the presence of Ca^{2+} ions at 200 mg·L^{-1} influent $[Al^{3+}]_{in}$ concentration, pH=12.1 of precipitant, and at 6 MR of $[OH^{-}]_{in}/[Al^{3+}]_{in}$.

micro fragments were formed at an alkaline pH of the effluent of 11.8. The XRD revealed the major diffraction peaks at 2θ values of the granules formed using Cu *K*α1-radiation (λ = 1.540598 Å) (Figure 6). The major peaks at 12°, 24°, 30°, 53°, and 61° represents the radiation (λ = 1.540598 Å) (Figure 6). The major peaks at 12°, 24°, 30°, 53°, and 61° represents the crystallographic characteristics of a tetra calcium dialuminum dodecahydroxide carbonate pentahydrate ($Al_2Ca_4H_{22}O_{20}$).

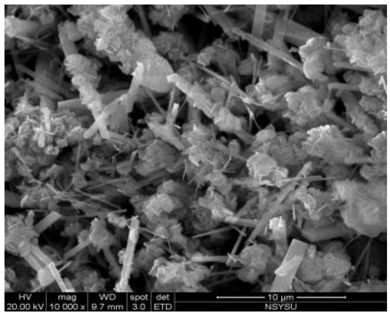

Figure 5. SEM image of the granules formed at 10, 000 magnification with 10 μm. diameter.

4. Conclusion

The removal of Al from synthetic wastewater was successfully done using FBHGP. The presence of Ca^{2+} ions affects the *Al removal (%)* and *GR (%)*. The Al granules was produced at 200 mg·L^{-1} influent $[Al^{3+}]_{in}$ concentration, pH of precipitant of 12.1 at pH_e of 11.8, and 6.0 MR of $[OH^{-}]_{in}/[Al^{3+}]_{in}$. The highest removal of 99.2% and GR of 98.9% in the presence of Ca^{2+} ions was achieved at L=1.15 kg·m^{-2} h^{-1} achieved the. The highest Al removal of 99.0% and GR of 97.6% was achieved at U=32.47 m·h^{-1}. The slight difference in the Al removal and GR with and without the presence of Ca^{2+} ion has no effect in the efficiency of the FBHGP. But, on the granules formed, its affects the characteristics. The presence of Ca^{2+} ions attached onto the surface of the Al ions. XRD revealed the crystallographic structure patterns that represents the tetra calcium dialuminum dodecahydroxide carbonate pentahydrate ($Al_2Ca_4H_{22}O_{20}$).

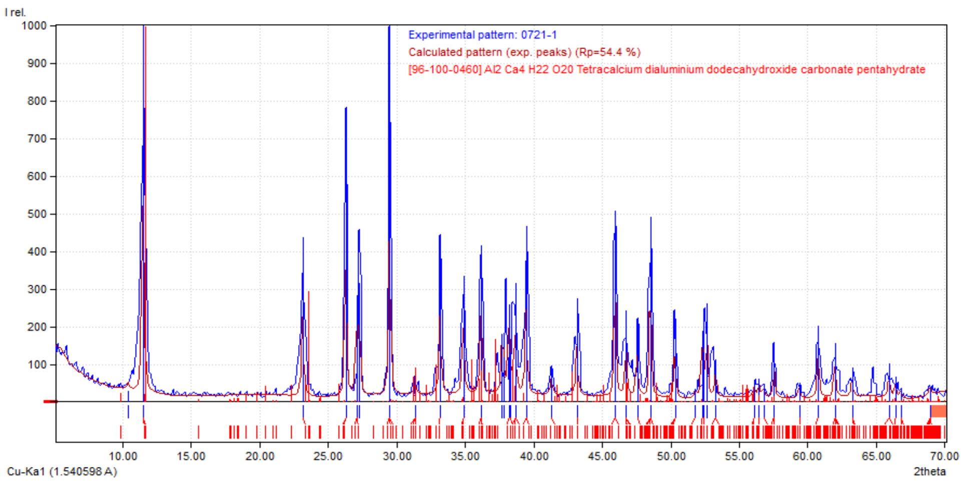

Figure 6. XRD spectrum of the granules formed at $[Al^{3+}]_{in}$=200 mg·L^{-1}, MR of $[OH^{-}]_{in}/[Al^{3+}]_{in}$=6.0, $pH_{(NaOH)}$=12.1 with pH_e=11.8.

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