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Desorption trials and granular stability of chromium loaded aerobic granular sludge from synthetic domestic wastewater treatment

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ABSTRACT

This study investigated Cr (VI) adsorption from aqueous solution onto aerobic granular sludge (AGS) and then its desorption to recover Cr and regenerate AGS. AGS adsorption was conducted using batch experiments. Alkaline (CH_3COONa, $NaHCO_3$, Na_2CO_3, and Na_2CO_3 containing Na_2HPO_4 or KCl) and HCl solutions were attempted to desorb Cr (VI) and Cr (III), respectively. Their effects on microbial activity and granular stability were also explored. 0.5 M $NaHCO_3$ was found to be the best desorption agent with desorption ratios of 62% for Cr (VI) and 10% for Cr (III). 0.1 M HCl could further desorb the remaining Cr (III), resulting in totally 81% of desorption ratio. Adsorption under acidic conditions decreased microbial activity, while desorption using alkaline solutions negatively affected granular stability to some extent, most probably attributable to cations release from AGS. These results for the first time suggest the possibility of Cr-loaded AGS regeneration by weak alkaline solutions.

1. Introduction

Heavy metals (HMs) in industrial wastewater are a serious issue which can severely impair human health and the environment. Chromium (Cr) is a common contaminant in surface water and groundwater, possibly due to its wide application in electroplating and other industries (Ellis et al., 2002). Hexavalent chromium (Cr (VI)) is highly toxic to living organisms and aqueous ecosystems with strong oxidizing properties.

Granular sludge with higher porosity structure compared with traditional activated sludge has been reported to be effective in adsorption and removal of various HM from wastewater. For instance, Cu (II) could be adsorbed by active functional groups like —OH, —COOH, and —NH_2 on aerobic granular sludge (AGS) (Jian et al., 2015), and those in wastewater with SO_4^{2-} could deposit in anaerobic granules as CuS precipitates (Cao et al., 2014). Pb (II) can be continuously removed from aqueous streams in anaerobic granular sludge system (Pat-Espadas et al., 2016), and together with Cu (II) adsorbed by chitosan modified granules (Liu et al., 2017b). Ni (II) can be adsorbed by both aerobic and anaerobic granular sludge, and the key functional groups for Ni (II) sorption are reported to be —OH and —NH_2 (Li et al., 2017). Sb (V) adsorption by AGS could be enhanced by introduction of Fe (III) to the surface of AGS (Wan et al., 2014; Wang et al., 2015; Wang et al., 2014a). Wei et al. (2016) found that the protein-like compounds of extracellular polymeric substances (EPS) in AGS was the key component to quench with Zn (II). As for Cr, Yao et al. (2009) removed Cr (III) from aqueous solution by using AGS. Moreover, AGS modified with polyethylenimine (PEI) exhibited a significant increase in adsorption capacity for the removal of Cr (VI) (Sun et al., 2011; Sun et al., 2010).

Clearly, it can be seen that although granular sludge has been reported to effectively adsorb HMs and remove them from industrial wastewaters, desorption of HM has not been received much attention. Up to the present, little information is available on how to desorb or recover the HM-loaded AGS to purposefully reuse HM and AGS respectively, the crucial aspect to maintain the sustainable operation of AGS system and HM recovery. Most importantly, an effective and environmentally friendly desorption method is preferred.

As it is well known, the traditional adsorbents like activated carbon can realize its regeneration by some physical means, such as heating (Yu et al., 2016) and ultrasound (Liu et al., 2017a) methods. However, AGS with abundant microorganisms are not suitable to be directly heated when AGS is purposefully designed to return to the bioreactor for continuous contribution to pollutants removal or resources recovery. Chemical regeneration might be an economically feasible alternative for this purpose (Kow et al., 2016). As reported, activated carbon can be desorbed by NaOH solution (Kow et al., 2016), or ethanol and acetic acid solution (Ma et al., 2016), depending on the component adsorbed onto it. Han et al. (2000) applied granular activated carbon to adsorb Cr (VI), and then extracted the adsorbed Cr (VI) using dibasic potassium phosphate solution. Kołodyńska et al. (2017) successfully desorbed Cu (II), Zn (II), Cd (II), Co (II) and Pb (II) from both commercial

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activated carbon and biochar using 0.1 M HNO_3 solution. Restated, up to now, no report could be found on HM desorption from HM-loaded AGS for HM recovery and AGS regeneration.

Therefore, in this study, we tried to make up the research gap in the lack of desorption method for HM-loaded AGS. Cr (VI) was adsorbed on the AGS discharged from a long-term operated (>300 days) sequencing batch reactor (SBR) treating synthetic domestic wastewater. Chemical regeneration by different alkaline solutions was applied as a potential desorption method for Cr (VI)- loaded AGS. During these adsorption and desorption tests, the two most important aspects for AGS's stable operation, i.e. microbial activity and granular stability were also investigated.

2. Experimental

2.1. AGS used in this study

The AGS used in this study was sampled from a SBR after long-term operation (>300 days) in the lab by using synthetic domestic wastewater with the main characteristics as follows: 300 mg chemical oxygen demand (COD)/L (sodium acetate), 50 mg NH_4-N/L (NH_4Cl), 5 mg PO_4-P/L (KH_2PO_4), 10 mg Ca^{2+}/L ($CaCl_2 \cdot 2H_2O$), 5 mg Fe/L ($FeSO_4 \cdot H_2O$), and 5 mg Mg/L ($MgSO_4 \cdot 7H_2O$). The average granular size was determined by a stereo microscope (STZ-40TBa, SHIMADZU, Japan) with a program Motic Images Plus 2.3S (version 2.3.0).

2.2. Batch adsorption experiments

Cr (VI) solution was prepared with potassium dichromate ($K_2Cr_2O_7$). All the adsorption tests were conducted in 50 mL tubes. A 30 mL prepared Cr (VI) solution was mixed with 5 mL aerobic granules to the designated biomass concentration. After the sludge being dispersed in the solution, the tube was capped and then constantly shaken by using an oscillator at 25 ± 2° and 150 rpm for 18 h. To explore the influence of pH on the adsorption capacity of granules, the pH of Cr (VI) solution (100 mg/L) was adjusted from 1.68 to 10.10 with 0.1 M HCl or 0.1 M NaOH. pH value was measured by a pH meter (Mettler Toledo FE20, Switzerland). To investigate the adsorption isotherm of granular sludge, Cr (VI) solutions with concentration from 10 to 200 mg/L were used. Each of them was mixed with AGS and then the adsorption was performed as above with the initial pH being adjusted to about 2.0. After Cr adsorption, the granules were named as Cr-loaded AGS.

2.3. Desorption of Cr from Cr-loaded AGS

After adsorption, the Cr-loaded AGS was desorbed by using different alkaline solutions. Before desorption, the mixture of Cr (VI) solution and Cr-loaded AGS (obtained from Section 2.2) was centrifuged and the remaining Cr (VI) solution was then discharged to the designated wastewater tank. The Cr-loaded granules were washed by 20 mL deionized water which was then discharged after centrifugation. After being washed by deionized water for three times, the granules were dispersed in a 50 mL tube containing 20 mL alkaline solution (the desorption agent), and then constantly shaken at 25 ± 2 °C and 150 rpm for 18 h after being capped. The 6 alkaline solutions used in this study and their concentrations are listed in Table 1.

Table 1
Alkaline solutions used to desorb Cr-loaded AGS.

No.	Desorption agent	Concentration (mol/L)	Volume (mL)
1	Na_2CO_3	0.01, 0.05, 0.1, 0.25, 0.5	20/40
2	CH_3COONa	0.5	20
3	$NaHCO_3$	0.5	20
4	NaOH	0.1	20
5	Na_2CO_3 with Na_2HPO_4 (0.01 mol)	0.5	20
6	Na_2CO_3 with KCl (0.01 mol)	0.5	20

After desorption by each alkaline solution, the granules were further regenerated by 15 mL HCl at a concentration of 0.1 M to desorb Cr (III). The desorption procedure was as same as the alkaline desorption except that the desorption time was set at 1 h from our preliminary experiments.

2.4. Analytical methods

2.4.1. Cr quantification

The concentration of Cr (VI) in solution was determined by UV spectrophotometry (UV 1800, Shimadzu, Japan). After complexation with 1,5-diphenyl-carbazide in acidic medium (Gupta and Rastogi, 2009), Cr (VI) concentration was measured at 540 nm.

The concentrations of total Cr and other metal elements such as Ca, Mg and Fe were analyzed by ICP-OES (Optima-7300 V, Perkin Elmer). Samples were firstly digested with HNO_3 and H_2O_2 according to the method proposed by US EPA (Arsenic and Beryllium, 1996), and then filtrated through 0.22 μm membrane before injection. The concentration of Cr (III) was calculated as the difference between total Cr and Cr (VI). Average values were taken from triplicate tests of each sample in this study.

2.4.2. Microbial activity

Mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) were measured according to the standard methods (APHA, 2012). The microbial activity was expressed by specific oxygen uptake rate (SOUR) (Tang et al., 2016). 5 mL AGS with known concentration was mixed with 50 mL synthetic wastewater and loaded into a 100 mL glass flask. The mixture was aerated using an air pump (AK-30, KOSHIN, Japan) at 25 ± 2 °C till the dissolved oxygen (DO) reached relatively stable (no longer increase). Then the aeration was stopped and at the same time the flask was sealed (leaving the DO meter inside) with timely recording the decrease in DO due to the consumption of microorganisms. In these tests, DO was measured by a DO meter (DO-31P, TOA-DKK, Japan), and SOUR was calculated according to Eq. (1):

$$\mathrm{SOUR}\ (\mathrm{mg{-}O_2/g{-}VSS \cdot h}) = (DO_0 - DO_t)/(t \times \mathrm{MLVSS}) \quad (1)$$

where DO_0 (mg/L) is the initial DO of the solution, i.e. the DO value relatively stable before stopping aeration, DO_t (mg/L) is the DO value in the solution due to consumption by microorganisms at time t, and t (h) is the time duration after stopping aeration. MLVSS (g/L) is the granular biomass concentration in the flask.

2.4.3. Granular stability

The stability of AGS was expressed by integrity coefficient which is related to the strength of granules (Ghangrekar et al., 2005). Briefly, after being sampled, a 30 mL AGS being well mixed with 30 mL deionized water was added into a graduated cylindrical (100 mL) and settled for 1 min. After the supernatant being discharged, the volume of the mixture was adjusted up to 60 mL by adding some water. This process was repeated for 2 times. Then, after being mixed thoroughly 14 mL of the mixture was sampled, put into a 50 mL tube and capped, and placed in an oscillator shaken at 25 ± 2 °C and 200 rpm for 5 min. The mixture was then settled down for 1 min with the supernatant being separated. The integrity coefficient was expressed as the ratio of solids weight remaining in the supernatant to the total weight of granular sludge used for this test (14 mL of mixture) (Ghangrekar et al., 2005).

2.4.4. Statistical analysis

The adsorption process, the desorption process by alkaline solutions, the microbial activity detection and granular stability detection were conducted in triplicate for each experiment. All the data were expressed as mean ± standard deviation (x ± SD).