Desorption of Hg(II) and Sb(V) on extracellular polymeric substances: Effects of pH, EDTA, Ca(II) and temperature shocks

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HIGHLIGHTS

► Adsorption–desorption behaviors of Hg(II) and Sb(V) on EPS were investigated.
► Effects of EDTA, Ca(II), pH and temperature shocks on desorption kinetics were studied.
► Hg(II) and Sb(V) were bound with polysaccharides and protein-like compounds, respectively.
► EPS–Hg complex is a time bomb that may release Hg(II) in short time period under shocks.

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ABSTRACT

Extracellular polymeric substances (EPS) existed ubiquitously in biological systems affect the mobility and availability of heavy metals in the environments. The adsorption–desorption behaviors of Hg(II) and Sb(V) on EPS were investigated. The sorption rates follow Sb(V) > Hg(II), and the desorption rates follow reverse order. Applications of ethylene diamine tetraacetic acid (EDTA), Ca(II) and pH shocks affect desorption rates and desorbed quantities of Hg(II) from EPS–Hg complex. Temperature shock minimally affects the desorption rate of Hg(II). Conversely, the EPS–Sb complex is stable subjected to EDTA, Ca(II), temperature or pH shocks. The excitation–emission matrix (EEM) fluorescence spectroscopy and fast-Fourier (FT-IR) analysis showed that Hg(II) and Sb(V) principally interacted with polysaccharides and protein-like compounds in the EPS, respectively. The EPS–Hg complex presents a time bomb that may release high levels of Hg(II) in short time period under environmental shocks.

1. Introduction

Extracellular polymeric substances (EPS) are main constituents of numerous natural or engineered biological systems. The EPS are high molecular weight mixture secreted by bacteria and are mainly composed of carbohydrates, proteins, lipids, nucleic acids and various heteropolymers (Tu et al., 2012; Alasonati and Slaveykova, 2012; Bourven et al., 2012). The mobility and availability of heavy metals in the environments may be strongly influenced by EPS due to their ubiquitous presence and great metal binding capacity. The metal binding capacity of EPS can be a result of several physico-chemical and biological processes such as ion exchange, complex-ation and surface precipitation due to a variety of metal binding functional groups on surface of EPS (Aquino and Stuckey, 2004). The functional groups, including hydroxyl, carboxyl, phosphoric amine and amidocyanogen of proteins, polysaccharides and phospholipids (Morris and Meyer, 2006), can generate a negative surface charge and act as metal binding sites to form organo-metal complexes (Pagnanelli et al., 2009).

Mercury (Hg) is one of the most commonly found and most toxic heavy metals in the environment (Castro-Gonzáleza and Méndez-Armentab, 2008) and could be bound tightly to EPS of activated sludge or biofilms (Zhang et al., 2010). The behavior of Hg in aquatic systems is mainly controlled by adsorption and desorption processes depending on pH and organic matter (Ravichandran, 2004; Gorski et al., 2006). However, the desorption characteristics of the adsorbed mercury on EPS have not been studied. Antimony (Sb), as a global emergent pollutant, is ubiquitous in urban road dust which may be introduced into the activated sludge system with storm runoff (Smichowski, 2007). Sb can be concentrated

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in wastewater treatment plants (WWTP) in Sweden (Månsson et al., 2009).

The ultimate metal adsorption capacities are the focus of studies (Comte et al., 2006). How fast the adsorbed heavy metals can be desorbed from EPS under environmental shocks may be of even greater significance than their ultimate adsorption capacity since the accumulated heavy metals can be suddenly released under specific shock and induce the "time-bomb" effects (Chang et al., 1997). Compared with the adsorption studies, relatively fewer authors explored the desorption kinetics (Wang and Tian, 2007; Bai et al., 2009; Bashiri, 2011; Jafari et al., 2011; Wang and Lin, 2011). The objective of this study was to investigate the adsorption/desorption kinetics of Hg(II) and Sb(V) on EPS collected from activated sludge samples. The metal-adsorbed EPS were subjected to changes in ethylene diamine tetraacetic acid (EDTA) concentration, Ca(II) concentration, pH, and solution temperatures with the concentrations of released Hg(II) or Sb(V) ions being monitored.

2. Methods

2.1. EPS samples

The aerobic activated sludge was collected from Neihu wastewater treatment plant, Taipei, Taiwan. The activated sludge samples were centrifuged at $4300 \times g$ for 10 min at 4 °C in order to remove undissolved minerals and organic matters. The residues were recovered and re-suspended in milli-Q water and were extracted using ultrasound at 20 W for 5 min in an ice bath (Adav et al., 2010). Following ultrasonication, the suspension was centrifuged at $9000 \times g$ for 30 min at 4 °C. The supernatant was collected as the EPS sample. The EPS sample was then filtered through 0.22-μm acetate cellulose membrane and purified with dialysis membrane (3500 Da) for 24 h at 4 °C for at least three times.

The obtained EPS sample (>3500 Da) had the following characteristics: total organic carbon (TOC), 52.5 ± 0.06 mg l^{-1}; dried weight (DW), 197 ± 0.6 mg l^{-1}; volatile dried weight (VDW), 93 ± 0.5 mg l^{-1}; proteins, 55.99 ± 0.45 mg g^{-1} VDW; polysaccharides, 62.10 ± 0.22 mg g^{-1} VDW; humic acids, 2.66 ± 0.25 mg g^{-1} VDW. The organic fraction in EPS accounts for 47% of DW, and the PN/PS ratio of EPS sample was 0.9.

2.2. Adsorption/desorption tests

10 ml of EPS sample (>3500 Da, 197 mg l^{-1} DW) was transferred to dialysis sacks with molecular weight cutoff of 3500 Da. In adsorption tests, the dialysis sacks were sealed and placed into 150 ml conic flasks containing 90 ml of 30 mg l^{-1} Hg(II) or Sb(V) solution at 20 °C, with 0.5 ml of solution outside the sacks being sampled at fixed time points.

Following the 24 h adsorption tests, some dialysis sacks were transferred to 150 ml conic flasks with 90 ml of desorption medium for desorption tests. The desorption medium in the conic flasks could be milli-Q water at 20 °C. The other dialysis sacks were still kept in their sorption medium, respectively, and desorption tests were driven by changing these solutions: pH adjustment by adding 1 M HCl or NaOH at 20 °C, solutions at fixed concentrations of Ca(II) or EDTA at 20 °C, or desorption medium at 10, 20 or 30 °C. During desorption tests, 0.5 ml of solution outside the sacks was sampled at fixed time points for analysis.

Before tests all glassware were dipped in 0.1 M HNO$_3$ for 48 h, then rinsed with deionized water thoroughly and then dried. All chemicals were of analytical grade.

2.3. Analytical methods

The TOC contents of samples were determined with a TOC meter (Aurora 1030, Germany). The quantities of polysaccharides in samples were determined by the phenol–sulfuric acid method. Proteins and humic compounds were determined using the Lowry procedure (Frølund et al., 1995). Three randomly selected samples were collected and mixed with the wet weight and DW of mix being measured by weighing before and after drying at 105 °C for 24 h. The dried mix was then heated up to 550 °C for 1 h with the difference between the DW and the weight of the residue as the VDW.

For FT-IR analysis, EPS samples were dried at 60 °C and then the dried samples were mixed with solid KBr in the ratio of 1:100. The KBr–EPS pellets of 13 mm diameter of the mixture were prepared at 8×10^3 kg cm^{-2} pressure. The FT-IR spectra of the EPS samples were recorded with a FT-IR spectrophotometer (Lambaba Solution, USA). The fluorescent spectra were obtained with a fluorescence spectrophotometer (Eclipse Fluorescence spectrophotometer, Agilent, USA). Hg(II) concentrations in the filtrated samples were determined by ICP-AES (JY 2000, France). After every 10 measurements the ICP was calibrated by standard solutions.

3. Results and discussion

3.1. Adsorption/desorption Hg(II) and Sb(V) on/from EPS

Fig. 1 shows typical adsorption–desorption curves of Hg(II) and Sb(V) on the extracted EPS. Both Hg(II) and Sb(V) were quickly adsorbed onto EPS, with 81.4% of Hg(II) and 93.6% of Sb(V) adsorbed onto EPS in the first 30 min of contact, followed by a long tail to equilibrium. Bai et al. (2009) also demonstrated in their adsorption and desorption tests of calcium lignosulfonate on a porous dolomite rock a two-step pattern: a fast adsorption/desorption followed by a slow step. The maximum amounts of Hg(II) and Sb(V) adsorbed on EPS were 452.8 and 648.7 mg g^{-1} DW, respectively. When the samples were transferred to milli-Q water, a quick desorption process was noted for Hg(II). Not all Hg(II) are reversibly adsorbed onto the EPS surfaces: eventually only 183.8 mg g^{-1} DW was desorbed, accounting for 41% of the adsorbed Hg(II) on EPS. The initial desorption of Sb(V) occurred right after contact with milli-Q water, but only accounting for 9% of the total adsorbed (648.7–604.1 mg g^{-1} DW). The follow-up desorption proceeded slower than Hg(II), reaching 517.8 mg g^{-1} DW at 48 h. Restated, over 79% of Sb(V) was irreversibly adsorbed by EPS. In fact, in all following tests with environmental shocks, the desorption of Sb(V) was not enhanced in rate or in quantity. The Sb(V) has a much stronger affinity with EPS surface than Hg(II).
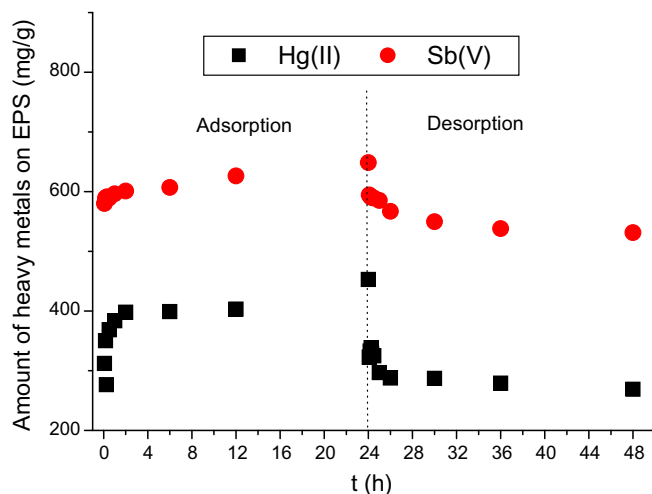

Fig. 1. Typical adsorption–desorption tests of Hg(II) and Sb(V) on sludge EPS at 20 °C. pH 7.37. Desorption in milli-Q water.
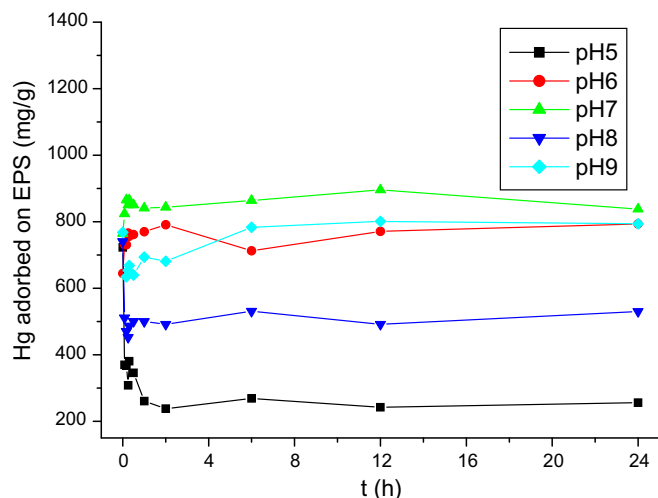
Fig. 2. Desorption of Hg(II) from EPS surfaces at various pHs.

3.2. Desorption: environmental shocks

3.2.1. pH shock

Solution pH affects metal speciation and surface charge characteristics of dissolved organic materials including EPS (Ravichandran, 2004). Desorption of Hg(II) from EPS was significantly influenced by pH. When solution was dropped in pH from 7 to 5, $467.0 \, mg \, g^{-1}$ of Hg(II) was desorbed from EPS surface in 15 min (Fig. 2). He et al. (2007) also noted that desorption quantity of Hg(II) increased from Al_2O_3 powers as pH was reduced. As pH was increased from 7.0 to 9.0, no Hg desorption was noted. Restated, the EPS–Hg complex is more stable in alkaline than in acidic environment.

3.2.2. EDTA shock

Fig. 3 shows the desorption tests of Hg(II) and Sb(V) in the presence of $10 \, mg \, l^{-1}$ EDTA. About 74.4% absorbed Hg(II) was released right after the EDTA shock. The EDTA can induce strong complexation to bound Hg(II) on EPS. Gao et al. (2003) noted that EDTA effectively enhances desorption of Pb and Cd from sediments. On the contrary, the EDTA shock did not pose any significant effects on the absorbed Sb(V).
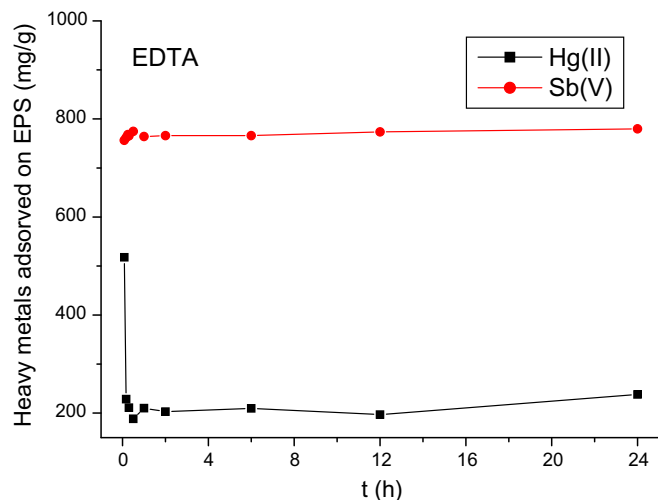

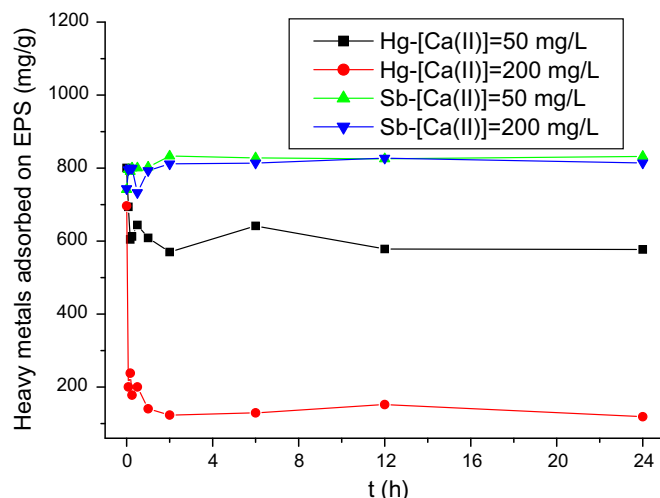**Fig. 3.** Desorption of Hg(II) and Sb(V) from EPS surfaces at EDTA concentration shocks.

Fig. 4. Desorption of Hg(II) and Sb(V) from EPS surfaces at Ca concentration shocks.

3.2.3. Ca(II) shock

The Ca(II) can compete with Hg(II) on EPS sites while increased Ca(II) concentration enhances desorption of Hg(II): at $50 \, mg \, l^{-1}$ Ca(II), 27.8% of absorbed Hg(II) was desorbed; while at $200 \, mg \, l^{-1}$ Ca(II), 77.5% of Hg(II) was desorbed. Meanwhile, no Sb(V) was desorbed at Ca(II) shock (Fig. 4).

3.2.4. Temperature shock

Over the temperature range of 10–30 °C, no desorption of either Hg(II) or Sb(V) was noted from EPS (data not shown for brevity sake). The weak temperature-dependence indicates that the formed EPS–Hg and EPS–Sb complexes were quite stable at room temperature range.

3.3. Fluorescence analysis

The EEM spectra of original EPS revealed strong protein-like fluorescence peaks and relative weak humic acid-like fluorescence peaks (Fig. S1a in Supplementary Data), correlating with the results in Mayer et al. (1999) and Liu and Fang (2002). The complexation with Hg(II) quenched both protein-like fluorophores and humic acid-like fluorophores on EPS (Fig. S1b in Supplementary Data). In the desorption test with milli-Q water the intensities of protein-like fluorophores were recovered (Fig. S1d in Supplementary Data). On the contrary, only the protein-like fluorophores of EPS were weakly quenched by the binding with Sb(V) (Fig. S1c in Supplementary Data). After desorption, the intensities of protein-like fluorophores on EPS were recovered (Fig. S1e in Supplementary Data). The increased intensities in the EEM spectra suggested that EPS–Hg complexes dissociated and Hg(II) was desorbed from the protein-like substances. This is in accordance with the results of batch desorption experiment which showed that 40.6% of Hg(II) was desorbed from EPS.

3.4. FT-IR spectra of EPS adsorption/desorption of Hg(II) and Sb(V)

The FT-IR spectra of EPS and EPS-complex are shown in Fig. S2 (in Supplementary Data). The characteristics of functional groups correlated with those noted in literature works (Zhang et al., 2006; Pagnanelli et al., 2009; Wang et al., 2009). A broad peak at $3150 \, cm^{-1}$ was contributed by stretching of O–H bond as hydroxyl functional groups of polysaccharides and proteins. The peaks at 2926 and $2853 \, cm^{-1}$ were due to C–H asymmetric and symmetric stretching vibrations of CH, CH_2 and CH_3 groups. The peaks at 1630

and 1580 cm^{-1} correspond to the amide I (C=O stretching) and amide II groups (N–H bending and C–N stretching), respectively. The spectra bands between 1150 and 1030 cm^{-1} exhibits C–O–C stretching groups of polysaccharide. The intense peak at 1405 cm^{-1} along with the peak at 1240 cm^{-1} is due to deformation vibration of CH$_2$ and C=O, respectively.

Detailed analysis on FT-IR spectra noted peak shift of hydroxyl functional groups of polysaccharides and proteins and the reduced peak intensities of carboxylate, amide and the C–O–C group of polysaccharides. The C–O–C groups of polysaccharides were changed after desorption of Sb(V) from EPS (Fig. S2c and e in Supplementary Data), indicating that Sb(V) combining on C–O–C group of polysaccharides released Sb(V). Conversely, the FT-IR (Fig. S2c and e in Supplementary Data) of the complex of EPS–Hg(II) cannot be found with obvious change, suggesting that EPS binding Hg(II) by electrostatic forces were easily desorbed. The distance between C=O and C–O stretching peaks can be diminuted due to the interaction among metals and carboxylic adsorbent sites (Figueira et al., 1999; Pagnanelli et al., 2003).

3.5. Discussion

3.5.1. Kinetic behaviors

The pseudo-second order rate equation was used to fit the sorption kinetics (Ho, 1995):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{1}$$

where k_2 is the rate constant of sorption/desorption (g/mg min), q_e is the amount of sorption/desorption at equilibrium (mg g^{-1} DW), and q_t is amount of sorption/desorption at time t (mg g^{-1}). The best-fit parameters for metal adsorption tests are listed in Table 1. The best-fit q_e correlated well with those noted in 48-h adsorption test, suggesting that the present adsorption tests had reached equilibrium. The best-fit k_2 indicated that the Sb(V) (13.9 × 10^{-3} g mg^{-1} h^{-1}) was adsorbed onto EPS faster than Hg(II) (3.12 × 10^{-3} g mg^{-1} h^{-1}).

Eq. (1) was also adopted to describe desorption kinetics of organic dyes on adsorbents (Wang and Tian, 2007; Bai et al., 2009; Jafari et al., 2011). The best-fit parameters of the pseudo-second order equation with the present desorption data in milli-Q water are also listed in Table 1. On the contrary, the first-order equation does not properly describe the desorption data (data not shown). The desorption rate constant (k_2) of Sb(V) is greater than that of Hg(II), opposite to those noted for adsorption tests. Restated, the Sb(V) is adsorbed faster than Hg(II) from EPS, but is desorbed slower than Hg(II).

The good fitting of adsorption (r^2 = 0.9534–0.9994) and desorption (r^2 = 0.9778–0.9997) data suggesting that the desorption of the both Hg(II) and Sb(V) from EPS can be approximated as a second-order reaction, a result suggesting that the dosed Hg(II) and

Sb(V) were in much higher quantities than the available adsorption sites on EPS surfaces.

3.5.2. Desorption behaviors under shocks

Eq. (1) was adopted to describe desorption kinetics of Hg(II) from EPS at pH shock (Table 1). The desorption rate constant (k_2) of Hg(II) is smaller than that at pH 7, but the desorbed quantity on the contrary is much higher. Subject to acid shock, the absorbed Hg(II) will be released at a low rate but eventually great quantity to solution. Regardless of solution pH change (5–9, data not shown), minimum desorption of Sb(V) from EPS was noted. Restated, the desorption of Sb(V) from EPS was not relevant.

The fitting of Eq. (1) for the desorption data of Hg(II) is satisfactory (r^2 = 0.9997) under EDTA shock (Table 1). The desorption rate constant (k_2) of Hg(II) is higher than that in milli-Q water, while the desorbed quantity reached 544.2 mg g^{-1} DW, comparable to that with acid shock (Section 3.2.1).

Eq. (1) was also used to describe the desorption data of Hg(II) at 50 or 200 mg l^{-1} Ca(II) shock (Table 1). The k_2 and desorption quantities of Hg(II) were increased with increasing Ca(II) concentration.

No kinetic parameters were evaluated for desorption data under temperature shock.

3.5.3. Environmental relevance

Chang et al. (1997) proposed two long-term scenarios for toxic metals in sewage sludge amended soils. The plateau theory claimed that the soil adsorbed metal will persist in its chemical stability in the soil and the metal concentration will reach a plateau value upon continuous sludge amendments. The time bomb hypothesis proposed that the soil–metal interaction may be weakened over time while the adsorbed toxic metals may then be released, so the sludge amended soil is a time bomb for plant phytotoxicity. The present study revealed a similar scenario. The EPS is redundant in natural or artificial water systems. Hg(II) and Sb(V) in an incoming water stream can be adsorbed (so is accumulated) by the protein-like and polysaccharide-like function groups of the incorporated EPS. When the upstream manufacturing plants incidentally released wastewater with EDTA, Ca(II) or waste acid to change aquatic conditions such as pH, the adsorbed Hg(II) is readily to be released in a short time period to yield a plume of high Hg(II) concentration that threats the downstream ecosystems. Hence, the present EPS–Hg complex is a time bomb for downstream organisms. Conversely, the desorption of Sb(V) from EPS cannot be triggered by EDTA, Ca(II) or pH shocks, indicating that the EPS–Sb complex is not a time bomb under the investigated environmental shocks.

The FT-IR observation together with the adsorption data presented in Section 3.1 that EPS adsorbed more Sb(V) than Hg(II) indicates that Sb(V) may be principally bound to the non-fluorescent components such as polysaccharides. Compared with Hg(II) loaded

Table 1
Kinetic parameters of EPS adsorption/desorption with Hg(II) and Sb(V).

Metal	Environmental shock	Pseudo-second order equation		R^2	q_e (mg g^{-1} DW) measured	Test
		k_2 (×10^{-3} g mg^{-1} h^{-1})	q_e (mg g^{-1} DW)			
Sb(V)[a]	–	13.9	645.2	0.9994	648.7	Adsorbed
	Milli-Q	16.1	118.2	0.9977	117.3	Desorbed
Hg(II)	–	3.12	440.5	0.9534	452.8	Adsorbed
	Milli-Q	30.4	182.8	0.9989	183.8	Desorbed
	pH 5	3.65	471.7	0.9778	466.5	Desorbed
	10 mg l^{-1} EDTA	31.3	515.5	0.9997	544.2	Desorbed
	50 mg l^{-1} Ca(II)	17.5	222.2	0.9907	222.8	Desorbed
	200 mg l^{-1} Ca(II)	28.5	571.4	0.9993	539.6	Desorbed

[a] All shocks applied herein had no effects on desorption of Sb(V) from EPS surface.

EPS, the EEM spectra of the Sb(V) loaded EPS also changed less after 24 h of desorption initiated by lowering metal concentration, suggesting stability of the complexes formed between the fluorescent components and Sb(V). Considering both the results of EEM fluorescence spectra and batch sorption/desorption, some information can be given: Hg(II) is prone to be bound to protein-like substances of EPS and also prone to be released when the water environment changes whereas Sb(V) seems to prefer the non-fluorescent components such as polysaccharides. The different desorption behavior of EPS–Hg and EPS–Sb complex may be attributable to the distinct interactions between dosed EDTA, Ca(II) and protons to the specific functional groups on EPS.

4. Conclusions

Desorption behaviors of Hg(II) and Sb(V) from EPS matrix were investigated under EDTA, Ca(II), pH and temperature shocks. The pseudo-second order rate equation can well depict the sorption/desorption of Hg(II) and Sb(V) on EPS. The maximum amounts of Hg(II) and Sb(V) desorbed from EPS were 183.8 and 117.3 mg g^{-1} DW, respectively. EEM and FT-IR proved that Hg(II) and Sb(V) bound on the different active sites of EPS and interacted with protein-like substances and polysaccharides of EPS. Hg(II) is bound with the protein-like compounds in EPS, which can be weakened by EDTA, Ca(II) or pH shocks. The EPS–Hg complex presents a time bomb that may release high levels of Hg(II) in short time period under environmental shocks. However, the complex of Sb(V)–EPS seems to be more stable under the effects of pH, EDTA, Ca(II) and temperature shocks.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2012.10.089.

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