Adsorption of U (VI) by Anaerobic Sludge Extracellular Polymeric Substances (EPS) in Wastewater

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Abstract. The different values of pH, EPS dosage, initial uranium concentration, dialysis temperature and other factors, were investigated of anaerobic sludge extracellular polymer (EPS) on U (VI) in wastewater by adsorption effect. The results show that, the best pH of EPS adsorption of uranium is 6, when the initial concentration of uranium is 20mg/L, EPS dosage is 56.1 g/L, the removal rate can reach 98.3%. The maximum adsorption capacity of U (VI) is 0.891mg/g EPS.

Introduction

Uranium deposit smelting has been produced a large amount of uranium-containing wastewater, it has the potential impact on the nature environment and body health. In the treatment process of uranium-containing wastewater at low concentrations, Bio-absorption method have the virtue of low cost, good selectivity, fast removal speed and extensive sources which become a focal point at issue relative to traditional physics and chemistry. Anaerobic sludge extracellular polymeric substances (EPS)exists widely in internal and surface of the sludge flocs, play role in bridging action among cells. Cells can also used it to carried on matter and energy transfer. Many scholars made major research of the EPS. Francois's[1] study demonstrate that EPS composes of various organic substances such as protein, polysaccharide and humic substances; Bourven[2] and Abazac[3] prove that mineral material of EPS is 20%~77%, and the mineral material has important influnce to the EPS character, Domínguez[4] studies shows that the molecular weight and the average distribution of EPS extracted by different methods are different, distribution is more uniform by chemical method, nevertheless, physical method is very unevenly distributed. Simon[5] used three different anaerobic granular sludge extraction EPS and analysed it by exclusion chromatography at the wavelength of 210~280 nm, results show that the structure of EPS extracted from different sorts of sludge varied widely, the structure of EPS by using different methods to extracted from the same kind sludge is not the same.

Many researches have demonstrated that it has good adsorption effect to heavy metal such as copper, cadmium, lead, nickel, chromium by EPS[6-7], nevertheless, it has not been reported that EPS extracted by anaerobic activated sludge adsorbed of uranium in wastewater. Because of EPS is a predominant sludge flocs component, about 60% of the dry weight sludge, EPS extract by sludge is used to remove the uranium in water bodies contaminated by uranium, due to its economical efficiency and cheap, its meaning is very important.

Materials and methods

Extraction of EPS. The source of the anaerobic sludge(Inoculated sludge) from anaerobic sludge of Hengyang Yanjing Beer factory EGSB anaerobic reactor, it was artificial by laboratory domestication at least 5 months before it was used. Culture volume is 2.5 L, removing supernatant 0.5 L weekly, adding 0.5L new culture medium, medium components is shown in table 1.

Table 1 Composition of nutrient solution

Name	Concentration(mg/L)	Name	Concentration(mg/L)
Glucose	3120	Yeast extract	450
$NaHCO_3$	1500	KH_2PO_4	76
H_3BO_3	0.06	$CuSO_4•7H_2O$	0.036
$CaCl_2$	63	NH_4Cl	320
$CoCl_2$	0.6	$MnCl_2$	2.5
$MgSO_4•7H_2O$	42	$NiSO_4$	0.04
$FeSO_4•7H_2O$	32	$ZnSO_4•7H_2O$	0.15

The sludge was pretreated by the following steps(applying a suitable amount of concentrated anaerobic sludge cultured device at the bottom of the anaerobic sludge, then cleaning by ultra pure water, standing for 30 minutes after the pour of the supernatant, repeated 3 times), the reserve sludge was obtained.

The crude EPS solution was contained by a refrigerated centrifuge method(the spare sludge pH : 11,slow mixing time – 10 minutes, then refrigerated centrifuge 15 minutes at 4 ˚C, 9000 r/min, filtering by 0.45 μm filter membrane later, retaining the filtrate).

The refinement of EPS: the crude EPS solution was obtained in the molecular weight cut-off of 8 000~14 000 dialysis bag, putting the dialysis bag into 1 L beaker, adding water 800 mL, magnetic stirring for 3 hours at a speed of 900 r/min, the water replaced every hour interval. The small molecular weight of EPS was removed by dialysis after 3 hours, the fine EPS solution was gotten. The colour of EPS solution obtained is slightly yellowish, the EPS concentration is 0.935g/mL by the test and analysis, the main components is protein and polysaccharide, it is agree with the results of experiment by Francois[1].

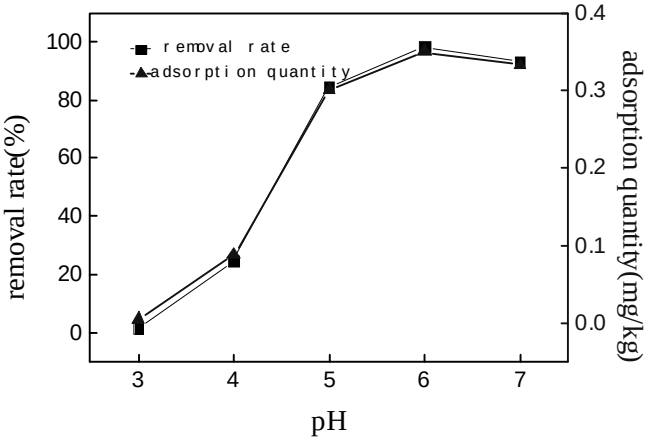
Preparation of uranium standard solution. The 1mg/mL standard uranium solution was prepared by using uranium reference reagents（U_3O_8）. It was diluted to the desired concentration as necessary in the experiment.

Test method for adsorption. The total solution is 100 mL including uranium standard solution, ultra pure water and quantitative EPS, adjusting the pH value , vibrating (150 r/min, 3 hours, 30 ˚C) in water bath box, sampling 50 mL to 8 000~14000 molecular weight cut-off of dialysis bag. The sample sealed with dialysis bag clip and ensured free of seepage, then the sample dialyzed 8 hours at 35 ˚C, mass concentration of uranium in water after dialysis was measured by atomic absorption spectrophotometry. The factors such as pH, the dosing quantity of EPS, initial concentration of uranium, dialysis temperature were discussed to the EPS adsorption effect of uranium, and the components of EPS were analyzed, the EPS were compared before and after adsorptive species in the inverted fluorescence display electronic microscope for morphology.

Results and discussion

Impact of pH on the adsorption effect. Adsorption can be effectively carried out only in the appropriate range of pH for the specific biological adsorbent[8]. Due to the alkaline conditions of uranium ions to produce hydroxide precipitation, It will seriously interfere with the effect of adsorption, this study examines the highest pH value of 7.The effect of pH for U (Ⅵ) adsorption was

investigated at a constant U (VI) concentration (20 mg/L), EPS dosage (6 mL).The results are shown in Fig. 1.



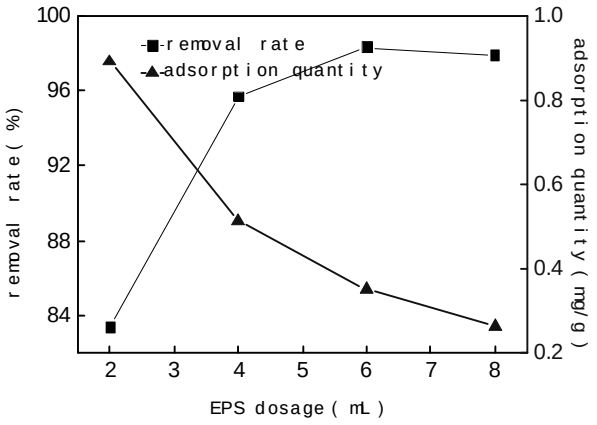


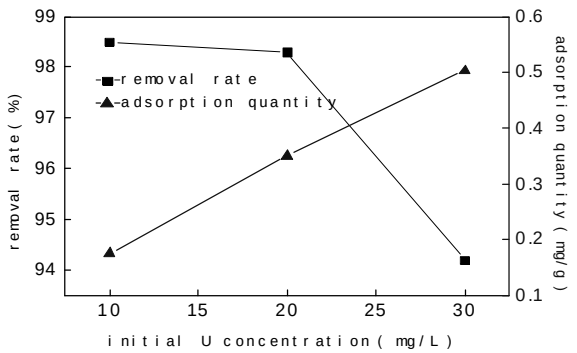
Fig.1 Effect of pH for U (VI) adsorption

Fig.2 Effect of EPS dosage for U (VI) adsorption

Fig. 1 shows the effect of pH on EPS adsorption of uranium significantly. When pH value is 3, the uranium removal rate is only 1.3%, the adsorption effect is poor, when the pH value is 6, the adsorption quantity is 0.35 mg/g EPS, the removal rate is up to 98.3%. The analysis show when pH is low, H^+ will occupy a large number of functional groups in EPS such as hydroxyl, carboxyl which can adsorb uranium, prevent the contact of the uranyl ion and the adsorption sites, furthermore, the H^+ made the EPS protonation, increasing surface repulsive force, so adsorbing ratio decreased.

EPS dosage effect on adsorption effect. The effect of sorbent dose on sorption process was studied by varying the sorbent dose from 2 to 8 mL at a constant U (VI) concentration (20 mg/L) and constant pH=6. The results are presented in Fig. 2.The dosage of EPS is 2 mL, adsorption capacity can reach 0.891 mg/g EPS, uranium removal rate has reached 83.3%; with the EPS dosage increase, the removal rate increases gradually , this reason is that the adsorbent dosage increase more conducive to U(VI) adsorption; The best adsorption effect can reach 98.3% when the dosage of EPS is 6 mL, The effect of increasing the EPS dosage on the removal rate is very small, the removal rate of measurement results drop to 97.9% and adsorption capacity is 0.262 mg/g EPS at this time, this may be the measurement error;This may be due to system U (VI) total unchanged, but the binding sites increases with the growth of amount of adsorbent, following the decrease of unit specific surface area, the mutual interference among groups also contributes to this trend.

The adsorption effect of different initial concentration of uranium. The effect of different concentrations of uranium on the sorption process was studied. The results obtained at pH = 6 and the EPS dosage(6 mL) are presented in Fig. 3.



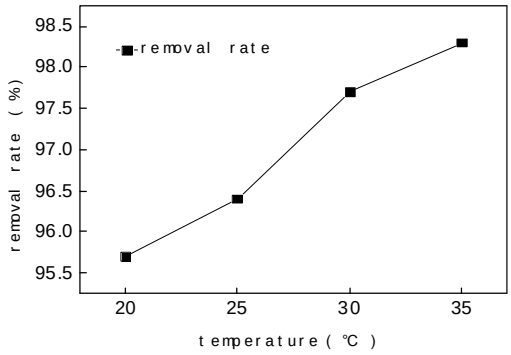


Fig.3 The adsorption ability under

Fig.4 Effect of dialysis for U (VI) adsorption

different U (VI) initial concentration

The removal rate of uranium (VI) decreases by degrees with initial U concentration increases, the highest removal rate is 98.5%, the lowest removal rate is 94.2%; the adsorption capacity increases with the initial concentration of U (VI) increases, the initial U (VI) concentration is 30 mg/L adsorption capacity can reach 0.503 mg/g EPS, when the initial concentration of uranium is 10mg/L, the adsorption quantity is 0.175 mg/g EPS. The increase of initial U(VI) concentration causes increase of the EPS adsorption uranium impetus effect, so the increase of adsorption.The removal rate of U (VI) drops as the concentration increases when the dosage of adsorbent is certain.

Effect of temperature on the adsorption effect of dialysis . The effect of temperature on sorption of dialysis was investigated at 20, 25, 30 and 35 ˚C, and the results obtained at U (VI) concentration (20 mg/L), constant pH= 7 , dialysis time(8 hours) and the EPS dosage(6 mL) are shown in Fig. 4. It can be observed that the adsorption rate is 95.7% at 20˚C, and 98.2% at 35˚C. The gap between the two is very small, the effect of temperature on adsorption effectvisible is very small. The molecular motion speed of the whole system faster with the increase of temperature, faster adsorption equilibrium, EPS is a kind of nonactivity, the main way for adsorption of uranium by complexation, ion exchange chelating , do not need to spend how much energy, the reaction is very fast, the effect of temperature is not obviously, can be carried out at room temperature.

Analysis of inverted fluorescence microscope. The EPS morphology changes was observed by using an inverted fluorescence electron microscopy in 400 times under the lens and contrast before and after adsorption of uranium, we can see that the color deepened after the EPS adsorption of uranium, EPS combines a number of uranium.It can be inferred from the experiments with NaOH extracted with EPS is a reticular cloverleaf structure, porosity, specific surface area is large, which is favorable for the development of adsorption, complexation reaction etc.

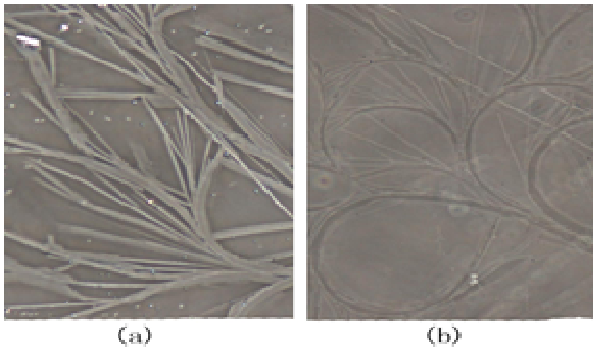


Fig.5 Observe the form of EPS under microscope (a) before U (VI) adsorption, (b) after U (VI) adsorption

Conclusions

Anaerobic sludge EPS extracted by NaOH method, showed good adsorption properties of uranium, when the initial uranium concentration is 20 mg/L at pH 6 with EPS dosage of 18.7 g/L, the adsorption capacity of uranium reached 0.891 mg/g EPS; when the initial concentration of uranium is 20mg/L at pH 6 with EPS dosage of 56.1 g /L, the uranium removal rate is up to 98.3%.

The pH is one of the most important factors influencing the uranium adsorption of EPS, The adsorption effect is the best when the pH value is 6, nevertheless , the adsorption effect are not good when the pH value is below 3.

The effect of temperature on the adsorption of EPS is not obvious, the highest removal efficiency under 35 ˚C is only 2.8% higher than under 20˚C.

It Can be inferred from the observed by inverted fluorescence microscope, EPS extracted using this method is a structure of net interchange, pore specific and surface area are great, beneficial to adsorption reaction.

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