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Recycle of Alum recovered from water treatment sludge in chemically enhanced primary treatment

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ABSTRACT

An investigation was made to study the feasibility of recovering the Alum from coagulation sludges and reusing it in chemically enhanced primary treatment (CEPT) process to make the CEPT more cost-effective and recover the resource (Alum) efficiently. The optimum condition and efficiency of the acidification method for Alum recovery from coagulation sludge were investigated in the test. The results show that when the recovery rate of Alum reaches its highest level, 84.5%, the reduction rate of sludge is 35.5%. It turns out that the capability of recovered coagulant to remove turbidity, UV_{254} and COD are 96%, 46% and 53%, respectively. The results prove that the recovered coagulants could be used in CEPT and the efficiency of recovered coagulant to remove pollutants is similar to that of fresh coagulant. Although some substances will be enriched during recycle, they have little effect on the quality of treated wastewater. The experiments verify that it would be an advisable and cost-effective way to recover Alum from coagulation sludges in water treatment and chemical wastewater treatment, and it could be then recycled to CEPT as well as reduce sludge volume.

1. Introduction

Chemically enhanced primary treatment (CEPT) for municipal wastewater treatment is cost-effective and particularly suitable for rapidly growing mega-cities and developing countries, which could be used as an alternative for traditional wastewater treatment processes [1,2] and should be paid more attention to. The removal of suspended solid (SS), colloid and total phosphorus (TP) is significant with CEPT process: SS removal is about 90%, and TP is 80–90%. The main problems of CEPT are the costs of chemicals and the production of excessive sludge volumes. Conventional chemical treatment processes produce about 1.5–2.0 times more sludge than that produced by conventional primary treatment [3,4].

The cost of waste sludge disposal is a major factor in the operational cost of wastewater treatment plants, 30–50% of the annual operating costs are related to sludge dewatering alone [5]. Coagulation Sludge (after coagulation in water treatment and CEPT process) contains a large amount of coagulant, so the sludge as resource recovered from CEPT could be an effective way to reduce the disposal sludge volume as well as save the dosage cost [6]. Generally, four ways of coagulant recovery employed for water treatment in recent years are acidification, basification, ion exchanging, and membranes.

The principle of coagulation involves adding coagulant which form aluminum hydroxide and within the flocs of the hydroxide, the destabilized colloids are enmeshed, and acidification involves neutralizing these flocs of hydroxide to release aluminum salt back in the solution including the release of some parts of the contaminants/heavy metals/TOC, etc.

Acidification is a high efficiency and low cost method for the recovery of coagulants among the four methods mentioned above. It is used firstly to recycle metal ions from water treatment sludge at a low pH value [7–11]. It mainly contains three steps [9,10]: dewatering, acidification and separation. Some researchers claim that the efficiency of acidification to extract Alum salt from sludge is high when pH is low [8].

Some researchers focused on the recovery of coagulants from drinking water treatment and its reuse in drinking water treatment several years ago [12,13]. However, as the quality requirement for drinking water is stringent, and harmful substances are increased during coagulant recycling, it is rare to use the recovery method for drinking water treatment nowadays, unless the quality of raw water is high, but recycled coagulant used in CETP could be possible. Although the enrichment of harmful substances may have some negative impact on water quality, the requirement for the quality of treated wastewater is not as stringent as that for drinking water.

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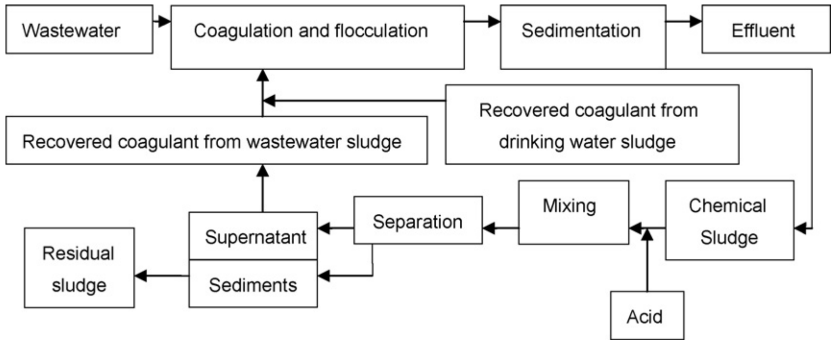

Fig. 1. Flow chart of recycle of Alum recovered from water treatment sludges in chemically enhanced primary treatment.

Table 1
Quality of raw water samples from Songhua River

Turbidity (NTU)	Color (HU)	Temperature (°C)	pH	TOC ($mg L^{-1}$)	UV_{254} (cm^{-1})
65–75	16–19	19–21	7.1–7.6	9.1–9.5	0.305–0.59

In this research, acidification is employed for the recovery of Alum coagulant from coagulation sludge produced from water and wastewater treatment. The recovered coagulant will be reused in chemical wastewater treatment to study the feasibility and efficiency of the removal of the pollutants by recovered coagulant, the impact of acidification on the reduction of sludge volume is also investigated. The flow chart was shown in Fig. 1.

2. Reagents and methods

2.1. Quality of water samples

Water samples used for the preparation of sludge from water treatment were collected from Songhua River, China, which has the same quality as the raw water used at the drinking water treatment plant in Harbin, China. The quality of water samples is shown in Table 1.

The wastewater samples for the experimentation of recovered coagulants from sludge in CEPT were collected from the resident zone of Harbin Institute of Technology. The wastewater quality is shown in Table 2.

Four different kinds of raw water were prepared by adding humic acid (HA) and heavy metals in raw river water. The qualities of each kind of raw water are listed in Table 3.

2.2. Reagents

All the reagents used in this study are analysis grade, except for the acid used in ICP-AES for heavy metals detection, which is chromatogram grade. The dosage of coagulant is measured in mass of Al.

Table 3
Quality of raw water samples ($mg L^{-1}$)

Water samples	HA	Hg	Cd	Cr	Pb
Raw water I	—[a]	—[a]	—[a]	—[a]	—[a]
Raw water II	—[a]	—[a]	—[a]	0.05	—[a]
Raw water III	5	—[a]	—[a]	—[a]	—[a]
Raw water IV	0.1	0.001	0.005	0.05	0.05

—[a] Not added.

2.3. Methods

All the analysis methods employed in this study for detection of water quality are according to Standard Methods for Examination of Water and Wastewater, 20th edition, prepared and published by APHA, AWWA and WEF, 1998.

(1) The hydraulic condition for coagulation in this study is fixed as shown below:
River water treatment:
500 rpm 30 s(G: 332.0; GT: 9960); 400 rpm 30 s(G: 246.0; GT: 17340); 300 rpm 30 s(G: 167.1; GT: 22353); 200 rpm 30 s(G: 96.8; GT: 25257); 100 rpm 2 min(G: 38.1; GT: 29829); 50 rpm 2 min(G: 15.0; GT: 31629); 30 rpm 5 min(G: 7.6; GT: 33909); 15 min, for sedimentation.
Wastewater treatment:
400 rpm 10 s(G: 246.0; GT: 2460); 120 rpm 1 min(G: 50.7; GT: 5682); 80 rpm 5 min(G: 28.2; GT: 14142); 50 rpm 10 min(G: 2.51; GT: 15648); 30 min, for sedimentation.
(2) All the sludge samples were prepared by centrifuging water samples at 3500 rpm for 5 min after coagulation and sedimentation with a certain amount of coagulant. Sludge samples were stored at 4 °C for further study.
(3) The acid used in this research is H_2SO_4, and the concentration is 1 M. The acid was added while the sludge was mixed simultaneously and it will be stopped as the pH of solution reached at certain value. During acidification, all the sludges were kept quiescent for 15 min after being adjusted to a certain pH. Afterward the adjusted sludges were being mixed at 170 rpm for a specific time and then centrifuged at 4000 rpm for 10 min.

Table 2
Quality of wastewater from resident zone

	Turbidity (NTU)	Color (HU)	Temperature (°C)	pH	COD_{Cr} ($mg L^{-1}$)	$SCOD_{Cr}$ ($mg L^{-1}$)	UV_{254} (cm^{-1})
Raw water	112				502.36	189.66	0.622
Settled water	73	56–72	15–22	7.1–7.9	355.65	178.55	0.585
Removal rate (%)	34.82				29.2	5.86	5.88

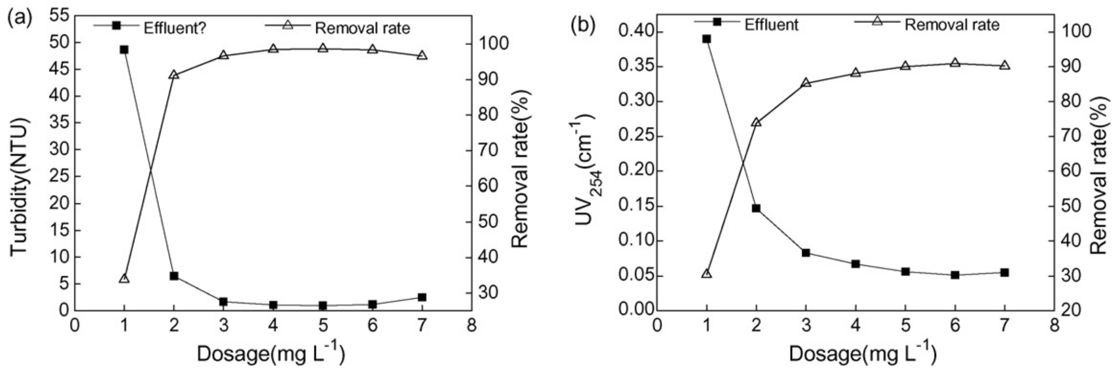

Fig. 2. Effect of $Al_2(SO_4)_3$ dosages on coagulation properties in water treatment. (a) Removal of turbidity and (b) removal of UV_{254}.

(4) The pH of the recovered coagulant solution is only a little higher to the pH of the initial acidified mixture. All the recovered coagulants with different concentrations were diluted to 8000 mg L^{-1} when it was stored at 4 °C. When the recovered coagulant was added to raw water it was diluted to 1000 mg L^{-1}. It has little affection to the pH value of treated water.

3. Results and discussion

3.1. Preparation of sludges

3.1.1. Preparation of sludge from water treatment

3.1.1.1. Optimum dosage and preparation of sludge. It can be seen that dosage 3–6 mg L^{-1} is the best dosage range (Fig. 2), and the optimum dosage of $Al_2(SO_4)_3$ was selected as 4 mg L^{-1} (measured by Al). The optimum dosage of $Al_2(SO_4)_3$ was added to each water samples for coagulation. The qualities of four kinds of sludges prepared from four kinds of raw water are listed in Table 4.

Table 4
Contents of heavy metals in water treatment sludges (mg g^{-1} dried sludge)

Sludges	Fe	Al	Hg	Cd	Cr	Pb
Sludge I	0.85	4.72	—[a]	0.00001	0.0050	0.0057
Sludge II	0.86	4.86	—[a]	0.00001	0.0099	0.0058
Sludge III	0.52	4.53	—[a]	0.00007	0.0050	0.0056
Sludge IV	0.57	4.57	—[a]	0.00197	0.0095	0.0281

—[a] Not detected.

3.1.2. Preparation of sludge from chemical wastewater treatment

3.1.2.1. Optimum dosage and preparation of sludge. It can be seen (Fig. 3) that as the dosage of $Al_2(SO_4)_3$ is over 10 mg L^{-1}, all the parameters of treated wastewater quality are satisfactory,

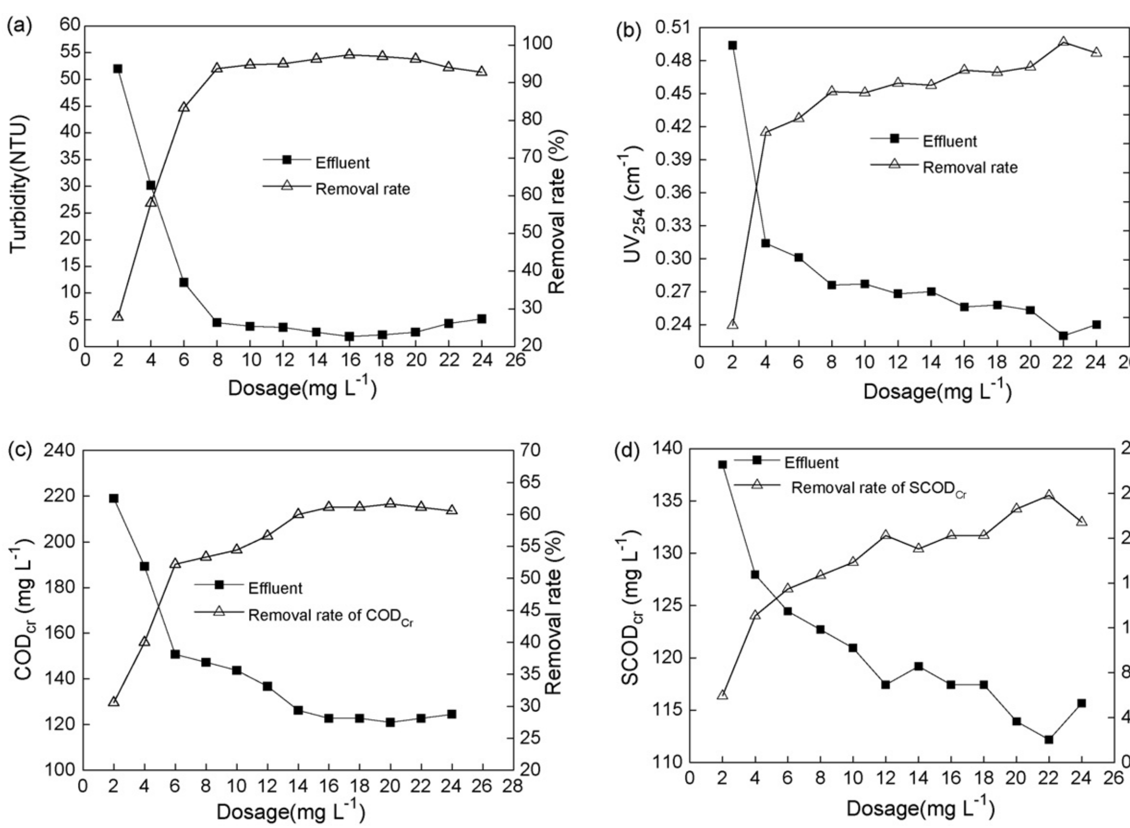

Fig. 3. Effect of $Al_2(SO_4)_3$ dosages on coagulation properties in wastewater treatment. (a) Removal of turbidity, (b) removal of UV_{254}, (c) removal of COD_{Cr} and (d) removal of $SCOD_{Cr}$.

and the optimum dosage is selected at 12 mg L^{-1}. The optimum dosage of $Al_2(SO_4)_3$ (12 mg L^{-1}) was added to each water sample for coagulation, and after centrifugation the sludges were stored at 4 °C.

3.2. Recovery of Alum coagulant

3.2.1. Optimum pH for recovery

The recovery rates of Alum coagulant in sludges from both water and wastewater treatment were observed at a series of pH levels for 1 h acidification in order to obtain the optimum pH level for recovery of Alum coagulant. The relationship between pH value and recovery rate of coagulant in sludge is shown in Fig. 4a.

From Fig. 4a it can be seen that with the decline of pH value the recovery rate of coagulant from sludge increases. In the sludge from water treatment, when pH is 2.5 the recovery rate is 83.6%. When the pH value continues to decline after it has reached 2.5, the recovery rate will not increase significantly. So the optimum pH for recovery of coagulant in sludge from river water treatment is selected at 2.5.

It also can be seen that when pH for acidification is 2.5 the recovery rate is 84.2% in sludge from wastewater treatment, which is comparable to that of coagulant in sludge from water treatment.

3.2.2. Optimum mixing time for recovery

Sludge samples were acidified and adjusted to initial pH 2.5, and then they were kept quiescent for 15 min after being adjusted to pH 2.5 and prepared for a series of mixing times. The recovery rates in sludge were observed, and the results are shown in Fig. 4b.

As it is shown in Fig. 4b, in the acidification of sludge from water treatment when the mixing time is 30 min the recovery rate is about 80%. When the mixing time is over 30 min the recovery rate only increases slightly. So the optimum mixing time for acidification is sited at 30 min in this study.

When mixing time is 30 min for the acidification of sludge in wastewater treatment the recovery rate of Alum coagulant is 65.9%. When the mixing time has reached 60 min the recovery rate is 83.5%, and it only increases slightly with the increase of mixing time afterward. Thus the optimum mixing time for recovery of coagulant in sludge from wastewater treatment is selected as 60 min.

It is obvious that the mixing time for coagulant recovery in sludge from wastewater treatment is as much as twice that of the mixing time for coagulant recovery in sludge from water treatment. This may be due to the high content of pollutants in wastewater which significantly slow down acidification.

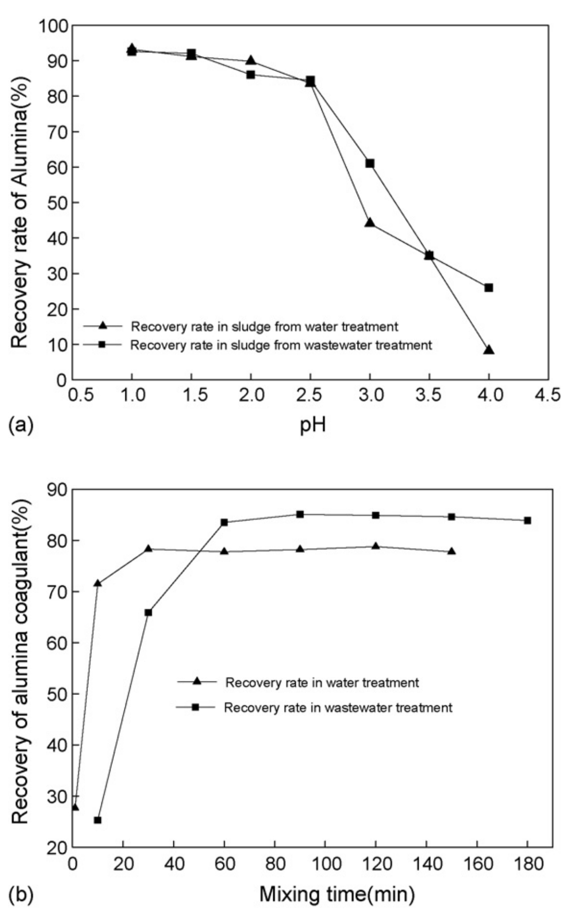

Fig. 4. Impact of pH and mixing time on the recovery rate of Alum in sludges. (a) Impact of initial pH on the recovery rate of Alum in sludges and (b) impact of mixing time on the recovery rate of coagulant in sludges.

3.2.3. Impact of sludge qualities on recovery of Alum coagulant

Four different kinds of sludge prepared from water were acidified, and then the recovery rates of coagulant from these sludges were measured. The results are shown in Fig. 5.

From Fig. 5 it can be seen that when the pH for acidification is high, the recovery rate in sludge III and IV is lower than that in sludge I and II. This is because the HA added in raw water of sludge III and IV effect the reaction between Alum coagulant and acid. When the pH for acidification is low, the differences between the recovery rates in four kinds of sludges are not significant. When the pH is 2.5, the recovery rates are 83.6%, 58.3%, 80.8% and 79.6%, respectively.

3.2.4. Relationship between reduction of sludge and recovery of Alum

During acidification Alum and some substances in sludge are dissolved out, so a significant reduction of sludge is expected, which is very valuable for reduction of operation cost. In this study the relationship between reduction of sludge and pH was obtained, and the results are shown in Fig. 6a.

Because most of the substances dissolved during acidification are metals, the reduction of sludge should have a close relationship to the recovery rate of coagulant. So the relationships between recovery rate and reduction of sludge were observed, and the results are shown in Fig. 6b.

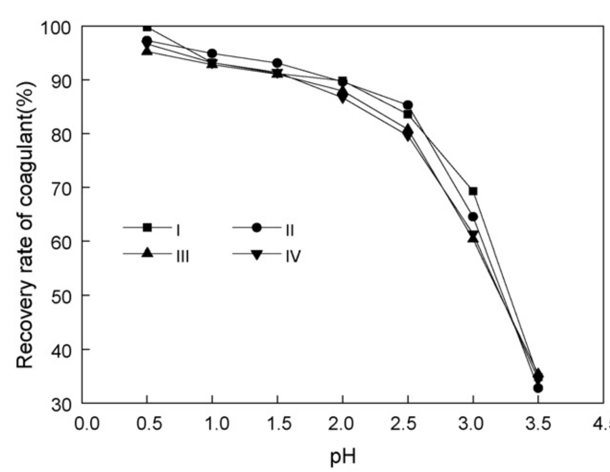

Fig. 5. Recovery rate of Alum in four kinds of sludges prepared from water treatment.

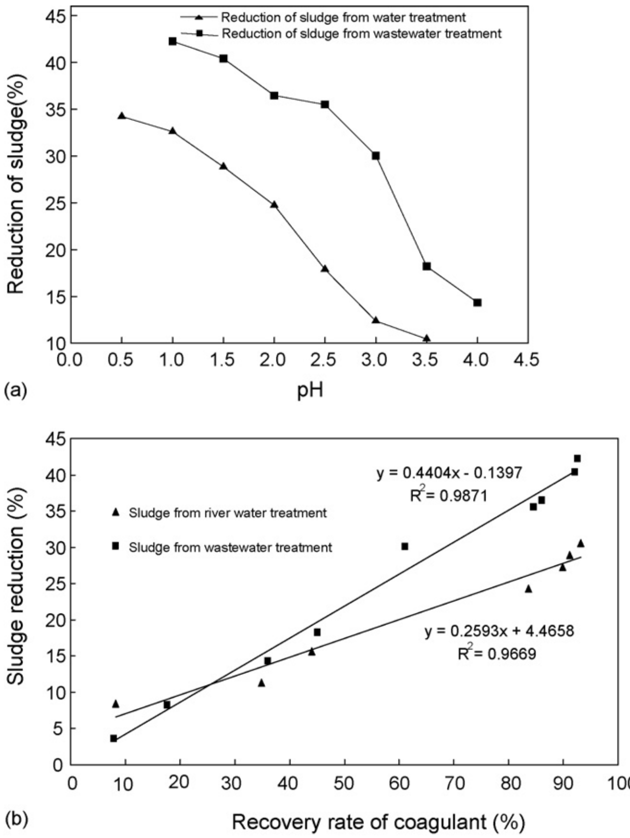

Fig. 6. Reduction of sludges by pH and its relationship to the recovery of Al coagulant. (a) Impact of pH on reduction of sludges and (b) relationship between sludge reduction and recovery of Al coagulant.

In Fig. 6b it is obvious that there is a linear relationship between reduction of sludge and coagulant recovery. With the increase of the recovery rate of Alum coagulant the reduction of sludge increases. For example, when the recovery rate is 84.5% the reduction of sludge is 35.5%. As the recovery rate is the same, the sludge reduction rate in water sludge is less than that in wastewater sludge. The reason may be that the Alum dosage in water treatment is less than that in wastewater treatment.

3.2.5. *Repeated recoveries of coagulant*

In order to test the impact of repeated recoveries of Alum on sludge reduction and coagulant recovery, coagulant was recovered repeatedly 4 times, and the recovery rate and sludge reduction were obtained. The results are shown in Fig. 7. It is showed that the recovery rate of coagulant and sludge reduction have little decline with the increase of the frequency of coagulant recovery.

3.3. *Analysis of recovered coagulants*

During acidification some organic compounds such as HA and metals such as Cr, Pb and Mn are recovered together with coagulant. So the recovered coagulant has relatively high color and heavy metal contents. When the coagulant recovered from sludge is employed in water treatments, the heavy metals and organic compounds will possibly enriched in treated water and therefore impact the water quality. Thus, here the influence of the heavy metals in the recovered coagulant was analyzed.

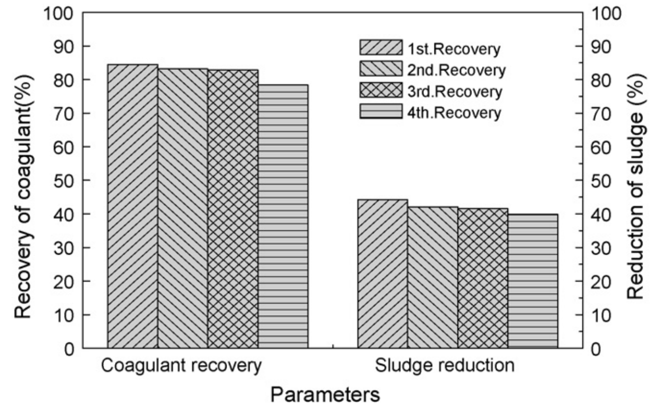

Fig. 7. Alum recovery and sludge reduction within four continuous recovery cycles.

3.3.1. *Content of heavy metals in recovered coagulant*

The contents of heavy metals in both fresh coagulant and coagulants recovered from each kind of sludges were measured in order to obtain the differences between fresh coagulant and recovered coagulant. The results are shown in Table 5.

It can be seen in Table 5 that all the levels of heavy metals in recovered coagulants are higher than that in fresh coagulant. The coagulant recovered in the sludge prepared from raw river water which did not have heavy metals added contains a bit higher level of Cr than that in fresh coagulant. As 0.05 mg L^{-1} of Cr was added to water sample II and IV, recovered coagulant II and IV contains as about 4 times the amount of Cr as that in coagulant I and III. Hg cannot be detected in any of the coagulants. The contents of Fe and Mn in recovered coagulants are obviously higher than that in fresh coagulant.

The high level of heavy metals in recovered coagulant may be for two reasons. Firstly, raw water contains some heavy metals, and naturally the coagulant recovered from the sludge prepared from raw water will have a higher concentration of heavy metals. Secondly, the HA contained in raw water has a strong adsorption capability for heavy metals, and when they are combined together they will easily to be separated in water treatment and enriched in sludge. Therefore the existence of HA in raw water enhances the separation of heavy metals during coagulation, and will probably increase the concentration of heavy metals in recovered coagulants.

Also the raw water usually contains relatively high levels of Fe at test site, so it will be enriched in the recovered coagulant. Its function is in a similar way as Alum, but the Fe concentration is much lower than the amount of the recovered Alum coagulant, so the main function of the coagulation is caused by recovered Alum coagulant although Fe is positive to the coagulation.

3.3.2. *TOC and UV_{254} in recovered coagulant*

TOC and UV_{254} in recovered coagulants were measured in order to evaluate the content of organic compounds in coagulants recov-

Table 5
Contents of metals in coagulants (μg mg^{-1} Al)

Metals	Fresh coagulant	Recovered coagulant			
		I	II	III	IV
Cr	0.015	0.033	0.136	0.031	0.116
Cd	0.009	0.010	0.008	0.011	0.226
Hg	—[a]	—[a]	—[a]	—[a]	—[a]
Pb	0.02	—[a]	—[a]	—[a]	1.655
Fe	18.3	168	173	156	149
Mn	0.2	3.12	3.25	3.12	3.06

—[a] Not detected.

Table 6
TOC and UV_{254} in recovered coagulants from water treatment sludge

Parameters	Recovered coagulant in sludge from river water treatment				Coagulant of repeated recovery			
	I	II	III	IV	1st	2nd	3rd	4th
TOC ($mg\,L^{-1}$)	340.6	340.4	366.7	369.3	403.1	446.6	492.8	550.2
UV_{254} (cm^{-1})	0.384	0.382	0.389	0.398	0.225	0.233	0.256	0.269

ered from different sludges and to measure the changes of organic concentration during repeated recoveries. The results are shown in Table 6.

It can be seen in Table 6 that TOC level in coagulant III and IV is higher than that in coagulant I and II, due to coagulant III and IV being recovered from water samples III and IV in which HA was added. Thus it can be said that the amount of organic compounds in recovered coagulant strongly depends on quality of raw water.

As the cycles of coagulant recovery increase, TOC content in recovered coagulant increases gradually. After the fourth recovery cycle, TOC has increased from 403.1 to 550.2 $mg\,L^{-1}$, which demonstrates that organic compound amount will be enriched during repeated recoveries. It also can be seen in Table 6 that TOC in recovered coagulant from sludge in wastewater treatment is higher than that of recovered coagulant from sludge in river water treatment. The reason is that there is a high level of organic compounds in wastewater.

The UV_{254} value of coagulant recovered from sludge (raw water with HA added) is not significantly higher than that in other coagulants. The reason is probably that HA is easy to remain in sludge at low pH during acidification. So the content of HA in recovered coagulant whose raw water contained HA is only a little higher than that in fresh coagulant.

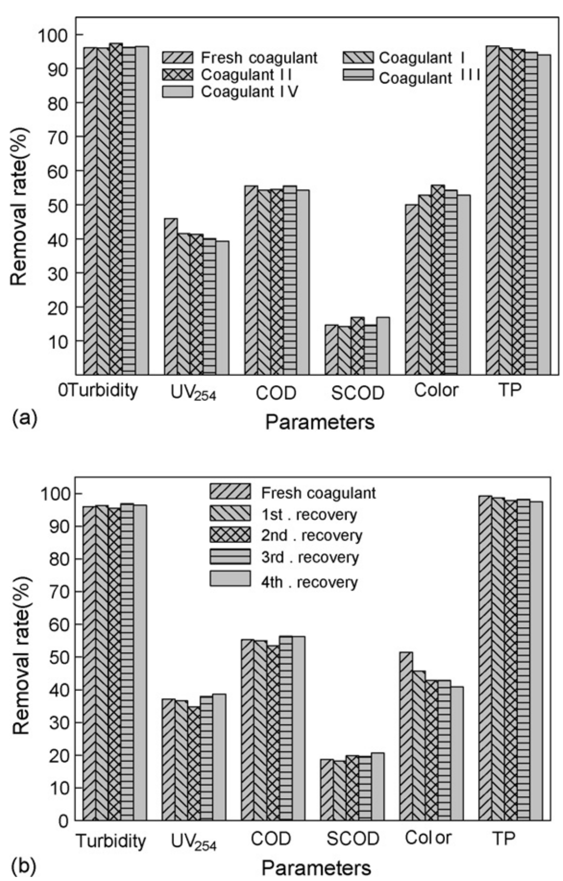

Fig. 8. Efficiencies of recovered coagulants in wastewater treatment. (a) Efficiency of coagulant recovered from river water treatment and (b) efficiency of coagulant recovered from wastewater treatment.

3.3.3. *Efficiency of recovered coagulant in CEPT*

Recovered coagulants were used at wastewater treatment by the optimum condition obtained in this study. Then qualities of treated wastewater were measured, and the results are showed in Fig. 8.

In Fig. 8a turbidity of all the treated wastewater is lower than 3NTU, and the removal rates are all above 96%. The efficiency of recovered coagulant to remove turbidity is a bit higher than that of fresh coagulant. This is because during acidification some metal ions such as Ca^{2+}, Mg^{2+}, Fe^{3+} are recovered together with Alum coagulant, and those are positive for the removal of turbidity. Fresh coagulant has the highest efficiency to remove UV_{254}, which is 46%. The efficiencies to remove COD_{Cr} and $SCOD_{Cr}$ by all the coagulants are similar. All the coagulants are good at removing TP, and all the removal rates of TP are more than 94%. Water treated by coagulant IV contains 0.0005 $mg\,L^{-1}$ of Cr, 0.0011 $mg\,L^{-1}$ of Cd and 0.0082 $mg\,L^{-1}$ of Pb.

In Fig. 8b it can be seen that there are no obvious differences between the efficiencies of fresh and recovered coagulants by the increasing of repeated cycles to remove turbidity, and the turbidities of all the treated wastewaters are about 4NTU. Each coagulant has removal rate of UV_{254} over 34%. The removal rate of COD_{Cr} and $SCOD_{Cr}$ are about 53% and 18%, respectively for all the coagulants. With increased cycles of recovery, the efficiency of recovered coagulant to remove color declines slightly.

4. Conclusions

Acidification can effectively recover Alum from sludge of both water and wastewater treatment. In addition, during Alum recovery, sludge volume is significantly reduced. The quality of treated wastewater by recovered and fresh coagulant is similar, and the effect of recovered coagulant might be better than that of fresh coagulant in some respects, such as turbidity removal. The tests show that it could be a better way to recover resource and reduce sludge volume for the recovery of Alum from the sludges of water treatment and chemical wastewater treatment. More importantly, the recycling of the recovered Alum to chemical wastewater treatment could make the CEPT process more cost-effective.

References

[1] D. Harleman, S. Murcott, The role of physical-chemical wastewater treatment in the mega-cities of the developing world, Water Sci. Technol. 40 (1999) 75–80.
[2] C.S. Poon, C.W. Chu, The use of ferric chloride and anionic polymer in the chemically assisted primary sedimentation process, Chemosphere 39 (1999) 1573–1582.
[3] J.C. Huang, L. Li, An innovative approach to maximize primary treatment performance, Water Sci. Technol. 42 (2000) 209–222.
[4] L. Semerjian, G.M. Ayoub, High-pH-magnesium coagulation-flocculation in wastewater treatment, Adv. Environ. Res. 7 (2003) 389–403.
[5] L.H. Mikkelsen, K. Keiding, Physico-chemical characteristics of full scale sewage sludges with implications to dewatering, Water Res. 36 (2002) 2451–2462.
[6] G.R. Xu, W.T. Zhang, G.B. Li, Absorbent obtained from CEPT sludge in wastewater chemically enhanced treatment, Water Res. 39 (2005) 5175–5185.
[7] M.M. Bishop, A.T. Rolan, T.L. Bailey, D.A. Cornwell, Testing of alum recovery for solids reduction and reuse, J. AWWA 79 (1987) 76–83.

[8] T. Panswad, Aluminium recovery from industrial aluminium sludge, Water Supply 10 (1992) 159–166.
[9] P.G. Fulyon, Recover alum to reduce waste-disposal costs, J. AWWA 66 (1974) 312–318.
[10] M.S.E. Abdo, K.T. Ewida, Y.M. Youssef, Recovery of alum from wasted sludge produced from water treatment plants, J. Environ. Sci. Health A 28 (1993) 1205–1216.
[11] C.W. Li, J.L. Lin, S.F. Kang, C.L. Liang, Acidification and alkalization of textile chemical sludge, Sep. Purif. Technol. 42 (2005) 31–37.
[12] D. Cornwell, J. Susan, Characteristics of acid-treated alum sludges, J. AWWA 71 (1979) 604–608.
[13] W. Chu, Lead metal removal by recycled alum sludge, Water Res. 33 (1999) 3019–3025.