# The performance of enhanced coagulation for treating slightly polluted raw water combining polyaluminum chloride with variable charge soil

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## ABSTRACT

The feasibility and effectiveness of treating pollutants in slightly polluted raw water by variable charge soil and polyaluminum chloride (PAC) was investigated. Removal efficiencies of turbidity, phenol, aniline, algae and heavy metals ($Cu^{2+}$, $Zn^{2+}$ and $Pb^{2+}$) were used to evaluate the coagulation performance. The results indicated that the addition of variable charge soil as a coagulant aid is advantageous due to the improvement of removal efficiencies. The tests also demonstrated that the presence of variable charge soil increased the removal of turbidity rather than adding residuary turbidity. The use of variable charge soil produced settleable flocs of greater density and bigger size. The main mechanism involved in the PAC coagulation was supposed to be sweep flocculation as well as charge-neutralization. Variable charge soil played a promoted aid role by adsorption in the enhanced coagulation process. It is concluded that the enhanced coagulation by PAC and variable charge soil, as coagulant and adsorbent, is more effective and efficient than traditional coagulation.

**Key words** | enhanced coagulation, PAC, pollutants removal, variable charge soil

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## INTRODUCTION

Water is considered as an important and scarce resource around the world. Natural waters contain many different compounds, both natural and anthropogenic (Tomaszewska *et al.* 2004), such as organic matter, algae, heavy metals. Most of these compounds are hazardous and bio-refractory products, which might cause adverse effects on public health and environmental safety. Moreover, heavy metal ions are an important issue in drinking water and have received significant attention for environmental applications (Jiang *et al.* 2014). To reduce its influence directly or indirectly, available and effective methods have to be developed.

Historically, coagulation has been used for particle and turbidity removal, drinking water regulations have emerged expanding the use of this process beyond its traditional role (Uyak *et al.* 2007). Nowadays, a better strategy, enhanced coagulation, has been reported, which has been identified as among the best available techniques for removal of disinfection by-product precursor in water treatment (Yan *et al.* 2008; Yu *et al.* 2011; Aryal *et al.* 2012). In addition, polyaluminum chloride (PAC) has been found to be superior to the traditional aluminum (Al)-based coagulants for particulate and/or organic matter removal under some conditions (Yan *et al.* 2008). On the other hand, previous studies have used PAC with clay or diatomite to removal algae (Jiang & Kim 2008; Wu *et al.* 2011).

Variable charge soil, distributed over large areas in tropical and subtropical regions of Southern China (Yu *et al.* 2004), was chosen as the coagulant aid in the present study. As previous researches reported, variable charge soil, which is rich in iron (Fe) and Al oxides, usually carries both positive and negative charges on its surface and thus can absorb both anions and cations under some conditions (Jiang *et al.* 2012). Variable charge soil has been investigated for treatment of *p*-nitrophenol (Zhang *et al.* 2014), pentachlorophenol (Hyun & Lee 2004) and organic acids (Hyun & Lee 2004). In addition, adsorption of heavy metal ions such as $Cu^{2+}$, $Pb^{2+}$ and $Cd^{2+}$ has been studied; (Ugochukwu *et al.* 2012; Bolan *et al.* 2013; Xu & Zhao 2013). However, researches on a combination of PAC and variable charge soil have been hardly reported so far.

The principal objective of this paper was to study the feasibility and effectiveness of combined processes of variable charge soil-adsorption with PAC-coagulation in the

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treatment of turbidity, phenol, aniline, algae and heavy metals. The zeta potential of the flocs was also conducted for a better understanding the mechanisms.

## METHODS

### Test water

Model water was prepared with tap water and kaolin suspension until a specific concentration of turbidity was achieved. The model water had the following characteristics: turbidity $= 20.5 \pm 0.5$ NTU, pH $= 7.7 \pm 0.2$, temperature $= 20 \pm 1$ °C, zeta potential $= -13.6 \pm 1.0$ mV, conductivity $= 77.8 \pm 1.0$ μS/cm, alkalinity $= 79.6 \pm 2.0$ mg/L. In the case of evaluating the removal efficiencies of different matter such as phenol, aniline, algae, $Cu^{2+}$, $Zn^{2+}$ and $Pb^{2+}$, these were added to achieve specific initial concentrations.

### Chemicals and coagulants

Variable charge soil was obtained from Guangzhou, China. Soil samples were collected from a depth of 20–40 cm within the soil profile, air dried at room temperature, crumbled gently, passed through a 100-mesh sieve, and then stored in jars for experimental use. Some basic characteristics such as organic compounds, main chemical composition, organic matter, cationic exchange capacity (CEC), Brunauer, Emmett, Teller surface, X-ray powder diffraction analysis and Fourier transform infrared spectroscopy analysis, can be found in Zhang *et al.* (2014).

The stock solution of PAC (containing 30% as $Al_2O_3$, stock solution 5 g/L as Al) was prepared in deionized water. The stock solution of $Al_2(SO_4)_3$ (5 g/L as Al) was prepared by directly dissolving $Al_2(SO_4)_3 \cdot 18H_2O$ into deionized water. Aqueous stock solutions of phenol and aniline were 1.0 g/L and 3.5 g/L, respectively. The stock solutions of 0.50 g/L $Pb^{2+}$, 0.75 g/L $Zn^{2+}$ and 1.00 g/L $Cu^{2+}$ were prepared from $Pb(NO_3)_2$, $Zn(NO_3)_2 \cdot 6H_2O$ and $CuSO_4 \cdot 5H_2O$.

*Microcystis aeruginosa* (obtained from the Institute of Hydrobiology, Chinese Academy of Sciences) was cultivated in axenic BG11 (Blue-Green Medium) at $24 \pm 1$ °C under fluorescent light (1,000 lx, 12 h light/12 h dark). The composition of BG11 medium was the same as previously reported (Wu *et al.* 2011). All model water experiments were carried out with the cells in the late exponential growth stage.

### Jar test

Coagulation was conducted by using a jar test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd, CHN) under different conditions. Each 1.0 L solution was subjected to rapid mixing (200 rpm) for 2 min, and then continuously rapidly mixed for 30 s, followed by a slow mixing for 30 min at 30 rpm, and at last a settling for 30 min. Variable charge soil and PAC were added before and after the first mixing step, respectively. Zeta potential of flocs was analyzed before the slow mixing step. After sedimentation, the supernatant sample was carefully withdrawn for measurements of turbidity, phenol, aniline, algae, $Cu^{2+}$, $Zn^{2+}$ and $Pb^{2+}$. The water samples were prefiltered using 0.45 μm fiber membranes before testing phenol, aniline, $Cu^{2+}$, $Zn^{2+}$ and $Pb^{2+}$.

### Analytical methods

Turbidity was measured by using a 2100AN Turbidimeter (Hach, USA). pH value was determined in a PHS-3C meter (Shanghai Precision Instruments Co. Ltd, CHN). Zeta potential was analyzed with a Zetasizer ZS90 (Malvern Instruments, UK). A particle size and shape analyser (Eye Tech, Ankersmid, The Netherlands) was used to monitor the floc size during the flocculation process. The concentration of phenol or aniline was analyzed by using a UV-visible spectrophotometer (UV-5800, Metash, CHN). Blanks were also used.

For chl-a analysis, samples were pump filtered through a 0.45 μm filter and the membranes containing chlorophylls were extracted using 20 mL acetone (90%). After centrifuging for 10 min (5,000 rpm), the optical densities of the extracts were measured at 665 and 750 nm by using a spectrophotometer (Lorenzen 1967). And a blank with deionized water was run prior to sample analysis.

A Perkin Elmer Optima 5300DV (USA) inductively coupled plasma-optical emission spectrometer instrument with AS-90 plus autosampler was used to determine concentrations of $Cu^{2+}$, $Zn^{2+}$ and $Pb^{2+}$ in the permeate (Wu *et al.* 2011).

## RESULTS AND DISCUSSION

### Removal of turbidity

Initially, optimization tests were performed to ascertain the optimum type and dosage of coagulant on the basis of removal of turbidity. Figure 1 showed the effect of coagulant dosage (2 to 30 mg/L) of PAC and $Al_2(SO_4)_3$ on removal efficiencies of turbidity and zeta potential of flocs. For $Al_2(SO_4)_3$, it can be seen that the removal of turbidity increased slightly at a low dosage and then decreased with further increase of the dosage, reaching the highest removal of turbidity (95.0%) at 10 mg/L. In the case of PAC, the removal of turbidity increased rapidly and remained at a relatively high efficiency beyond 97.1% during the test range. The zeta potential of the two kinds of flocs showed a parallel increasing trend, while the zeta potential of PAC flocs were lower than that of $Al_2(SO_4)_3$ constantly. Flocculation with $Al_2(SO_4)_3$ or PAC has been suggested to be achieved by the mechanism of charge-neutralization and bridge-formation (Gao *et al.* 2005). In this study, high removal efficiencies of turbidity by PAC were achieved, although zeta potentials of the flocs were rather positive. The results can be explained by sweep flocculation mechanism playing a key role, owing to the precipitation of amorphous hydroxide. When zeta potential further increased, the positive charge became more dominant, which led to electrostatic repulsion between particles (Zhao *et al.* 2011).

Then, enhanced coagulation combined PAC with variable charge soil was investigated, with increasing dosage (0 to 100 mg/L) of the soil under conditions of three kinds of PAC dosages (Figure 2). For the enhanced coagulation, great turbidity reduction was achieved. When the dosages of variable charge soil changed from 20 to 100 mg/L, a slight increase of turbidity removal appeared. At soil dosage of 40 mg/L, the increases of removal efficiencies of turbidity were 2.6%, 1.7% and 3.0% at PAC dosages of 5 mg/L, 10 mg/L and 15 mg/L, respectively. More than 99.0% of turbidity can be removed at PAC dosage of 10 mg/L and soil dosage of 40 mg/L. Using the particle size and shape analyser for determining the size of flocs, it was found that the mean sizes of the flocs were 7.70 and 4.14 μm by PAC (10 mg/L) coagulation, with (40 mg/L) and without the soil, respectively. The bigger the sizes of flocs, the faster the settling process. The reason why adding the soil can improve the removal of turbidity, could be due to the big size, the high density and the adsorption capacity of the soil. In other words, the soil absorbed parts of turbidity easily settled down to clarify the water. Figure 2 also showed that the soil has inapparent effects on the zeta potential of flocs, whereas zeta potential increased with increasing dosage of PAC. The unobvious effect of the soil on zeta potential was probably owing to the fact that the zeta potential of soil (1:300 with deionized water) was negative (about −7.61 mV), which has similar charge properties to the experimental water, and the soil remained in its original state in the water. Considering the highest removal of turbidity, the PAC dosage of 10 mg/L was selected to perform the following experiments. A similar trend has been observed by Chung *et al.* (2013) who demonstrated that flocs formed by the mixture of chitosan and aluminium sulfate showed higher settling velocities and could further reduce overall expenditure.

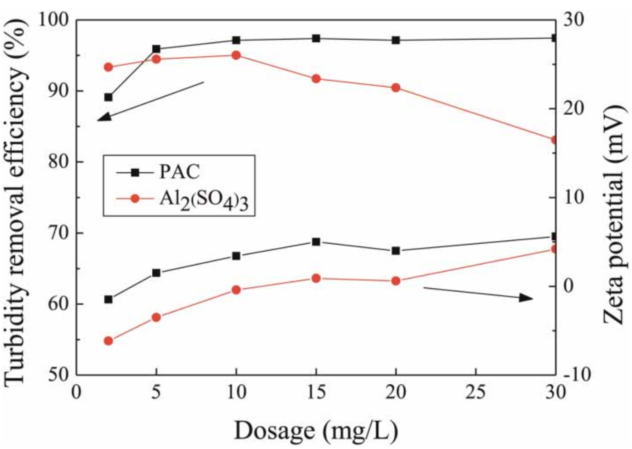


**Figure 1** | Effect of the coagulant dosage on removal efficiency of turbidity and zeta potential of flocs with PAC and $Al_2(SO_4)_3$.

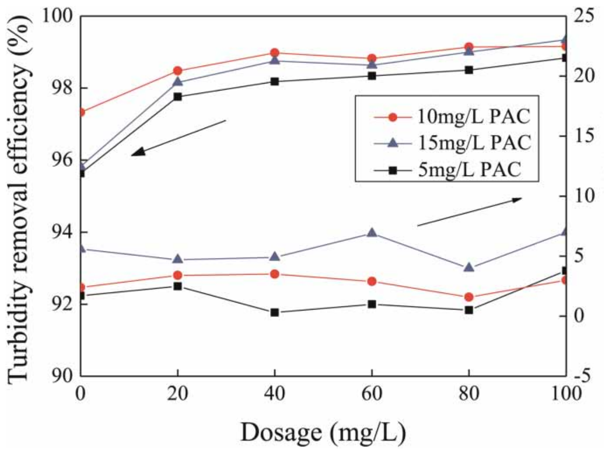


**Figure 2** | Effect of the dosages of variable charge soil on turbidity removal efficiency and zeta potential with PAC coagulant.

## Removal of aniline and phenol

The removal of aniline and phenol in water by enhanced coagulation was conducted. The concentrations of phenol or aniline after coagulation were analyzed. Figure 3 shows

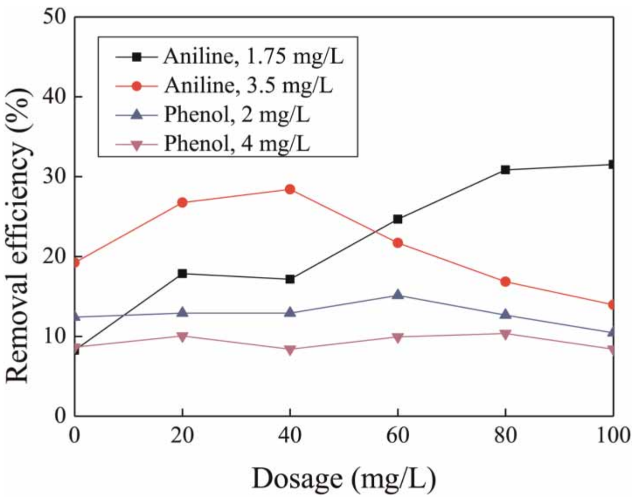


**Figure 3** | Effect of the dosages of variable charge soil on aniline and phenol removal efficiency.

that the removal efficiency of phenol was lower than that of aniline. This can be explained as follows. Phenol has the molecular structure of a tight aromatic ring coupling with the oxygen and a relatively loose bond between the oxygen and hydrogen, so that the hydrogen atoms in the hydroxyl group are easily dissociated. In other words, phenol ionized hydrogen ions and was negatively charged. Once the ionization of phenol happened, the active sites on its soil surface with a negative charge controlled the absorption of phenol. On the contrary, the hydrolysis reaction of aniline could occur so that aniline could carry a positive charge. Under this circumstance, the presence of variable charge soil on the surface with a negative charge promoted the absorption of aniline. There were two horizontal lines in the case of the removal of phenol, that is, the addition of soil had little effect on the system. In addition, the removal efficiency of phenol at the initial concentration of 2 mg/L was higher than that of 4 mg/L, which means that the enhanced coagulation process with variable charge soil has low capacity toward phenol removal. For the aniline removal process, the trends were more complicated compared to phenol. When the initial concentration of aniline was 1.75 mg/L, the removal efficiency of aniline was increased from 8.3% to 31.5% when the soil dosage increased from 0 to 100 mg/L. When the initial concentration of aniline was 3.5 mg/L, the removal efficiency declined after the highest removal efficiency (28.4%) was achieved. The reason why the decrease happened will be further researched in the following study. However, variable charge soil combined with other technologies may improve the treatment.

## Removal of algae

Generally speaking, the contamination of surface water with algae is a concern (Teixeira & Rosa 2006). In this part, the removal of algae was studied with two initial concentrations of algae. It can be seen from Figure 4 that two clear trends appeared. The removal of algae increased gradually as the soil dosage increased. It should be noted that the removal efficiencies increased by factors of 1.7 (10 mL algae) and 2.4 (15 mL algae), respectively, which proved that the absorption of the soil played a significant role in decreasing the amount of algae. The removal of algae contributed to PAC coagulation, whose main mechanism is sweep flocculation and charge-neutralization, as well as variable charge soil adsorption. Adding variable charge soil as a coagulation aid improved the density of the flocs produced by PAC, so that the settling of the flocs was accelerated. Another enhanced coagulation combining PAC with diatomite (Wu *et al.* 2011) reported that the removal of algae was enhanced by adding diatomite at the same time or before PAC.

## Removal of heavy metals

High concentrations of heavy metals in water may cause long-term risks to ecosystems and humans, and are persistent and difficult to remove or decompose (Xu & Zhao 2013). Variable charge soil can decrease the mobility and bioavailability of heavy metal ions in the soil due to its adsorption capacity, CEC and so on (Jiang *et al.* 2012). Figure 5 showed the removal efficiencies of $Cu^{2+}$, $Zn^{2+}$ and $Pb^{2+}$ under two different initial concentrations by enhanced coagulation. It is notable that the order of removal

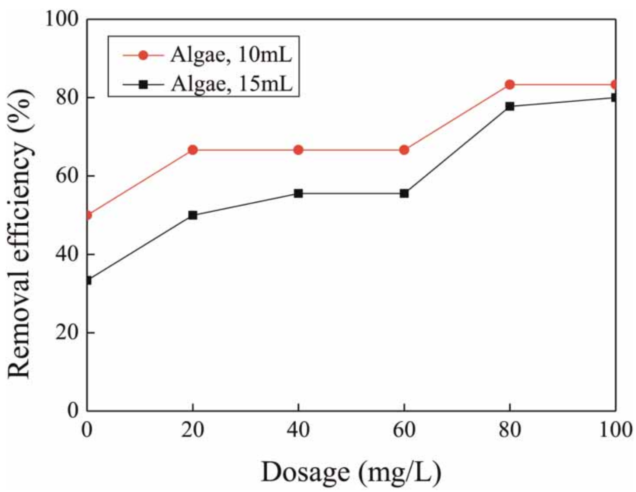


**Figure 4** | Effect of the dosage of variable charge soil on removal efficiency of algae.

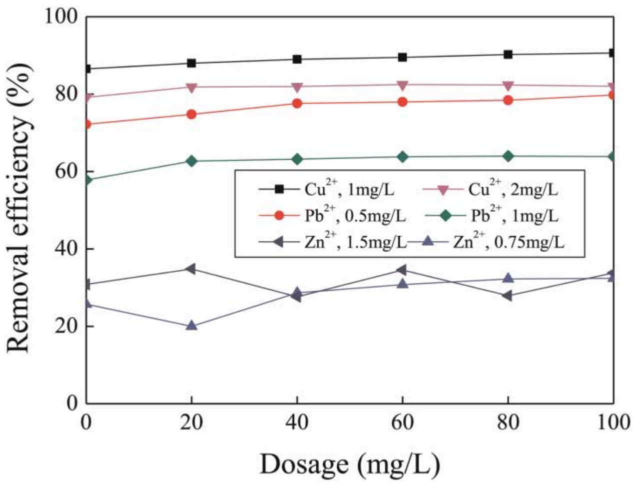


**Figure 5** | Effect of the dosages of variable charge soil on removal efficiency of heavy metals.

efficiency was $Cu^{2+} > Pb^{2+} > Zn^{2+}$. Compared to the cases without soil added, there was a moderate increase in removal of $Cu^{2+}$, $Zn^{2+}$ and $Pb^{2+}$ with added soil (20 mg/L). However, an obvious increase for the removal of the heavy metals was not observed when the addition levels of variable charge soil were raised from 20 to 100 mg/L. It was deduced that most of the heavy metals removal was afforded by coagulation. The results also showed that the removal of these three kinds of heavy metal ions increased with the increasing initial concentrations, which means that PAC coagulation had excellent performance on the removal of heavy metals. Li (2006) also reported that the surface charge of variable charge minerals had an important influence on the removal of $Cu^{2+}$, $Cd^{2+}$ and $Pb^{2+}$ ions.

## CONCLUSIONS

The present study has first demonstrated that enhanced coagulation combining PAC and variable charge soil possessed the capacity for the removal of turbidity, phenol, aniline, algae and heavy metal ions. The following conclusions are drawn from this study:

1. Variable charge soil could be used as a kind of coagulant aid, considering that it can achieve turbidity removal up to 99.0% at PAC dosage of 10 mg/L and soil dosage of 40 mg/L.
2. The removal efficiencies of turbidity, aniline and algae were related to the presence of the soil. The removal order of heavy metal was $Cu^{2+} > Pb^{2+} > Zn^{2+}$.
3. The settleability of formed flocs could be enhanced by adding variable charge soil.
4. The main mechanism involved in the enhanced coagulation is sweep flocculation and charge-neutralization during the PAC coagulation as well as adsorption onto variable charge soil. Therefore, good coagulation performance could be achieved by the combination of these two advantages.

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## REFERENCES


Aryal, A., Sathasivan, A. & Vigneswaran, S. 2012 Synergistic effect of biological activated carbon and enhanced coagulation in secondary wastewater effluent treatment. *Water Science and Technology* **65** (2), 332–339.

Bolan, N., Mahimairaja, S., Kunhikrishnan, A. & Naidu, R. 2013 Sorption–bioavailability nexus of arsenic and cadmium in variable-charge soils. *Journal of Hazardous Materials* **261**, 725–732.

Chung, Y. C., Wu, L. C. & Chen, C. Y. 2013 The removal of kaolinite suspensions by acid-soluble and water-soluble chitosans. *Environmental Technology* **34** (3), 283–288.

Gao, B. Y., Chu, Y. B., Yue, Q. Y., Wang, B. J. & Wang, S. G. 2005 Characterization and coagulation of a polyaluminum chloride (PACl) coagulant with high Al13 content. *Journal of Environmental Management* **76** (2), 143–147.

Hyun, S. & Lee, L. S. 2004 Hydrophilic and hydrophobic sorption of organic acids by variable-charge soils: effect of chemical acidity and acidic functional group. *Environment Science and Technology* **38**, 5413–5419.

Jiang, J. Q. & Kim, C. G. 2008 Comparison of algal removal by coagulation with clays and Al-based coagulants. *Separation Science and Technology* **43** (7), 1677–1686.

Jiang, J., Wang, Y., Xu, R. K. & Yang, C. 2012 Adsorption of chromate on variable charge soils as influenced by ionic strength. *Environmental Earth Sciences* **66** (4), 1155–1162.

Jiang, W. J., Cai, Q., Xu, W., Yang, M. W., Cai, Y., Dionysiou, D. D. & O'Shea, K. E. 2014 Cr(VI) Adsorption and reduction by humic acid coated on magnetite. *Environmental Science and Technology* **48** (14), 8078–8085.

Li, L. Y. 2006 Removal of multiple-metals from contaminated clay minerals. *Environmental Technology* **27** (7), 811–822.

Lorenzen, C. J. 1967 Determination of chlorophyll and pheo-pigments: spectrophotometric equations. *Limnology and Oceanography* **12** (2), 343–346.

Teixeira, M. R. & Rosa, M. J. 2006 Comparing dissolved air flotation and conventional sedimentation to remove cyanobacterial cells of *Microcystis aeruginosa*: part I: the key operating conditions. *Separation and Purification Technology* **52** (1), 84–94.

Tomaszewska, M., Mozia, S. & Morawski, A. W. 2004 Removal of organic matter by coagulation enhanced with adsorption on PAC. *Desalination* **161** (1), 79–87.

Ugochukwu, N., Ali, I., Fu, Q. L., Zhu, J., Jiang, G. J. & Hu, H. Q. 2012 Sorption of lead on variable-charge soils in China as affected by initial metal concentration, pH and soil properties. *Journal of Food Agriculture and Environment* **10** (3–4), 1014–1019.

Uyak, V., Yavuz, S., Toroz, I., Ozaydin, S. & Genceli, E. A. 2007 Disinfection by-products precursors removal by enhanced coagulation and PAC adsorption. *Desalination* **216** (1–3), 334–344.

Wu, C. D., Xu, X. J., Liang, J. L., Wang, Q., Dong, Q. & Liang, W. L. 2011 Enhanced coagulation for treating slightly polluted algae-containing surface water combining polyaluminum chloride (PAC) with diatomite. *Desalination* **279** (1–3), 140–145.

Xu, R. & Zhao, A. 2013 Effect of biochars on adsorption of Cu(II), Pb(II) and Cd(II) by three variable charge soils from southern China. *Environmental Science and Pollution Research* **20** (12), 8491–8501.

Yan, M. Q., Wang, D. S., Yu, J. F., Ni, J. R., Edwards, M. & Qu, H. H. 2008 Enhanced coagulation with polyaluminum chlorides: Role of pH/alkalinity and speciation. *Chemosphere* **71** (9), 1665–1673.

Yu, S., He, Z. L., Huang, C. Y., Chen, G. C. & Calvert, D. V. 2004 Copper fractionation and extractability in two contaminated variable charge soils. *Geoderma* **123** (1–2), 163–175.

Yu, W. Z., Gregory, J., Liu, T., Yang, Y. L., Sun, M. & Li, G. B. 2011 Effect of enhanced coagulation by KMnO4 on the fouling of ultrafiltration membranes. *Water Science and Technology* **64** (7), 1497–1502.

Zhang, J. Y., Wu, C. D., Jia, A. Y. & Hu, B. 2014 Kinetics, equilibrium and thermodynamics of the sorption of p-nitrophenol on two variable charge soils of Southern China. *Applied Surface Science* **98**, 95–101.

Zhao, Y. X., Gao, B. Y., Shon, H. K., Cao, B. C. & Kim, J. H. 2011 Coagulation characteristics of Ti salt coagulant compared with Al and Fe salts. *Journal of Hazardous Materials* **185** (2–3), 1536–1542.

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