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Characteristics Analysis of Different Coagulants in the Removal of Organic Matters of Raw Yellow River Water

[1]Chen Yan, [2]Li Le, [2]Gao Yan-Hong and [2]Xiao Zi-Wen
[1]Engineering Research Center for Cold and Arid Regions Water Resource Comprehensive Utilization Ministry of Education, Lanzhou Jiaotong University, Lanzhou, Gansu 730070, China
[2]School of Environmental and Municipal Engineering, Lanzhou Jiaotong University, Lanzhou, Gansu 730070, China

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Abstract: In this study, the coagulation treatment of raw Yellow River water is conducted with $FeCl_3$, $Al_2(SO_4)_3$, polyacrylamide (PAM) and then the treated water is detected by the means of fourier transform far infrared spectroscopy(FTIR) and molecular-weight gradation. The results showed that organic matters with MW greater than 30KDa. The removal rate of $FeCl_3$ for organic matters with MW greater than 3KDa was higher than that of $Al_2(SO_4)_3$ the removal efficiency of PAM was higher than those of $FeCl_3$ and $Al_2(SO_4)_3$ for. With the dosing quantity of $FeCl_3$ increasing, the quantity of organic matters with MW ranging from 30 to 10KDa decreased and the quantity of organic matters with MW range from 3 to 1KDa increased; With the dosing quantity of $Al_2(SO_4)_3$ increased it had just the opposite effect.

Key words: Raw yellow river water, organic compounds, molecular weight distribution, FTIR

With the speeding industrial pollution and soil and water loss, the Natural Organic Matter (NOM) content of source water of Yellow River gradually rose accordingly and its composition became more and more complex. These organic matters can cause a series of apparent water quality problems in color, smell, turbid degree etc. They may also raise other practical problems, for example they can increase the dosing quantity of water treatment process and the quantity of sludge. Thus, the removal characteristics of these organic matters have become a key and hot point in water treatment field. Coagulation as an important component of the water treatment, is one of the most effective, convenient and economical technology for NOM removal(Yao *et al*., 2008). The choice of coagulant is key to the coagulation treatment. The coagulants currently widely used are polyacrylamide (polymer coagulant) and metal salt coagulant: Aluminum salt and ferric salt. And remove water NOM with aluminum salt and ferric salt is the most basic and important way in water treatment (Yan, 2000). So, in this study we selected $FeCl_3$, $Al_2(SO_4)_3$ and PAM as coagulants in the treatment of raw Yellow River water and detected the treated water by the means of fourier transform far infrared spectroscopy and molecular-weight gradation, to learn more about of the treatment efficiency of those three coagulants.

The shape and size of the organic matter are import factor in its physical, chemical and biochemical behavior in the water. So found out its Molecular Weight (MW) distribution and characteristics will help us in the choice of water purification process (Li *et al*., 2008). Thus, we took the source water of lanzhou section of the yellow river as research object in this study.

EXPERIMENTAL PART

Determination of water quality indexes: The pH was determined with PHS-3C pH meter(Shanghai Precision & Scientific Instrument Co., Ltd.); turbid degree (NTU) with HACH-2100P Portable Turbidimeter; UV_{254} analyze with 752N Ultraviolet Visible Spectrophotometer; and COD by acidic potassium permanganate titration.

Detection conditions of FTIR: IRPrestige-21. Fourier Transform Infrared Spectrophotometer (Shimadzu Corporation, Japan) for infrared spectrum analysis, scanning range: 400, 4000 cm^{-1}, resolution: 0.5 cm^{-1}, scanning times: 10; sample presser (Shimadzu Corporation, Japan).

The samples were pressed into transparent sheets for infrared spectrum analysis with KBr disk method.

Determination method of the distribution of organic molecular weight: Distribution of molecular weight was monitored using ultrafilter membrane with the ultrafilter from Shanghai REX Instrument Co., Ltd. Parallel method:

Corresponding Author: Chen Yan, Engineering Research Center for Cold and Arid Regions Water Resource Comprehensive, Utilization Ministry of Education, Lanzhou Jiaotong University, Lanzhou, Gansu 730070, China

The water samples to be determined were first filtered with the mixed cellulose ester membrane (Shanghai peninsula Industrial Co., Ltd.) , after that filtered with YM30, YM10 and YM1 ultrafiltration membranes (Millipore Corporation), filtration pressure: 0.1MPa and then detected COD_{Mn} and UV_{254} indexes of filtrates; Range of organic content of the molecular weight distribution is obtained by subtraction.

RESULT AND DISCUSSION

Characteristic analysis of raw yellow river water: Routine indexes of raw Yellow River water: The main water quality indexes of temperature, turbid degree, pH, COD_{Mn} and UV_{254} etc. were shown in Table 1.

FTIR spectrum of raw yellow river water: FTIR spectrum of raw Yellow River water was shown in Fig. 1. It can be seen from Fig. 1: There were typical O-H stretching vibration absorption peak at 3411cm^{-1} C = O stretching vibration absorption peak at 3411 cm^{-1}; and maybe the peak at 1643 cm^{-1} was C = O stretching vibration absorption peak of amino acid (Lee, 2003), or the " ghost peak " caused by the absorption of moisture of KBr which occurred in the sampling process easily (He *et al*., 2006); the absorption peak caused by the combination of the in-plane stretching vibration of C-O and O-H of carboxylate ion was at 1420 cm^{-1}(Mei *et al*., 2007): The C-O anti-symmetrical stretch vibration absorption peak was at 1130 cm^{-1}; The C-H out-of-plane deforming vibration absorption peak was at 872 cm^{-1} (Zhang *et al*., 2002);The C-Br stretch vibration absorption peaks were at 617 and 716 cm^{-1}. Fewer types of organic pollutants in raw water of the Yellow River can be seen, mainly containing hydroxyl and carboxyl compounds and contain a certain amount of bromide ion.

Table 1: Quality of raw water in yellow river

Sampling date	2009.10.21 Oct 21, 2009
Water temperature °C	10.0
Turbid degree/NTU	47.7
pH	8.05
COD_{Mn} mg L^{-1}	3.56
COD_{Mn} mg L^{-1}	0.04

Distribution of organic molecular weight of raw yellow river water: The distribution of organic molecular weight of raw Yellow River water was shown in Fig. 2. It can be seen from Fig. 2: There was a good correlation between COD_{Mn} and UV_{254} indexes in the respect of characterization of dissolved organic matter content. Dissolved organic matters of the raw water were mainly small molecule organic matter. And organic matters with molecular weight less than 3KDa, took 69.6 and 60% of the total COD_{Mn} and UV_{254}, respectively.

Effects of different coagulants and dosing quantities on removal efficiency: It can be seen from Fig. 3: There was basically no change of the peaks' position of the FTIR spectrum of raw Yellow River water after coagulation treatment of $FeCl_3$, $Al_2(SO_4)_3$ and PAM. But the height and the width of peaks were significantly different. This indicated that different coagulant has different effect on coagulation treatment efficiency. After coagulation treatment, the height and the width of O-H stretch vibration absorption peak at 3411 cm^{-1} increased distinctively. This indicated that the addition of those

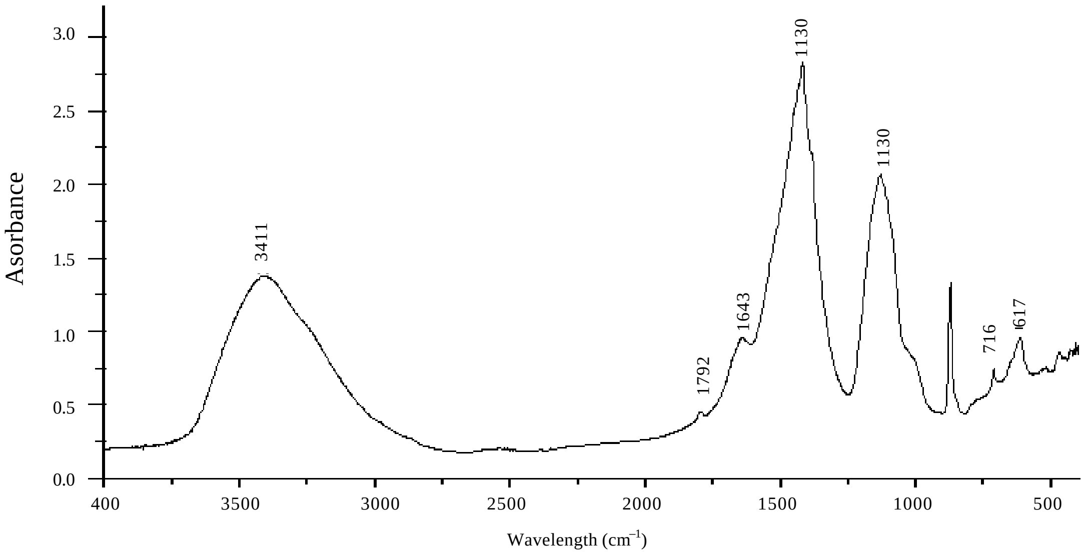

Fig. 1: FTIR spectrum of raw yellow river water

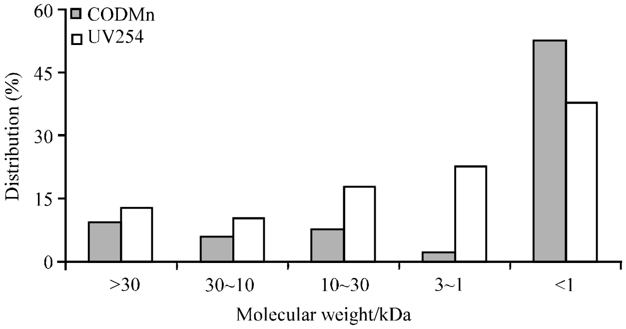

Fig. 2: Histogram of organics with various MW in raw yellow river water

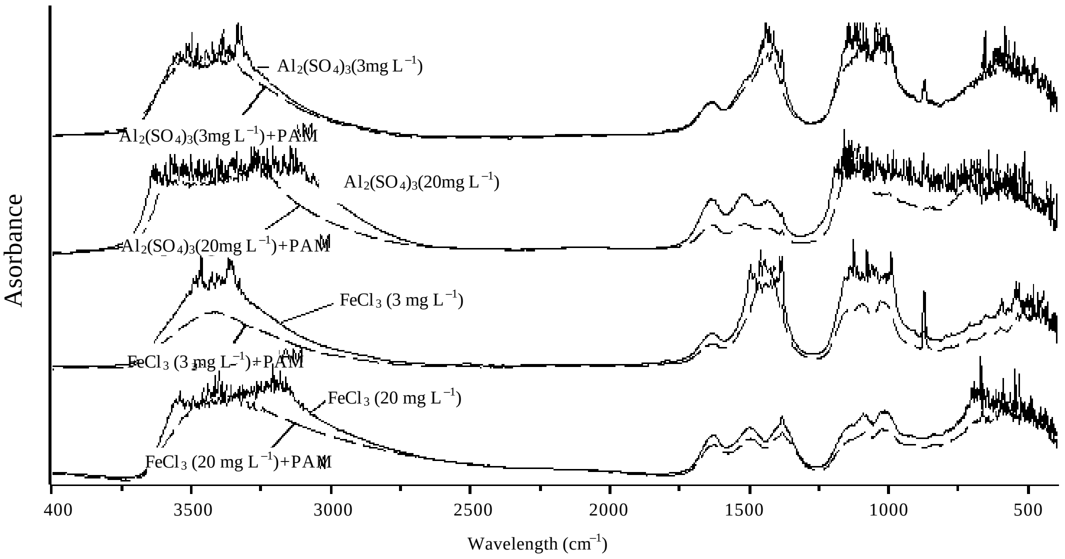

Fig. 3: FTIR spectra of water samples treated with different coagulants and coagulant dosage

three coagulants increased the hydrophilic matters of the water on the contrary. The obvious decline of those three absorption peaks at 1420, 1130 and 872 cm^{-1}, indicated that the coagulation removal efficiency to hydrophobic matters were high. For $FeCl_3$ and $Al_2(SO_4)_3$, the greater the coagulant dosing quantity is, the higher the removal efficiency is. But the dosing of PAM had just the opposite result: the greater the dosing quantity, the lower the treatment efficiency. This was consistent with the results indicated in Fig. 4 and 5.

It can be seen from Fig. 4 and 5, as for the COD_{Mn} and UV_{254} of which the molecular weight is larger than 3KDa, the removal efficiency of $FeCl_3$ and $Al_2(SO_4)_3$ was higher and with the dosing quantity increasing, the removal efficiency increased greatly, for macromolecular organic matter has strong hydrophobic nature and often contains many negatively charged functional groups. Hydroxide generated by the hydrolysis of $FeCl_3$ and $Al_2(SO_4)_3$ with increased coagulant dosing quantity, the positive charge carried by the hydrolysate improved (Wang *et al*., 2005). And the electric charge neutralization between the hydrolysate and the organic matters enhanced. And the removal efficiency of organic matters increased accordingly. Moreover with low pH, the protonation degree and hydrophobic nature of organic matter improved. This made the removal of organic matter by coagulation and adsorption became easier(Dong *et al*., 2003).

$FeCl_3$ and $Al_2(SO_4)_3$ had different organic matter removal efficiency in each molecular weight range. But the removal efficiency of organic matter with MW less than 3KDa was very poor with the coagulant added, those organic matters increased on the contrary. With the dosing quantity of $FeCl_3$ increased, the quantity of organic matters with MW range from 30 to 10KDa decreased and the quantity of organic matters with MW

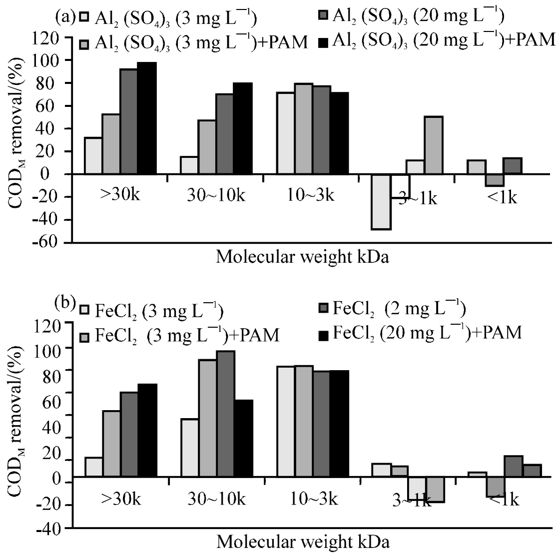

Fig. 4(a-b): COD_{Mn} removal rate in different MW range, (a) $Al_2(SO_4)_3$, $Al_2(SO_4)_3$+PAM, (b) $FeCl_3$, $FeCl_3$+PAM

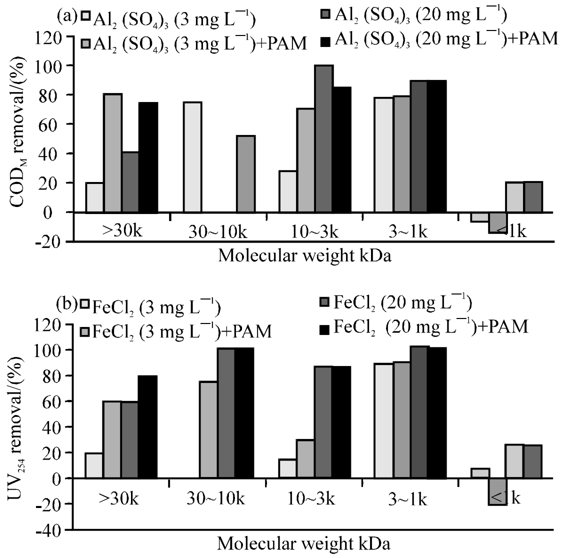

Fig. 5(a-b): UV_{254} removal rate in different MW rang, (a) $Al_2(SO_4)_3$, $Al_2(SO_4)_3$+PAM, (b) $FeCl_3$, $FeCl_3$+PAM

range from 3 to 1KDa increased; with the dosing quantity of $Al_2(SO_4)_3$ increased it had just the opposite effect: the quantity of organic matters with MW range from 30 to 10KDa increased and the quantity of organic matters with MW range from 3 to 1KDa decreased. This is probably because macromolecule with negatively charged moieties (i.e. hydroxyl and carboxyl), formed a kind of sponge-like structure at near-neutral pH values. This sponge-like structure contains many "cavity". Adsorption and complexation reactions occurred between small molecule organic matters and oxygen-containing functional groups existed on its huge inner and outer surface. When coagulants were added to water, metal cations generated from hydrolysis reacted with negative charged macromolecular organic matters through electrovalent bond, complexation reaction or surface adsorption and forms a more stable complex, thus greatly weakened the combination between macromolecule and small molecule organic matters. Finally small molecule organic matters were released. Thus exhibited small molecule organic matters increased phenomenon(Luo *et al*., 1998). It is also possible that residual Fe^{3+}, Al^{3+} of the water reacted with macromolecular organic matters and formed complex. And now functional groups of macromolecular organic matter were sheltered by Fe^{3+} and Al^{3+}. This made the molecular chain contracted. The result was the superficial size of the complex became smaller and the organic content of small molecular range would increase.

At dosing quantity of 3 mg L^{-1}, removal efficiencies of $FeCl_3$ and $Al_2(SO_4)_3$ for organic matters with MW greater than 3KDa were 46 and 40%, respectively. At dosing quantity of 20 mg L^{-1}, removal efficiencies were 82% and 80% respectively. This is because the solubility product(Ksp) of $Fe(OH)_3$ is 3.2×10^{-38} whcih is far less than that of $Al(OH)_3$($Ksp = 1.9\times10^{-33}$). So the hydrolysis, polymerization and polymerization abilities of ferric salts were much stronger than those of aluminum salts (Liu *et al*., 2007). On the other hand, as the Al^{3+} is lazy-gas-type with high charge and small volume, thus it has poor deformability. And Fe^{3+} is non-lazy-gas-type it has an electronic configuration of $3d^5$ it has much more deformability and polarization ability it can occur stronger mutual polarization with its ligands and form firm combination. So Fe^{3+} has much more removal ability for organic matters.

The removal efficiency of PAM for organic matters with MW greater than 30KDa was very high, higher than it of $FeCl_3$ or $Al_2(SO_4)_3$. This is because the MW of PAM is very high, under the same stirring conditions, the greater the gyration radius of macromolecules in the water, the faster speed of the adsorption between macromolecular organic matters and macromolecules and the flocculation speed up naturally. In addition macromolecules have much greater chain length and have strong combination ability. The floc they formed has a big skeleton. The floc size is big. And high porosity which caused the inner permeability of the floc increased. The fluid resistance decreased in the process of flocculation settlement, thus speed up the settlement rate (Li *et al*., 2006). The removal efficiency of PAM for organic matters with MW less than 10KDa was very poor, even negative. This is probably because the stirring caused the breakdown of the long molecular chain which adsorbed organic matters.

It can be seen from Fig. 4 and 5: $FeCl_3$, $Al_2(SO_4)_3$ and PAM had different removal rates for COD_{Mn} and UV_{254} indexes. This is because COD_{Mn} and UV_{254} indexes stand for different organic matters. COD_{Mn} indexes stand for the total quantity of the organic matters which consists of all kinds of organic matters of different properties (Qiu *et al*., 2006; Jiang *et al*., 2007; Dong *et al*., 2003).

CONCLUSIONS

The removal efficiency of all those three coagulants: $FeCl_3$, $Al_2 (SO_4)_3$ and PAM, were high. PAM had the highest removal efficiency of those three and the greater the dosing quantity, the higher the removal efficiency. The removal rate of $FeCl_3$ for organic matters with MW greater than 3KDa was higher than it of $Al_2 (SO_4)_3$.

With the dosing quantity of $FeCl_3$ increased, the quantity of organic matters with MW range from 30 to 10KDa decreased and the quantity of organic matters with MW range from 3 to 1KDa increased; With the dosing quantity of $Al_2 (SO_4)_3$ increased it had just the opposite effect: the quantity of organic matters with MW range from 30 to 10KDa increased and the quantity of organic matters with MW range from 3 to 1KDa decreased.

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