Study Progress in the Preparation Coagulant by Industrial Waste

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Abstract. In the progress of industrial production, coal gangue, fly ash and other wastes was produced, which contains aluminum, iron, silicon and other important components of coagulants. Made full use of those materials could change it from waste into valuable products and used for wastewater treatment which is of great significance. The preparation steps of coagulants and the influence conditions in the process of coagulant preparation were elaborated in this paper. The coagulant application to organic waste water, turbidity wastewater, etc., and research status and development trend of coagulant were summerized.

Introduction

Large amounts of industrial waste are produced in the process of industrial production. For example: in the process of coal production will produce coal gangue[1], fly ash. And cigarette factories and all kinds of aluminum foil packaging production process will produce large amounts of waste aluminum foil. In the process of power plant operation will produce a large amount of fly ash and in the process of titanium white production will produce large amounts of iron. All of them contains a lot of aluminum, iron, silicon dioxide, which are renewable resources. If regard them as waste, not only brings serious environmental pollutions, but also generate resources waste. Coal gangue and fly ash could dip into the acid solution after calcined, then aluminum, iron and silicon dioxide was dipped into the solution, which could prepared for coagulants and used for water treatment[2]. It could solved the problem of environmental pollution at the same time make full use of waste to create more economic benefits. This paper reviews the preparation of coagulant by industrial waste, its application to waste water treatment and coagulation sedimentation principle.

The preparation steps of different coagulants

Coal gangue, fly ash and iron slag contain different kinds of minerals, so the preparation ways and the types of coagulants are different. The preparation methods of coagulant included calcination, impregnation and aggregation. Table 1 summarized the preparation for various coagulants and its preparation methods.

Table 1 Different kinds of diatomite complex with coagulants and its application

industrial waste	preparation way	poly aluminum chloride silicate (iron)
rice bran[3]	calcination+acid dipping+aggregation	poly aluminum chloride silicate (iron)
coal gangue	pickling+alkali soluble+aggregation	poly aluminum silicate, poly aluminium chloride
blast furnace slag	pickling+aggregation	poly aluminium sulfate silicon
metal pickling waste liquor[4]	negative pressure evaporation+oxidation+polymerization	iron coagulant
titanium slag iron	hydrolysis+oxidation+polymerization	poly iron coagulant
the fly ash[5]	microwave polymerization	poly aluminium chloride
	pickling+ethanol impregnation poly aluminium chloride, high purity aluminum sulfate	poly silicon aluminium sulphate
pyrite firing residue	pickling+aggregation	silicon polymer ferric sulfate
scrap aluminum foil[6]	pickling+aggregation	polymerization aluminium sulphate (chloride)
acid drainage of coal mine[7]	the aggregation	polymeric aluminum sulfate iron
coal pyrite in tailings[8]	biological leaching ore+aggregation	ferric sulfate coagulant

Calcination. Fly ash and coal gangue have low chemical activity, crystal structure, insufficient reaction with acid, low leaching rate of Al_2O_3, so which need to be calcines in the process of preparation coagulant. The purpose of calcination is to remove moisture in the raw meal lattice and destroy the crystal structure, generate high surface activity kaolinite, change Al_2O_3 into γ-Al_2O_3. γ-Al_2O_3 can reacts with hydrochloric acid or sulfuric acid rapidly and easily. And the leaching rate of Al_2O_3 can reach 90%, the process of calcined dehydration as follows:$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O$.

Dipping. Aluminum , iron and silicon of flying ash, waste aluminum foil and iron titanium slag are exist in the form of Al_2O_3, Fe_2O_3 and SiO_2. The aluminum and iron could be dipped into the solution after hydrochloric acid or sulfuric acid steeping, the reaction with acid[9] as follows:

$$Al_2O_3+H_2SO_4 \rightarrow Al_2(SO_4)_3+H_2O;\ Fe_2O_3+H_2SO_4 \rightarrow Fe_2(SO_4)_3+H_2O\ ; \quad (1)$$

$$Al_2O_3+HCl \rightarrow AlCl_3+H_2O;\ Fe_2O_3+HCl \rightarrow FeCl_3+H_2O\ ; \quad (2)$$

$$Al_2O_3 \cdot 2SiO_2+HCl \rightarrow AlCl_3+SiO_2\downarrow\ ;\ Al_2O_3 \cdot 2SiO_2+H_2SO_4 \rightarrow Al_2(SO_4)_3+SiO_2\downarrow\ ; \quad (3)$$

Alkali Leaching. Coal gangue, fly ash contains a lot of SiO_2. When it diped by NaOH, sodium silicate solution was got. Under the action of sulfuric acid, poly silicic acid coagulants was got after a series of synthetic[10]. Equation is expressed as:$SiO_2+2NaOH=Na_2SiO_3+H_2O$ (heating).

Biological Impregnated. Some microbes have strong ability to decompose, and some mineral compositions can be degraded by them. Angéli[11] studyied the acidophilic bacteria could speed pyrite which in tailings dissolution rate. It could dissolve the iron from pyrite to solution, which could used for coagulants preparation.

Aggregation. Aggregation is which in order to make iron salt or aluminum salt and silicate

hydrolysis completely by adding $Ca(OH)_2$、$NaHCO_3$ into it under certain conditions. The formation of polymeric aluminum sulfate (iron) experienced from low molecular polymer to high-molecular polymer, which could strengthen the adsorption bridging and electricity neutralization, improve the effect of coagulation. The polymerization reaction equation is as follows:

$$2AlCl_3 \cdot 6H_2O \rightarrow Al_2(OH)_nCl_{6-n} + (12-n)H_2O + nHCl \quad (4)$$

$$2FeCl_3 \cdot 6H_2O \rightarrow Fe_2(OH)_nCl_{6-n} + (12-n)H_2O + nHCl \quad (5)$$

$$nAl_2(SO)_3 \cdot 14H_2O + \frac{m+n}{2}Ca(OH) + xH_2O = [Al_2(OH)_m(SO_4)_{3-\frac{m}{2}}]_n + \frac{mxn}{2}CaSO_4\downarrow + yH_2O \quad (6)$$

The influence factors of coagulant preparation

Calcination temperature, acid concentration, acid leaching temperature and time, ratio between aluminum and iron and silicon are important factors affecting coagulant properties. Table 2 summerized the factors in the process of preparing coagulant.

Table 2 The influence factors in the process of coagulant preparation

coagulants tyes	acid (alkali) concentration	pickling time	pickling temperature	The quality ratio of different material (mass ratio)
poly aluminum silicate sulfate[12]	w(NaOH)=15%~20%	45(min)	80~90(℃)	n(Al):n(Si)=1:1
poly aluminium chloride(liquid)	HCl=14%	2(h)	120℃	/
polymeric silicate sulfate[13]	H_2SO_4=65%	12h	180℃	n(Si):n(Fe)=0.8
poly aluminium sulfate iron[14]	H_2SO_4=2mol/L	30min	100℃	n(Al):n(Fe)=5:1
poly aluminum chloride iron silicate	HCl=10%~15% w(NaOH)=15%~20%	2h 3h	70~80℃ 150℃	n(Al+Fe):n(Si) =1:4
phosphorus ferric sulfate[15]	H_2SO_4(industrial-grade)	1h	50~60℃	$n(SO_4^{2-})$:n(Fe)=0.65 n(P) :n(Fe)=0.05

The Influences of the Calcination Temperature. Some substances containing Al_2O_3 and other oxides. Due to its low activity and not easy to react with acid, so it need to be roasted, which could change inert metal oxide into reactive oxide. If calcination temperature is too low, can only turn it into amorphous type or half crystal type, can't completely reaction with acid. If calcination temperature is too high, γ-Al_2O_3 crystal growed, tissue compression make the particles increased

and surface area reduced, activity reduced. When the temperature above 850 ˚C, γ-Al_2O_3 gradually transition intoα-Al_2O_3, and the activity disappear. And the leaching rate of aluminum from clay to solution, so the optimum calcination temperature is 550 ~ 700˚C.

The Influence of Acid (alkali) Concentration, Acid (alkali) Immersion Time and Temperature. It general use hydrochloric acid or sulfuric acid to dip aluminium, iron oxides from industrial scrap material. And the acid (alkali) concentration, acid (alkali) immersion time and the temperature have important influences to the dipping rate of aluminium[14]. If the concentration of the acid is low or dipping time is short, aluminum and iron leaching rate is low. High concentration of hydrochloric acid is easy to volatile, the concentration of sulfuric acid is over high, the aluminum dipping rate is not changed obviously and could waste time, so we should control the concentration of acid and acid leaching time. Generally the concentration of hydrochloric acid in 10%~15%[14], the concentration of sulfuric acid in 50%~60% is the best, the temperature 200~240 ˚C, pickling time about 10 h is the best.

The Influence of the Amount of Coagulant Compositions. The coagulant structure, crystal forms and quality is different with the different proportions of the of aluminum, iron and silicon in the progress of preparation coagulant. So the proportions of the of aluminum, iron and silicon decide the nature of polymerization aluminum sulfate iron, silicon polymer aluminum sulfate, poly aluminum sulfate silicon iron coagulant. Sun studied prepared the poly silicon iron coagulant aluminum sulfate using fly ash. When (Al+Fe):Si was14:1, the structure of coagulant is chain structure, and it has high removal rate of COD. Sun studied the preparation of poly silicon aluminum sulfate iron coagulant by oil shale. When (Al+Fe):Si was14:1, the peak of Si-O-Al, Si-O-Al was obviously, and the prepared coagulant was good.

The Application of Coagulant

The polymerization aluminum sulfate, polymeric ferric sulfate, polymer aluminum sulfate iron coagulant prepared by industrial waste material, are often used to the life sewage, turbidity wastewater, printing and dyeing wastewater treatment.

Sewage Treatment. The polymeric aluminium sulfate (iron), poly aluminium chloride (iron) coagulant, has the stronger adsorption bridging role, for the removal of organic matter in water effect is better. The removal of organic matter in water is better. There are a lot of researches studied the coagulants used for sewage treatment.

Deng studied the preparation of poly aluminum silicate coagulant by fly ash used for sewage treatment. It could replace poly aluminium chloride at the same time, and it can reduced its costs and its has low residual aluminum content. Yan studied the preparation of poly aluminium chloride coagulant by scrap aluminum foil used for waste aluminum foil. And use it for city sewage and river water treatment. It could produced flocculation and absorbed the organic compounds, and the water clear after coagulant. Qiu studied the preparation of polymeric aluminum ferric chloride coagulant by hydrochloric acid and used for sewage treatment. The removal for turbidity, COD_{Cr}, total phosphorus, ammonia nitrogen removal rate reached 95%, 70%, 80% and 70% respectively.

Turbidity Waste Water Treatment. The colloid, suspended material in water usually has negative charge, and polymer sulfate aluminum iron has positive charge, so it can play a role of coagulant adsorption and electrical neutralization function. And the suspended materials in water can be removed by them.

Zhang studied the preparation of polymeric aluminum sulfate coagulant by waste aluminum

slag and used for sewage treatment. And it good for diatomite turbidity water removal. Chen[12] studied the preparation of poly aluminium chloride coagulant by coal gangue and used for low turbidity, turbidity and high turbidity treatment. And the water turbidity removal rate reached 91.5%, 91.5% and 91.5% respectively. Li[6] studied the preparation of polymeric sulfate aluminum iron by scrap aluminum foil and iron scale and used for urban sewage treatment. And it good for diatomite turbidity water removal. It suitable for the raw water (pH range from 6 to 9), the removal rate of turbidity over 98%. He[16] studied the preparation of poly silicon aluminium sulphate coagulant by fly ash and used for sewage treatment. And it good for diatomite turbidity water removal. It has the advantages of low dose, good floc sedimentation performance, wide applicable scope.

Dyeing Wastewater Treatment. Printing and dyeing wastewater not only contain organic matters, but also have refractory chromaticity.When polymerization aluminium sulphate hydrolysis occurs in water, it can form high polymer organic polymer, adsorption and bridging role, which can remove organic matter and colority in water.

Wang[12] studied the poly ferric sulfate coagulant by titanium slag iron and used for dyeing wastewater treatment, and COD_{Cr} removal rate can reach to 91.3%, and increased 1.5% by polymeric ferric sulfate. Lv[8] studied poly aluminum chloride silicate coagulant by Gu displacement fluid and industrial sodium silicate and used for bagasse paper wastewater which produced in the middle of it. The decolorization rate of waste water was 95.20%, COD_{Cr} removal rate can reach to 47.90%, and the residual turbidity was 2.59. Lu studied the poly sulfate aluminium silicon coagulant by blast furnace slag and used for simulated printing and dyeing wastewater treatment. And the decolorization rate was over 90%. Sun[17] studied the aluminum and iron composite coagulant by red mud and used for tobacco wastewater treatment, the results show that in the pH between 6 and 10, COD_{Cr} removal rate reached over 60%, and had good decolorizing effect.

Other Wastewater Treatment. Coagulants prepared by industrial waste materials have different qualities. They could be used for different kinds of wastewaters treatment. Such as: printing and dyeing wastewater, turbidity wastewater, slaughter wastewater, industrial production wastewater, heavy metal ion wastewater, etc.

Angéli[11] studied the ferric sulfate coagulant prepared by pyrite which impregnated by bacteria and used for wastewater treatment. Abo-El-Enein[3] studied the coagulant prepared by rice bran and used for ground water, sewage and industrial wastewater treatment. And the removal rate of Fe^{2+},Mn^{2+} comes from surface water.reach to 99% and 97% respectively. The removal rate of COD_{Cr}, BOD and TSS reached to 90%, 92% and 92%, respectively. Di studied the composite coagulant by scrap aluminum, iron and fly ash and used for slaughter wastewater treatment. The removal rate of COD_{Cr} can reach to 91.3%, the removal rate of SS was 98.7%, the removal rate of turbidity was 98.4%, the removal rate of chroma was 96.6%.

The Coagulation Sedimentation Mechanism of Coagulant

A series of coagulants prepared fly ash, scrap aluminum foil, blast furnace slag. They dispose wastewater by adsorption and coagulation function. The main ingredients of coagulants was Fe^{3+}, Al^{3+}, Si^{4+}, also contain Fe^{2+}, Ca^{2+}, Mg^{2+}, SiO_2, and other coagulant compositions. The coagulants can release a lot of Fe^{3+}, Al^{3+}, which could reduce or eliminate the water suspension colloid particle zeta potential so that make it steady. The waste materials could prepared polymerization sulfate aluminum , polymeric sulfate ferric , polymerization silicate aluminum coagulant after acid treatment and certain synthetic process. Coagulants in the hydrolyzed process can form many complex nuclear complexes, which more conducive to the adsorption of suspended colloid

impurities in waste water. Coagulants containing $Al_2(SO_4)_3$、$FeCl_3$、$AlCl_3$、$Fe_2(SO_4)_3$、$FeSO_4$、H_2SiO_4 compositions, so it is easy to absorb suspended particles in the water.

Conclusion

The composite coagulants prepared by fly ash and other industrial waste after calcinations, acid leaching and polymerization process. It could reduced the cost, improve the quality of products, reduced the waste emissions , reused waste materials. But the composite coagulant prepared by industrial waste, coagu-flocculation mechanism and flocculation morphology research are few, and it still needs to be strengthen the research in this field.

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