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A Brief Guideline of

the Applications of Ferrous Sulphate Heptahydrate in Water Treatment

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1. PRODUCT INFORMATION

Product: Ferrous Sulphate Heptahydrate

Synonyms: Ferrous sulphate; Green vitriol; Iron sulphate.

Category: Inorganic chemical

Molecular Formula: FeSO4 - 7H2O

Molecular Weight: 278.01

CAS No.: 7782-63-0 (Heptahydrate) 7720-78-7 (Anhydrous)

Properties: Ferrous sulphate is a kind of green monoclinic crystal, or crystalline powder, odourless. Its relative density is 1.8987 and the melting point 64^{o}C. Soluble in water (48.6g/100ml at 50 ^{o}C) and anhydrous methanol, slightly soluble in alcohol. It begins to lose molecular water at 57^{o}C, losing 6 molecular water when heated to 64-90^{o}C and becoming anhydrous at 300 ^{o}C. When it decomposes, it forms iron oxide and releases SO_2 and SO_3. It is caustic with pH value 3.0-5.0, efflorescing in the dry air and being oxidized in wet air.

2. QUALITY SPECIFICATIONS

Iron (Fe) …….……………............... 19.7% min.
$FeSO_4.7H_2O$ ……………..……..……. 98.0% min.
Lead (Pb) …………………………. 20ppm max.
Arsenic (As) ………………………. 5ppm max.

3. GENERAL REVIEWS

Being used as a flocculant, ferrous sulphate is a very economical raw material for wastewater treatment of printing, dyeing and electroplating. It has a good flocculation and decolorization ability, removing the heavy metal ions, oils and phosphorus, disinfection and other functions. Especially has an obvious effect for decoloring the printing and dyeing waste water, removal of COD and depositing the ferrite in the electroplating wastewater.

Characteristics:

Ferrous sulphate is a blue inorganic water purifying agents. When it is used to handle the printing and dyeing wastewater with coagulation powder, it has the advantages of low cost, effectiveness and wide use. It is the best election in dyeing Wastewater treatment. Ferrous sulphate has the best decolorization effect than any of Fe^{3+} and Al^{3+}. When it is coagulated with the dye of wastewater and additives, it will become flocculation, which is an ideal dyeing wastewater treatment agent with the characters of rapid prototyping, large cluster and quick settlement.

Textile dyeing industry is an industry that disposals lots of industrial wastewater. Wastewater contains a variety of dyes, slurry, surfactant and other additives. Wastewater, characterized by high concentrations of organic, complex ingredients, poor biodegradability and high color changes, is a kind of industrial wastewater that is hard to deal with.

Coagulation Mechanism:

The decolorization Fe^{2+} and Fe^{3+} in the molysite coagulant are different. Fe^{3+} removes the dye adsorption by the compression-electron shell and its adsorption of the hydrolysates and other coagulation functions. This role has a high efficiency in removing the colloidal dye, but lower in removing the real solution form of the hydrophilic dye. Active hydrophilic has a good hydrophile, mainly because it has one or a number of sulfonic elements($-SO_3$),and a majority of molecules has $-NH_2$， -OH and other groups. All of these groups have not-shared electronics, which are strong coordination bodies. If we control the conditions, it will make complexation reactions with Fe^{2+}, and become the complicated structured cromolecular complexes, reducing its water-soluble, so that the dye molecules will has the colloidal chatacter, and then through the coagulation of the ferrous sulphate hydrolysate to remove it. However, it has a higher requirement in the above reaction conditions (PH and dosage).

Ways to operate

It has good result to deal the dyeing wastewater with lime and ferrous. The ferrous is easily hydrolyzed in alkaline conditions. It may use the reverting function of the ferrous to decolor according to the PH to add the lime dosage, that is, when the PH is 9.5 to 10.5 is the best. The best dosage of the ferrous sulphate is when it is out of water, it’s not bright green. These two medicaments must be added continuously, that is, the ferrous can be stopped for a while temporarily. When the lime stopped, the PH would be dropped, the result will be not so good. Besides, we should also pay attention to the preservation of the ferrous. When the ferrous becomes yellow, it means it has invalidated and has become the basic ferrous sulphate which lack of coagulation effects. About the dosage calculation, we can determine the dosage according to the PH and the water color without changing its thickness, which it’s very convenient.

In addition, we can also make the PH to 6-7 by wastewater in the pretreatment phase before adding fading ferrous sulphate precipitation to it. Then add PAM (polyacrylamide) to accelerate the settlement. After that we make the second flocculation sedimentation. If lime and aluminum sulphate flocculates and sedimentates, the water would fade, the SS lower, and COD would be much lower too.

If the COD value is still high, we add the depigmenting agents to it after it's out of water, and the hydrogen peroxide can be used. Then make the second flocculation sedimentation. It can also achieve the emissions requirement, but its costs are higher.

4. SEVERAL WAYS TO REMOVE THE COLORS OF THE DYEING WASTEWATER

If the color of the industrial printing and dyeing wastewater is bright, it will adversely affect the appearance of the drainage of printing and dyeing wastewater. At the same time these colored pollutants are often toxic for the environment and are related to other indicators in a certain extent. When we are doing the engineering design of dyeing wastewater treatment, we cannot only meet the color emission standards. The removal of the color and pollutants, such as COD should be considered, to ensure that the sewage treatment system can meet the requirements. Therefore, when we are doing the decolorization of the dyeing wastewater treatment, we'll choose the biological treatment process for priority.

The biological treatment for decolorization is to use the microbial enzyme to oxidize or to revert the dye molecules, and to destruct its unsaturated bond and color group. Decolored microbe firstly adsorpt the moleculars, then make the biodegradation. Dye molecules would eventually be degraded into simple minerals or inorganic nutrients and protoplasts through a series of oxidation, reduction, hydrolysis, cooperation and other life activities.

Subtle changes in molecular structure would significantly affect the dye decolorization rate. Different microbes can affect the removal efficiency greatly on different structure dyes; Dye concentration affect the decolorization to a certain level. High concentrations of dye (dye which itself has a strong biological toxicity) would inhibit the microbial activity and impact the decolorizing effect.

Aerobic process is a common technology. However, due to the strong anti-biodegradation of the dye molecules and the decline of the BOD5/COD ratio in the process (the biodegradability becomes worse), the removal rate of ordinary aerobic process to remove the wastewater color and COD is not high (60-70%). Adding molysite 、activated carbon and other adsorption materials to the aeration tank, can extend the staying of refractory materials in the system, improve the activated sludge concentration of the aeration and reduce the sludge load. Thereby it would increase the system removal rate of the decolorization and COD. In recent years, the development of the anaerobic (acid hydrolysis) can make up for deficiencies of the aerobic treatment process to some extent. Refractory dye molecules and their auxiliaries break down into small molecules under the hydrolyzation and acidification of the anaerobes, then break down into inorganic molecules by aerobic microbes. But if we only use the biological treatment technology, we can't meet the requirements of sewage pollution color and COD standards.

According to the production and different water quality of the company, we should choose the project facilities that is technically sound, economically viable, reasonable cost under some necessary circumstances, to pretreat and follow-up treat the wastewater, so that to ensure the color and other pollutants can meet the emission standards.

There are desizing wastewater, refining wastewater, bleaching wastewater, mercerizing wastewater and dyeing wastewater in the woven cloth dyeing process. This is a typical dyeing wastewater that is reported more on the books. With high alkalinity, high color, high COD and higher temperature, this kind of wastewater use of a wide range of dyes. Sometimes they use sulfur dyes in the production process, which cause the wastewater contains a certain amount of sulfide. If we use the PVA as if slurry, the mixed wastewater may contain a certain amount of PVA of poor biodegradability. If we only use this simple anaerobic-aerobic or extended aeration process to treat this kind of wastewater, the COD and the color will be difficult to meet the standards. When we add the strong oxidant to the system, the sulfide will be converted into sulfur precipitation. The water is white like the rice soup, so the color is still not fulfilled.In this type of wastewater treatment, if we increase the physical and biological treatment facilities, ferrous sulphate and PAC depigmenting agents before the treatment, we can remove 80% of the color, 95% of the sulphides, about 40% of COD. In this process, we have removed part of the refractory macromolecules dye, and then use the good designed biochemical process, COD and colors of such wastewater would fully meet the standards.

The cowboy yarn pulp dyeing wastewater's color and COD are high. Particularly in recent years, the mercerized blue, mercerized black, especially blue, black and other special dyeing process developed by foreign market, largely use the sulfur dyes, printing and dyeing auxiliaries such as sodium sulfide. Therefore the wastewater contains large amounts of sulfide, which is often as high as 200~1000mg/L, and color as much as 2000~3000 times. This kind of wastewater must be materializely pretreated, then biochemicaly treated, and then can meet the emission standards stably.

Rinse wastewater of the jeans contains dye, slurry, surfactant and other additives. This kind of wastewater has a large quantity, low concentration and color. If we only use the physical-chemical treatment, the COD is only between 100 and 200mg/L, and color also can meet the emissions requirements, but it would largely increase the sludge. The costs of sludge disposal are relatively high and would easily make the secondary pollution. When the environmental requirements are stricter, we should consider the biological treatment system. The conventional biological treatment process can meet the color and the COD emissions requirements.

Knitted fabrics (yarn) of knitwear printing and dyeing wastewater often use cationic dyes, reactive dyes and disperse dyes. Such wastewater often uses the ferrous sulphate as the main depigmenting agents and white lime powder as the flocculant in the first physico-chemical treatment. It has a good decoloring effect. However, the addition of lime will lead the fouling to plug the pipelines, and then it will be very difficult for the sludge to discharge from the sedimentation pond and the workload of system maintenance would be very heavy. In recent years, some companies have developed some polymer depigmenting agents, which is targeted and has a good result. However, due to large fluctuations in the quality of sewage discharged by dyeing enterprises, it is difficult to achieve universality. Besides, there are often a certain high-price patents and technology inside, which causes the wastewater treatment fee high, the production costs increased and the simple materialized treatment can not meet the emission standards.

Knitted fabrics (yarn) and knitwear printing and dyeing wastewater would often go to the anaerobic-aerobic biological treatment directly via simple pretreatment. The good designed anaerobic treatment systems could remove 80% of the color. But sometimes the chroma increases in the aerobic system and the water come out from the secondary sedimentation tank was tea-brown. This means the biochemical system operates well. But at this time the removal of residual color by biological treatment except the strong oxidizing agent, the other depigmenting agents' results are not so good. The contacting reaction time of the wastewater and strong oxidizing can be controlled in 30-60 minutes. Such wastewater should also consider the impact of fluctuations of water quality. When the companies receive a number of sulfide dyeing orders, they often discharge the wastewater containing sulfur within a week or 10 day. As the microbial adaptation, the sulfide of the discharged wastewater would strongly inhibit the microbial activity, and make a big impact on the biochemical system. The result is the COD and colors are sub-standard in different degrees. This part of wastewater should be materialized pretreated first and then biologically treated.

5. THE DECOLORATION EXPERIMENT USING THE DYEING WASTEWATER AS THE MAIN COMPONENTS

One of the notable features of dyeing wastewater, is of its higher chroma. After the biochemical treatment, the water color has been reduced, but still with a deep color and it's difficult to achieve the emission standards. Therefore, decolorization is an important part in the dyeing wastewater treatment. Nowadays there are tens of thousands of dyes species around the world. In these dyes, the reactive dye is more widely adopted because of its bright color and complete chromatogram. However, the physical and chemical characters of the reactive dye make it become one of the dyes that it's most difficult to remove in the dyeing wastewater. Although the chemical coagulation has a good decoloring effect on the hydrophobic dye, it has a very uncertain decoloring effect on the reactive dye and other hydrophilic dyes. We have conducted a pilot study on how the chemical coagulation methods affect the factors and the control conditions of the decolorization of the reactive dyes.

1、Tests

1.1 Major equipments

721 spectrophotometer

DBJ-621Joint-six timing blender

PHS-2 pH meter

800 centrifuge

1.2 Test water and Pharmacy

Pure dying solution : active K-2BP solution (24mg/L).

Alkali polyaluminum chloride (PAC) solution (homemade), thereinto the mass fraction of Al_2O_3 is 10.0%；Ferrous sulphate ($FeSO_4$)；Cationic PAM (polyacrylamide, hundreds of thousands of molecular weight)；Anionic PAM (molecular weight 850 million).

Wastewater for test: Dying wastewater is from a dye house's conditioning ponds, whose dyes are mainly K, KN- reactive dyes and direct dyes as supplement. It shows red, yellow, blue, green and other colors, most of them are red and yellow. The temperature is 20-35 °C and pH is 8-9.The color is 200-1000 times and the COD is 200~1400mg/L.

1.3 Ways to Test

1.3.1 Measuring Steps of the Decolorization Rate

(1) Deposit the water naturally first, and then remove suspended solids of the water samples by the centrifuge;

(2) Dilute the water and choose the colorimetric plate appropriately. Try to make the peak of absorbance within 1.00%;

(3) Use the pure distilled water as a reference;

(4) On the 721 spectrophotometer, choose one point at every 20nm in the visible wavelength range (420~700nm). Altogether 15 points' absorbance will be measured.

(5) On the coordinates paper, choose the longitudinal superscript as the absorbance, and the beam as the wavelength to plot the absorbance-wavelength curves.

(6) Calculate the decolorization rate according to the following formula:

Decolorization rate = [(ΣE1 before the decolorization-ΣE2 after the decolorization) /ΣE1 before the decolorization] × 100%

E1 stands for the absorbancy of the former water, E2 stands for the absorbancy of the water after the coagulation treatment.

1.3.2 Test steps to determine the least amount of coagulant

Add 200ml water to the graduated cylinder, then add 1ml coagulant each time and stir it slowly and constantly. When the alum coagulant appears, take a note of the coagulant dosage, and convert it to mg/L. So this amount shall be the least coagulant dosage.

1.3.3 Test steps to determine the optimal dosage

(1) Take six 1000mL beakers, puts the same quality printing waste water 1000 ml in them separately, put them on the platform of six-associations mixers;

(2) Test the original water characteristics, PH, luminosity and so on;

(3) Adjust the original water PH to a certain number. Add different amounts of coagulant to six beakers (at least 25%~200% of the coagulation dosage) Stir fast for 2 minutes (rotational speed is 300r/min), then stir slowly for 15 minutes (rotational speed is 30~50r/min), finally set the precipitates for 20 minutes.

(4) Take the supernatant serum in the beaker and measure the luminosity.

1.3.4 Steps to determine the optimum PH

The testing sequences are basically the same with 2.3.3. The difference is in the 2nd step. Adjust the PH of the original water to different values while the coagulant dosage are the same (both are the best dosages).

2 Results and Discussion

The influence factors to the coagulation effect of the printing wastewater are mainly water, temperature, PH and the dye variety. The printing wastewater’s temperature is generally high. It may accelerate the hydrolysis process of the inorganic salts coagulants, and it’s is favorable for the coagulation.

PH may meet our demands by manually adjustment. Therefore, the dye variety becomes the primary factor to influence the coagulation effect. It is also the main basis to choose the coagulant. In the inorganic coagulants, the alkali aluminum chloride and the ferrous sulphate have a certain effect in processing the dye printing wastewater which contains water-soluble dyes [2]. In the following steps we’ll carry on the discussion on the aluminum chloride and the ferrous sulphate’s decolorization effect to the printing wastewater which use the reactive dyes as the principal constituent.

2.1Decolorization effect to pure dye solutions

Takes 2 shares 1000mL active red K-2BP solutions, join the ferrous sulphate solution separately (the increasing dosage is according to the non- crystal water $FeSO_4$, 750mg/L, pH is 8.2 when reacted), the PAC solution (the increasing dosage is according to the Al_2O_3, pH is 6.2 when responded), to carry on the coagulating. The fore-and-aft luminosity - wave curve of decolorization like chart 1 shows.

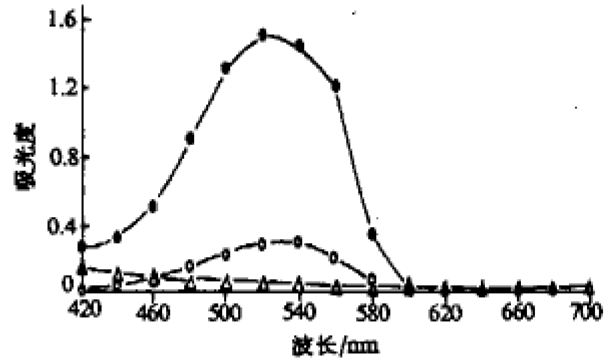

Chart 1 The absorption curve of the active red K-2BP solution before and after the decolorization

●—— Before decolorization;

△——After adding the 750mg/L ferrous sulphate;

○——After adding 750mg/L PAC.

From Chart 1, we know that compared with the original curve, the shape of the absorption curve after join the ferrous sulphate has changed. This indicates that the red dye molecule has had the chemical reaction. The decolorization rate would reach 90.1% after the computation. But the absorption curve after the PAC processing and the original curve are similar in shape. This means that there are red dye molecules remained in the water. The decolorization rate was 82.4%. The same dosage, but the ferrous sulphate decolorization rate is higher than PAC.

2.2 The influence of dosage to decolorization rate

Divide the wastewater into two groups. Join different dosage of ferrous sulphate into one of the group, and PAC to another group. Adjust the original water PH to 10 to decolor.

Because the flocculation PAC produced is tiny and loose, the settling rate is slow. Thus we use its adsorption bridging function to accelerate its flocculation reaction to add positive PAM. The PAM increment is 2mg/L, and the result as the chart 2 shows.

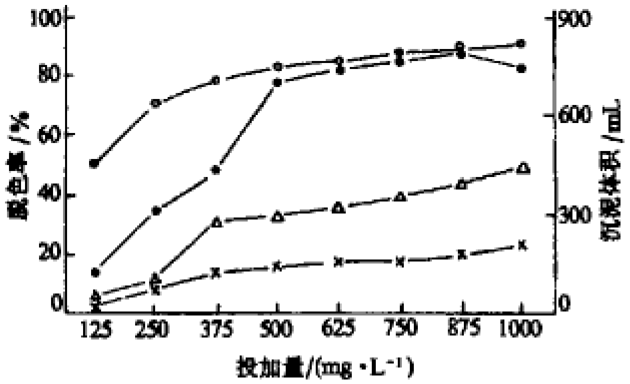

Chart 2 The decolorization rate and liman volume when add different the ferrous sulphate and PAC dosage

○——decolorization rate after adding PAC+PAM;

●——decolorization rate after adding ferrous sulphate;

△——The liman volume after adding PAC+PAM;

×——The liman volume after adding ferrous sulphate;

From chart 2 we know that:

(1) Speaking of adding PAC+PAM, when the PAC adding dosage increases from 125mg/L to 400mg/L, the decolorization rate would increase very quickly, from 50% to 80%; When the adding dosage increases from 400mg/ L to 1000mg/L, the decolorization

rate is slow. Although the decolorization rate is slightly enhanced as we increase the adding dosage, the sludge quantity would remarkably increase, which will increase the wastewater processing cost. Therefore the suitable adding dosage of PAC is between 700mg/L and 900mg/L.

(2) Speaking of adding the ferrous sulphate, when the adding dosage is smaller than 500mg/L, the decolorization rate would increase very quickly, from 14% to 78%; When the increment is 500 ~ 1000mg/L, the decolorization rate is 80% ~ 85%; When the increment is bigger than 1000mg/L, the decolorization rate starts to drop. Therefore the suitable increment of ferrous sulphate is between 750 mg/L and 950mg/L.

(3) When the increment of PAC and the ferrous sulphate are the same, the decolorization rate of adding PAC+PAM is higher than adding the ferrous sulphate, and the sludge quantity produced by adding PAC+PAM is also bigger than adding the ferrous sulphate.

2.3 The influence of pH to decolorization rate

PH is an important factor affecting the coagulation decolorization. Because the printing wastewater is not high to the change cushion degree of the PH, after we add the strong acid weak basicity ferrous sulphate or PAC, it can cause the coagulation pH drop largely. The PH which influence the coagulation decolorization effect not refers to the original water pH, but the coagulation responsing pH after adding the medicament [4]. Divide the experimental wastewater into two groups, adjust the original water PH to one series, one group added 900mg/L ferrous sulphate, and the other group added PAC 800mg/L、PAM2mg/L. The test result showed in the Chart 3, Chart 4.

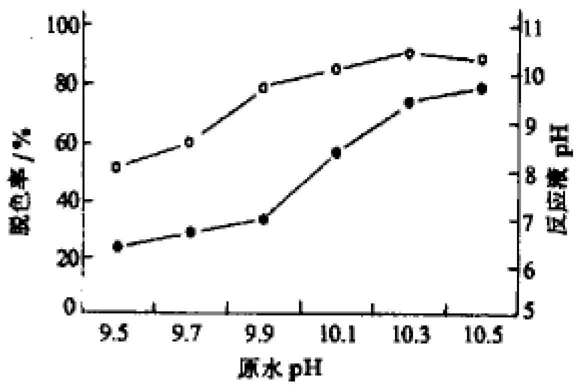

Chart 3 The change of decolorization rate of original water pH and response fluid PH (uses ferrous sulphate coagulation) at different time
○——decolorization rate; ●——Response fluid PH.

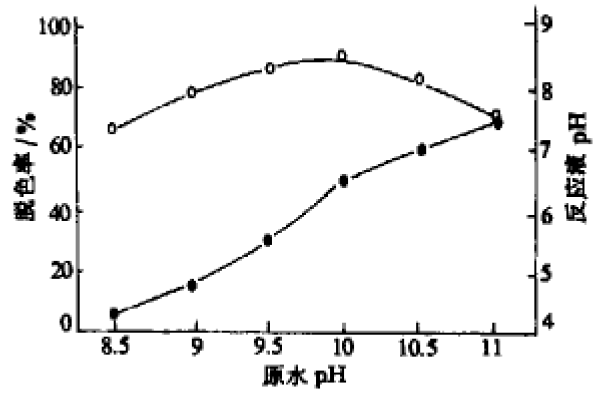

Chart 4 The change of decolorization rate of original water pH
and response fluid PH (uses the PAC+PAM coagulation) at different time

○——decolorization rate; ●——Response fluid PH.

From the chart 3, we know that although the ferrous sulphate increments are all 900mg/L, but because the original water pH is different, the coagulation response PH is different and the decolorization rate is dissimilar too. When the coagulation response pH controlled to 8.1 ~ 9.2, the decolorization effect is good.

From the chart 4, we know that although the ferrous sulphate increment are all 800mg/L and the PAM increment is 2mg/L, but because the original water pH is different, the coagulation response pH is different and the decolorization rate is dissimilar too. When the coagulation response pH controlled to 5.2 ~ 7.0, the decolorization effect is good.

2.4 The influence to decolorization rate when add macromolecule flocculant

As the quality difference of wastewater, sometimes if we only use the abioflocculant, we can not to be able to obtain a good processing effect, so we need add flocculant. The vitriol flower produced by PAC is small, and the garrulous is not easy to subside. If we use it with the PAM, we may obtain the remarkable coagulation effect[1]. Takes the 1000mL experiment wastewater, add 700mg/L PAC, then add few positive ions PAM and anion PAM separately. Add the positive ion PAM before the fast stirring over, then add the anion PAM in the intermediate coagulation stage. The test result shows as Figure 5.

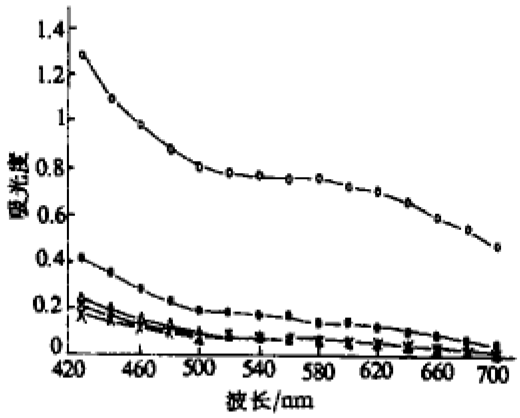

Chart 5 the coagulation decolorization comparison of using the PAC and the PAC+PAM

○——original wastewater absorption curve;

●——absorption curve after adding 700mg/L PAC;

△——absorption curve after adding 700mg/L PAC+2mg/L positive ion PAM;

□——absorption curve after adding 700mg/L PAC+2mg/L positive ion PAM+0.2mg/L

×——absorption curve after adding 700mg/L PAC+2mg/L positive ion PAM+0.1mg/L

From the Chart 5, we know that after adding 700mg/L PAC, and then add 2mg/L positive ion PAM, the decolorization rate increases from 73.7% to 88.9%, which means that the positive ion PAM has an obvious effect to help congealing. Except adding the PAC+ positive ion PAM, add 0.1mg/L anion PAM, the decolorization rate would be enhanced to 91.2%. However, when the PAM is excessive, the decolorization rate would reduce.

3 Coagulation decolorization mechanism analysis

The decolorization Fe^{2+} and Fe^{3+} in the molysite coagulant are different. Fe^{3+} removes the dye adsorption by the compression-electron shell and its adsorption of the hydrolysates and other coagulation functions. This role has a high efficiency in removing the colloidal dye, but lower in removing the real solution form of the hydrophilic dye. Active hydrophilic has a good hydrophile, mainly because it has one or a number of sulfonic elements(-SO_3),and a majority of molecules has -NH_2, -OH and other groups. All of these groups have not-shared electronics, which are strong coordination bodies. If we control the conditions, it will make complexation reactions with Fe^{2+}, and become the complicated structured cromolecular complexes, reducing its water-soluble,so that the dye molecules will has the colloidal chatacter, and then through the coagulation of the ferrous sulphate hydrolysate to remove it.However, it has a higher requirements in the above reaction conditions (pH and dosage).

Speaking of PAC, Al^{3+}may provide the coordinate space, the median allocation may reach 6. Thus there's the possibility that it could coordinate with-NH_2, -OH groups on the reactive dyes. Because one Al^{3+} cannot coordinate with many dyes, the rest space of Al^{3+} get in touch with the garrulous produced in the coagulation through bridge association function of the-OH in the hydrolisis process. After add the flocculant PAM, its intense adsorption bridging function may improve the flocculation's structure and make the tiny loose flocculation body to be thick and dense, accelerate the agglutination subsidence[2]. But if the flocculant adds excessively, then the surface of the colloidal particle gathered by the dye molecules would be saturated by the macro-molecule chain, so it cannot bridge with other granule, instead it causes the dye granule to disperse once more and reduces the decolorization effect.

4 conclusions

(1) Using the ferrous sulphate to deal the reactive printing and dying wastewater with coagulation processing, when the increment is controlled to 750 ~ 950mg/L and the response pH controlled to 8.5--9.5, the decolorization rate may achieve 85% ~ 92%; When using the PAC+PAM coagulation processing, adding 2mg/L PAM, PAC's increment controlled at 700 ~ 900mg/L and the response pH controlled at 5.2 ~ 7.0, the decolorization rate may achieve 85% ~ 93%.

(2) From the increment of the medicament, no matter we use the ferrous sulphate or PAC to decolor the reactive printing and dying wastewater, it would cost much more increment (ferrous sulphate about 100mg/L, PAC about 110mg/L) than dealing hydrophobic dye.

(3) Look from the pH, the ferrous sulphate has a narrow request to the original water pH, which increase some difficulty for the actual operation and make the leaking water to be alkalescence; To PAC, the original water pH scope is wider, and the water is neutral meta-acid.

(4) Look from the sludge quantity, the sludge quantity of PAC+PAM produced is much less than the ferrous sulphate. But after the water lays aside for a period of time, it would be the sorrel muddy shape. Maybe the residual Fe^{2+}oxidates to $Fe^{3+}$and produces $Fe(OH)_3$ colloids. This can make the water turbidity advance, meanwhile can reduce the dissolved oxygen in the water.

5. DISCLAIMER