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Full Length Research Paper

An overview of the treatment of print ink wastewaters

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Based on a large number of domestic and international literatures, the characteristics of print ink wastewaters such as high concentration and chroma, complex of the wastewater composition, poor biodegradabilitiy, and the present treatment of it were summarized. It has made a comment on treatment for ink wastewaters.

Key words: Print ink wastewaters, treatment, COD_{cr}, decolor.

INTRODUCTION

Ink are mainly applied in books, magazines and low-grade prints, corrugated paper and low-required printing industries, the packing of cigarette factory, brewery, pharmaceutical factory, cosmetic, children toy, milk and drink, and other carton packing industries. According to the United States (U.S.) census of printing inks, the quantity of lithographic and offset inks sold in 1992 amounted to a total of 378.6 million kg, including 48.9 million kg of sheet fed inks. The inks for engraving may be of drying oil type or of solvent type formulated with a resin and suitable solvents. Solvent inks are made by dissolving resins, such as nitrocellulose, maleic resins, vinyl acetate resin, Gilsonite, or natural resins in solvents, as xylol, toluol, and high-boiling mineral thinners.

Typically, printing ink is a complex, multi-component compound composed principally of dyes and pigments, resins, binders, solvents and optional additives. Obviously, the wastewater generated from the printing process is highly colored, and contaminated with organic minerals because of the afore-referred compounds. Hence, the wastewaters from such printing installation cannot be directly discharged into receiving streams without any treatment, not only due to its deleterious effect on human health and the environment, but aesthetically due to visibility of color even at low concentration.

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Characteristics of ink wastewaters

High concentration and chroma

Ink wastewaters are kind of high concentration organic wastewaters (Cai and Zhang, 2006; Li et al., 2007). The COD_{cr} of that is generally above 20000 mg/L and sometimes more than 100000 mg/L, SS about 800-1200 mg/L, higher pH commonly, the color dark blue with high chroma which is above 100000 tmes.

Great differences of water quality

Water quality varies with the different kinds of ink, which have different connected makings, pigments and additives. So the wastewaters have great differences correspondingly. The quality and quantity of wastewaters also varies with the different process section of the ink production.

Complex of the wastewaters composition

The main pollutants in wastewater of ink production are soluble resin of acrylic, organic with color group, alcohol bases of high molecular and phenyl dispersant. Moreover, acrylic resin is main component of COD_{cr} in wastewater, which is more than 80%. And it also contains tens of additives such as stabilizers, defoaming agent,

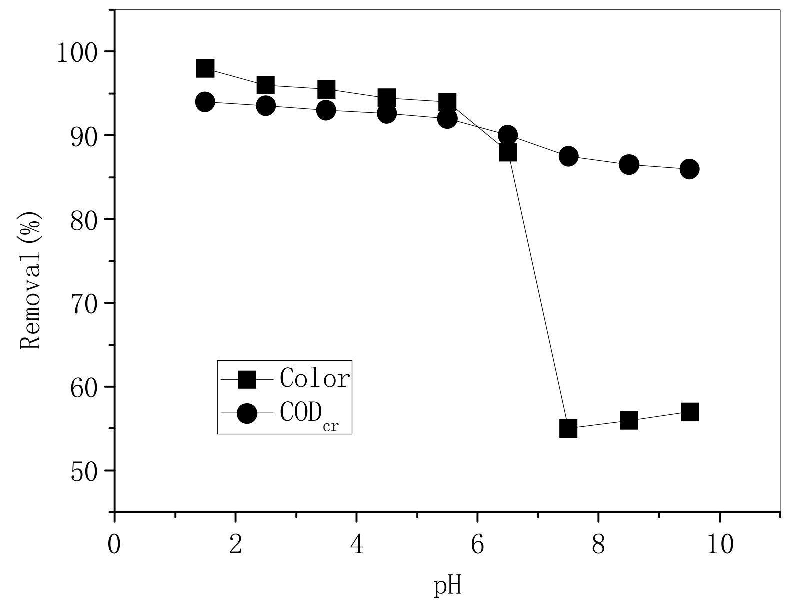

Figure 1. pH effect on the removal of ink wastewaters by PAMAM.

blockers, surfactants and preservative.

Poor biodegradabilitiy

Most of the components of wastewater are synthetic organic polymer with strong stability, which bring on the BOD_5/COD_{cr} of wastewaters is often lower than 0.4. Some wastewater has plenty of substances of inhibiting biological reaction and heavy metal ions, making for difficulty to be microbial decomposed and transformated.

Treatment methods of print ink wastewaters

Coagulation

Coagulation is a common method in wastewater treatments. Coagulation can reduce turbidity and chromaticity of ink wastewaters. It's important to choose coagulant in wastewater treatments. Considering about sediment time, decoloring rate and other factors, Wu et al., (2002) showed that COD_{cr} removal achieved 92.1%, decoloring rate achieved 97.4% after coagulation by polyferric chloride (PFC). Others (Cai and Zhang, 2006) indicated that the removal of decoloring and COD_{cr} were both low using ferrous sulfate as coagulants, while the decoloring rate can achieve 99% and COD_{cr} removal 45 to 60% using polymerization aluminium chloride (PAC). Tapas et al. (2003) demonstrated PAC was the best coagulant, in which decoloring rate, SS removal, BOD_5 removal and COD_{cr} removal achieved 95.9 to 96.5%, 96.5 to 97%, 61.3 to 65.8% and 54.8 to 61.8%, respectively.

However, due to the complexity of the actual wastewater and the strict request of the treatment effect, it needs a variety of coagulants to be used corporately. Metes et al. (2000) regarded chemical coagulation as a potential method. They selected a series of coagulants and found out the comparative effective combination: $AlCl_3 \cdot 6H_2O$ and $FeCl_3 \cdot 6H_2O$ united. Selecting $FeCl_3$ as flocculant and coagulant to treat water-based ink wastewaters, some researchers (Zhao et al., 2005) attained COD_{cr} removal 88.75% and chroma removal 99%. United PAC with Polyscrylamide (PAM) to pretreat packing and printing wastewaters, Sun et al. (2005) attained the removal of COD_{cr} and chroma above 50 and 90%, respectively. But coagulation will generate a lot of sludge which are difficult to dewater and disposing. So it will cause secondary pollution.

Adsorption

Adsorption is a process of using porous solid phase material to adsorb pollutants. Taking on pore structure and huge surface area, activate carbon is widely used to reduce chroma and COD_{cr} concentration. The results from Zhou et al. (2007) showed that active carbon has good efficiency for removing chroma and COD_{cr}. The wastewaters become colorless and transparent after adsorption. But active carbon tends to be saturated and high cost.

Zhang et al. (2010) use polyamidoamine (PAMAM) to modify zeolite and then treat ink wastewaters. The pH effect on the removal of ink wastewaters by PAMAM was shown in Figure 1 when the contact time 90 min. The chroma removal achieved 98% and COD_{cr} 93%.

Combined poly-dimethyl-diallylammonium chloride

Table 1. Proportion of H_2O_2 to $FeSO_4·7H_2O$ effect on the COD_{cr} removal and decolor.

$H_2O_2/FeSO_4·7H_2O$	4/1	3/1	2/1	1/1	1/2	1/3	1/4
COD_{cr} removal (%)	56.3	62.5	67.5	80.5	87.5	76.7	70.1
Decolor (%)	20	30	50	70	80	90	90

(PDMDAAC) and fly ash to treat ink wastewaters, some authors (Xiao et al, 2005) found the removal of chroma and COD_{cr} achieved 94 and 74%, respectively. Metes et al. (2004) used zeolites as adsorbent to treat ink wastewaters. The removal of COD_{cr} was 88% as dosage of zeolites being 5 g/L. The maximal adsorptional capacity was 34.48 mg/g When the ink wastewaters treated by adsorbent electroplate-compost (Netpradit et al., 2004).

Electrolysis method

Electrolysis method to treat wastewater mainly includes oxidation, reduction, agglomeration, air-floating in the electrolytic process to make pollutants transfer, degradation, mineralization, and reduce BOD_5, COD_{cr}, NH_3-N. Wang (2007) used iron as anode and aluminum cathode to treat print ink wastewaters under the strong electric current. The removal mechanism was iron dissolving into Fe^{2+} gradually in electrolytic process, and hydrolysis to Fe $(OH)_2$ which has agglomeration. At the same time, the cathode produces hydrogen which has strong reduction ability and occurs redox reactions with the pollutants in the wastewaters. Meanwhile macromolecular pollutants decompose into small molecules. The removal of COD_{cr} achieved 47%, BOD_5 60% and decoloring 84% after being treated.

Zhang et al. (2005) used iron electrolysis method to treat ink wastewaters. It is the comprehensive action of electroplating, Fenton action, coagulation and adsorption. Results showed chroma removal can attain above 90% and COD_{cr} about 50%. Electrolysis method has lots of advantages such as no secondary pollution, simple equipment, high chroma removal, but high cost and low COD_{cr} degradation.

Oxidation

The common oxidation methods are chemical oxidation and advanced oxidation. Oxidants in chemical oxidation are often NaClO, $KMnO_4$, O_3, $C_2H_2O_4·H_2O$. They can reduce most organic to a specified concentration, but not complete and the cost is high. Advanced oxidations such as Fenton oxidation, ultrasonic wave radiation oxidation, photo-chemical catalytic oxidation are new and effective chemical oxidation process in treating organic wastewater. The reaction mechanism is generally considered as the free radical oxidation composite oxidant, illumination, electricity or catalyst to induce and produce various forms of strong oxidation active substances. Especially oxyhydrogen free radicals can make most of the organic pollutants completely mineralization or partial decomposition.

Ma and Xia, (2009) used Fenton combining with coagulation to treat ink wastewaters. When pH was 4.5, H_2O_2 4.5 mg/L, $FeSO_4$ 25 mg/L, and PAC 700 mg/L after a stated contact time, the removal of chroma and COD_{cr} can be achieved 100% and 93.4%, respectively. Adopted H_2O_2 and $FeSO_4·7H_2O$ as oxidant, coordinated UV light to treat ink wastewaters, it can reduce COD_{cr} and decolor at the same time (Liang and Liang, 2005). Table 1 showed the proportion of H_2O_2 to $FeSO_4·7H_2O$ effect on the removal of COD_{cr} and decolor at pH 4. Si and Ma, (2009) introduced $FeCl_3$, CaO, ultraviolet radiation, TiO_2 at the same time to deal with the ink wastewaters. The removal of chroma and COD_{cr} can all be attained some 90%.

Chen (2010) used UV-Fenton to treat ink wastewaters from circuit board production which COD_{cr} removal achieved 92.3%. Using ultrasound (US) combining with Fenton oxidation to treat ink wastewaters (Chua and Loh, 2008), the experimental results (Figure 2) showed the treating effective for COD_{cr} from ink wastewaters by US-Fenton was higher than that of both simple sum, which COD_{cr} removal achieve 81.4% (He et al., 2009).

Biological method

Due to the poor biodegradabilitiy of ink wastewaters, biologiocal method is generally used as deeply treatment. Liao et al. (2009) adopted two-stage SBR process to treat the ink wastewater after pretreatment. The results showed that COD_{cr} removal remained above 93% and decoloring rate 80%. Using UASB reactor showed that the ink wastewaters after degradating in the sludge nitrification process was feasible and the decoloring rate can achieve 80% (Wu et al., 2005).

Thanks to the complexity of the actual ink wastewaters, it always combines several methods to treat ink wastewaters. Liang (2003) chose air-float-biochemical process to treat high concentration of printing ink wastewaters which made up the unsatisfactory effect of physic-chemical and biochemical. Some (Liu and Cui, 2001) adopted coagulation-air-float-micro-SBR process to treat carton packaging industry ink and adhesives wastewater to achieve National Level of Discharging Standard. Ceng et al. (2010) used sulfide precipitation – neutralization precipitation - coagulation precipitate – catalytic oxidation

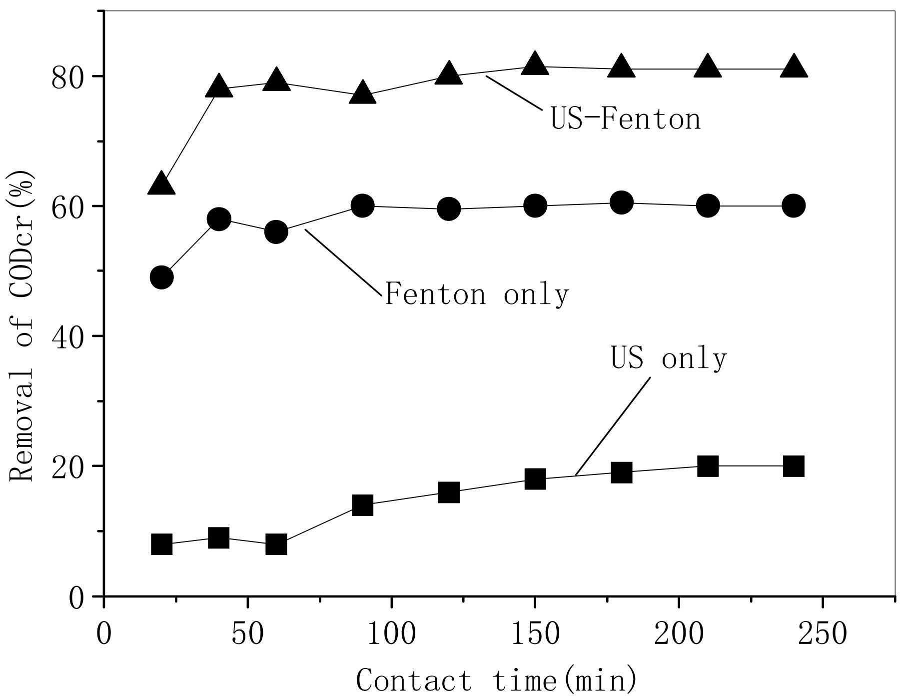

Figure 2. COD_{cr} removal treated by different methods.

combination process to treat high concentration ink wastewaters from print circuit board (PCB) manufacturer. The experimental results showed that the outlet of COD_{cr} was less than 90 mg/L, ρ(Cu^{2+}) less than 0.5 mg/L, SS less than 50 mg/L.

Some insufficiency on the treatment of ink wastewaters

Consulting larges of literatures from oversea and domestic can be known that most researchers saw about chroma and COD_{cr} as evaluating indexes for treating ink wastewaters. Few looked heavy metals and benzene as treating objects. Although the concentration of heavy metals and benzene is low, it is harmful to the water environment.

While there are a lot of reports about the technology of dealing with ink wastewaters, most of technologies (Cenek, 2004; Barredo et al., 2005; Zhang, 2004) are rest on the laboratory. It has a long way for industrialization.

Summary

The demand for ink will increases with the progress of social economy. In current, there are a lot of treatment methods for ink wastewaters. But deficiencies still exist for each kind of method. So it should continue to seek more effective and low cost treatment methods for print ink wastewaters.

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