

Pretreatment of wastewater from triazine manufacturing by coagulation, electrolysis, and internal microelectrolysis

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Received 6 March 2006; received in revised form 5 December 2006; accepted 13 December 2006

Available online 21 December 2006

Abstract

We studied the pretreatment of concentrated wastewater from triazine manufacturing by coagulation, electrolysis, and internal microelectrolysis. Results show that coagulation by polyaluminum chloride at dosage of 0.5 g/L could remove up to 17.2% chemical oxygen demand (COD) from the wastewater. Electrolysis using iron electrode achieved 33.2% COD removal at current of 2 A in 180 min, which was attributed to coagulation and oxidation of the organic contaminants in the wastewater by the radicals (OH^\bullet and O^\bullet) and oxidants (O_2 , O_3 , and H_2O_2) produced in electrochemical reactions. Internal microelectrolysis using iron chips and granular activated carbon (GAC) showed that up to 60.5% COD could be removed under the conditions of iron/GAC/wastewater volumetric ratio of 3:2:490, sparge ratio (ratio of air flow rate to volume of wastewater) of 2:490 min^{-1} , and reaction time of 132 h. COD reduction in internal microelectrolysis was attributed to a combination of chemical and physical processes, mainly oxidation by radicals and oxidants formed in electrochemical reactions, adsorption on, co-precipitation with, and enmeshment in ferrous and ferric hydroxides resulted from Fe^{2+} released during anode oxidation. The results suggest that internal microelectrolysis using iron chips and GAC is a promising, low-cost alternative for pretreating concentrated wastewater from pesticide manufacturing.

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Keywords: Triazine manufacturing wastewater; Coagulation; Electrolysis; Internal microelectrolysis; COD removal

1. Introduction

Wastewaters from pesticide manufacturing may originate from equipment cleaning after batch operation, spills and runoff during the synthesis processes. They usually contain toxic organics and pesticide residues, and pose a threat to the quality of surface and ground water. Treatment of concentrated wastewater from pesticide manufacturing with biological processes is often difficult because of microbial toxicity and mass transfer limitations [1]. High-temperature incineration and deep well injection can be very effective in treating such concentrated wastewaters, while other potential technologies such as wet air oxidation, solvent extraction, molten salt combustion, and microwave plasma destruction can also be applied [2]. However, these treatment

methods are costly and the technologies are not readily available in developing countries.

Traditional treatment technologies such as hydrolysis, biological treatment processes, chemical precipitation, chemical oxidation, activated carbon adsorption, resin adsorption, and steam or air stripping, etc. have been proposed and practiced for the treatment of wastewater from pesticide manufacturing [3]. Various innovative technologies, such as photocatalytic oxidation [4], photoassisted Fenton reaction [5], ultrasonic radiation [6], have also been proposed for treating pesticides in aqueous solutions at very low concentrations. However, many of these technologies suffer the limitations of either being too expensive or not being able to treat concentrated wastewaters from pesticide manufacturing.

For developing countries where there is a significant demand for agricultural pesticides while there is a lack of sophisticated wastewater treatment technologies, an ideal treatment scheme for concentrated wastewater from pesticide manufacturing is to

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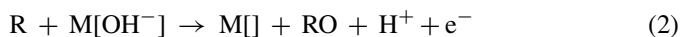
pretreat the wastewater by physiochemical processes to remove most of the organic contaminants and toxicity before biological treatment. The pretreatment processes should not only be low cost, but also robust in performance requiring relatively little maintenance.

One major wastewater treatment process used in removing colloids is coagulation, which is considered to encompass all reactions, mechanisms, and results in the overall process of particle aggregation within a water being treated, including *in situ* coagulant formation (where applicable), chemical particle destabilization, and physical interparticle contacts [7]. Mechanisms of coagulation have been well documented in water treatment literatures [7] and are not discussed here. Chemical coagulation by the use of inorganic coagulants such as alum, magnesium carbonate, ferrous salt, and clays has been successfully applied in removing color from dye-containing wastewaters [8–11]. It has been shown that hydrophobic dye can be more efficiently removed by coagulation using alum from wastewater compared to the hydrophilic counterpart with a high water solubility [9]. A recent study showed that both alum and FeCl_3 were effective in pretreatment of bakery wastewater by coagulation, and 55% of COD and 95 to 100% of suspended solids could be removed with coagulant dosage of 90–100 mg/L [12]. Compared to processes such as chemical oxidation, coagulation has been shown to be simpler and more cost-effective [9–11,13,14].

Recently, electrochemical methods have attracted significant attention for treating recalcitrant toxic wastes [15–19]. The toxic organic contaminants are usually destroyed by oxidants such as Cl_2 , ClO_2 , O_3 , OH^\bullet , O^\bullet , ClOH^\bullet , H_2O_2 , etc. that produced from anodic oxidation during the electrolysis [15,17–19]. The detailed electrochemical reactions taking place during the electrolysis of a brine solution are complicated and not entirely known. According to Comninellis [16], the electrochemical oxidation of organic matter dissolved in aqueous solutions proceeds in two steps. The first step is the anodic discharge of water, forming hydroxyl radicals that are adsorbed on the active sites of the electrode surface ($\text{M}[\cdot]$):



The absorbed hydroxyl radicals then oxidize the organic matter:

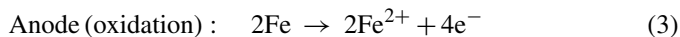


where RO represents the oxidized organic matter that can be further oxidized by the hydroxyl radicals formed from the continuous anodic discharge of water. The radicals, OH^\bullet , O^\bullet , and ClOH^\bullet , have very short half-lives due to their high oxidation potential and they either convert to other oxidants (such as Cl_2 , O_2 , ClO_2 , O_3 , and H_2O_2) or oxidize organic contaminants (direct oxidation) [20]. The primary (Cl_2 , O_2) and secondary (ClO_2 , O_3 , and H_2O_2) oxidants produced from the destruction of radicals have reasonably long half-lives and diffuse into the area away from the electrode, thus continuing the oxidation process (indirect oxidation) [21]. It is expected that organic contaminants cannot be fully oxidized to carbon dioxide and water by these oxidants, as in the case of direct oxidation by radicals, which

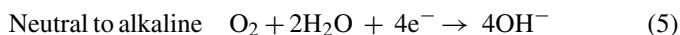
only occurs in an area around the electrode. Such anodic oxidation methods have been successfully utilized in treating olive oil wastewater [19], domestic sewage [22], landfill leachate [23,24], tannery wastes [20], and textile wastes [25].

When the anode is made of iron or aluminum, corrosion of the anode during electrolysis also releases active coagulant precursors (Fe^{2+} or Al^{3+}) into of the contaminated solution [26,27]. The *in situ* production of coagulating ions involves three successive stages [28]: (i) formation of coagulants by electrolytic oxidation of the sacrificial electrode; (ii) destabilization of the contaminants, particulate suspension, and breaking of emulsions; and (iii) aggregation of the destabilized phases to form floc. Studies have shown that organic contaminants in wastewater could be effectively removed by such electrocoagulation treatment [29–35], with processes such as adsorption and co-precipitation also contributed to the overall contaminant removal.

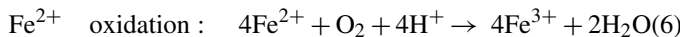
Internal microelectrolysis is believed to operate on the principles very similar to the above electrochemical methods with the exception that the electrons are supplied from the galvanic corrosion of many micro-scale sacrificial anodes instead of external power supply. For example, when a mixture of iron chips and granular activated carbon (GAC) particles is in contact with wastewater (electrolyte solution), numerous microscopic galvanic cells are formed between the particles of iron and carbon. The half-cell reactions can be represented as:



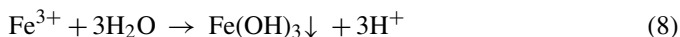
Cathode (reduction):



These half cell reactions occur at microscopic scales, but simultaneous occurrences of these reactions on the surfaces of a large number of iron chips and GAC particles can result in significant electron flows in the system. Coagulation in the treatment system is brought by the ferrous and ferric hydroxides formed from oxidation and precipitation of Fe^{2+} released from the anodes:



Precipitation:



It is believed that organic contaminants can be oxidized by radicals and oxidants produced during internal microelectrolysis. Furthermore, organic contaminants can also be removed through adsorption on, co-precipitation with, and enmeshment in the ferrous and ferric hydroxide floc. Additionally, GAC can also adsorb some of the organic contaminants, especially those hydrophobic ones [36]. Internal microelectrolysis method has been used in decolorization of bleaching alkali extraction effluent of chemical pulp [37], and in removing color and COD from wastewaters discharged by pharmaceutical, dye-printing, paper-making, and chitin-production plants [38–40].

Table 1
Comparison of the wastewater quality before and after pretreatment by coagulation, electrolysis, and internal microelectrolysis

Indicator	Before pretreatment	Coagulation ^a	Electrolysis ^b	Internal microelectrolysis ^c
Suspended solids	Visible	Invisible	Invisible	Invisible
Odor	Strongly pungent	Weakly pungent	Weakly pungent	Weakly pungent
Color	Dark red	Light brown	Light brown	Light brown
COD (mg/L)	97,850	81,000	65,400	38,630
COD removal (%)		17.2	33.2	60.5

^a Measured after pretreatment with 0.5 g/L PAC, mixed at 340 rpm for 1 min, then at 150 rpm for 10 min, followed by 85 min settling.

^b Measured after being electrolyzed at 2 A for 180 min.

^c Measured after for 132 h at iron/GAC/wastewater volumetric ratio of 3:2:490 and air sparge ratio of 2:490 min⁻¹.

Because of the concomitant occurrences of many physical and chemical processes in internal microelectrolysis, many factors may affect its treatment performance. Prior studies indicate that the treatment efficiency of internal microelectrolysis is influenced mainly by solution pH, reaction time, and aeration [37–40]. Under acidic conditions, both Fe²⁺ and Fe³⁺ are difficult to precipitate, while Fe(OH)₆³⁻ may form under alkaline pH, which interferes with coagulation. A pH range of 6–8 has been found to be optimal for Fe³⁺ precipitation in chemical coagulation and electrocoagulation [41,42]. Aeration can potentially accelerate oxidation of organic contaminants by supplying more oxygen to the treatment system. Meanwhile, this also accelerates the oxidation of Fe²⁺ to Fe³⁺, which is less soluble and a better coagulant [42].

This study investigated the pretreatment of concentrated wastewater from triazine manufacturing using coagulation, electrolysis, and internal microelectrolysis. We first studied COD removal from the wastewater by coagulation and electrolysis, then by internal microelectrolysis under different ratios of iron chips and GAC. The results provide valuable information for practical applications of internal microelectrolysis, whose potential usage is high owing to its low cost and operational simplicity, for pretreating high COD wastewaters.

2. Materials and methods

The wastewater used in this study was obtained from a pesticide manufacturing plant in Zhangjiakou, Hebei Province, China. Triazines were synthesized in this plant from raw materials including benzoyl chloride, methanol, dimethyl benzenes, methyl benzene, hydrazine hydrate, ethyl acetate, sulfuric acid, and sodium chloride. The wastewater contained triazines, the raw chemicals, and the reaction intermediates and by-products formed during pesticide synthesis. It had a dark red color and a strong pungent odor (Table 1). It also had a pH of around 8.3 and a high level of turbidity. COD of the wastewater was 97,850 mg/L, and most of the organic contaminants were aromatics, which are generally not amenable to biodegradation.

Coagulation was conducted using the experimental setup showing in Fig. 1a. Wastewater and poly-aluminum chloride (PAC) were added in 1000 mL of wastewater contained in a beaker. The wastewater was mixed at 340 rpm for 1 min, then at 150 rpm for 10 min (these conditions had been experimentally determined to be optimum). Coagulant dosage and settling time were varied to study their effect on COD removal.

The electrolysis experiments were conducted in an electrolysis apparatus shown in Fig. 1b. Three pairs of 15 cm × 22 cm iron plates were used as electrodes and were partially immersed in 3 L of wastewater contained in a 40 × 28 × 25 cm³ electrolysis vessel. The power was supplied by a HY1711-2 potentiostat (Yaguang Electronics, PR China), and electrolysis pretreatment was conducted at currents of 0.5 and 2.0 A in two separate experiments.

Internal microelectrolysis was conducted in the apparatus shown in Fig. 1c. The reaction column had a diameter of 25 cm, and an effective length (for liquid holding) of 101 cm. Iron chips (1.2–12 mm in length and 0.4–3.0 mm in width) were obtained as scrap metal from a metal machining shop and were degreased in a 10% hot alkali solution. They were then soaked in a diluted (2%) sulfuric acid solution to remove surface rusts, and finally cleaned by deionized water. The GAC used had a mean particle diameter of 1.5 mm with specific surface area >800 m²/g. The bulk densities of the iron chips and GAC were 7.78 and 0.48 g/cm³, respectively. Out of convenience, the amounts of iron chips, GAC, and wastewater were all expressed in the unit of volume. The reaction column was filled with 49 L of wastewater. Iron chips (100–300 cm³) and GAC (100–200 cm³) were first mixed together and then added into the reaction column. Air at a constant rate of 0.2 L/min was sparged into the bottom of the column through ceramic air diffusers, which led to a sparge ratio (ratio of air flow rate to volume of wastewater) of 2:490 min⁻¹. Air sparging also helped to keep the iron chips and GAC particles in the reaction column constantly mixed. The amounts of iron chips and GAC were varied in different sets of experiments to study their influence on system performance. To study the effect of wastewater pH on COD removal, pH of the wastewater was adjusted to 8.5, 5.5, 4.5, 3.5, 2.5, and 2.0 by adding diluted sodium hydroxide or sulfuric acid solutions. The residual COD in the wastewater was then measured after being treated under the conditions of $V_{\text{iron}}/V_{\text{GAC}}/V_{\text{wastewater}} = 3:2:490$ and 132 h reaction time.

Samples of the wastewater taken after coagulation were set still to allow complete settling of the floc before analysis. Wastewater samples from electrolysis and internal microelectrolysis were set in air to allow conversion of Fe²⁺ to Fe(OH)₃ and complete precipitation of the hydroxides. Supernatant of the water samples was diluted by 500 to 1000 times with deionized water, and the residual COD was determined by K₂Cr₂O₇ method [43]. Duplicate samples were taken with the mean value reported here. Reproducibility of COD measurements

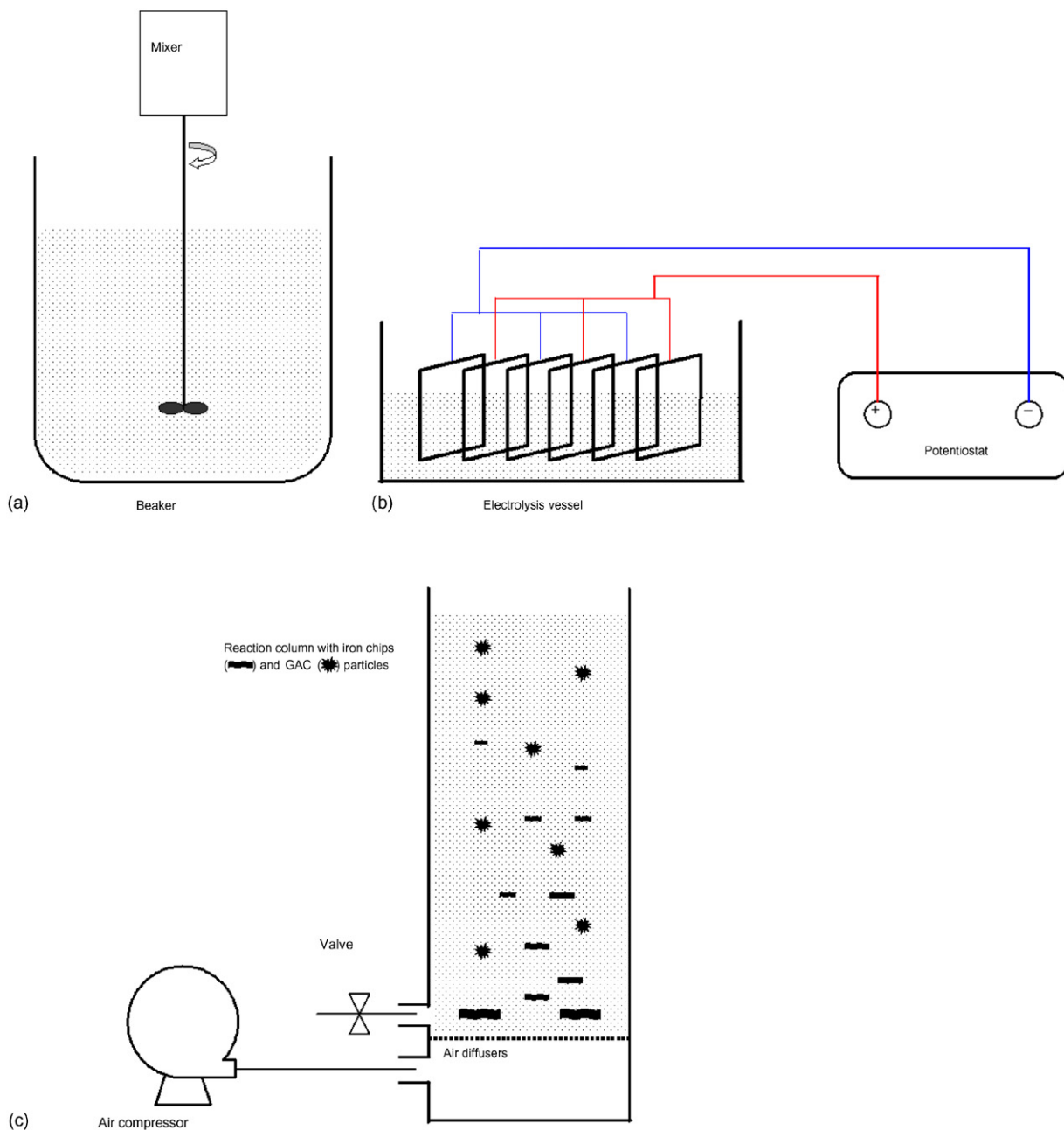


Fig. 1. Experimental setups (not to scale): (a) coagulation; (b) electrolysis; and (c) internal microelectrolysis.

determined by analyzing the same sample five times indicates deviations from the average were <5%.

3. Results and discussion

3.1. Coagulation

Fig. 2 shows that COD levels in the wastewater varied significantly with different settling time and PAC dosage. A clear solution with a pink color resulted from the turbid, dark red wastewater after coagulation. Organic contaminants in the wastewater were probably removed through an array of processes such as adsorption, electrostatic interactions, co-

precipitation, and enmeshment in the floc. These processes are affected by many factors, such as the stability and size of the floc formed. Despite the lack of a clear trend, the results indicate that higher PAC dosage and longer settling times did not improve COD removal. At 0.5 g/L PAC, which is the most economical coagulant dosage studied, residual COD stayed at 81,000 mg/L under all settling times. We also found that high flocculation mixing rates (>150 rpm) and long flocculation times (>15 min) had negative effect on COD removal (data not shown), probably due to breaking of floc by intensive and extended mixing [7].

Overall, the coagulation experiments suggest that 17.2% of the COD in the wastewater could be removed by coagulating with PAC at 0.5 g/L. This is much lower than the 55% COD

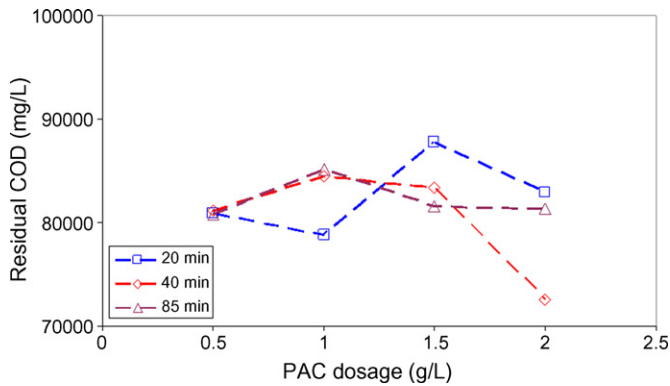


Fig. 2. Residual COD level in the wastewater influenced by coagulant dosage and settling time during coagulation pretreatment. After PAC addition, the wastewater was mixed at 340 rpm for 1 min, then at 150 rpm for 10 min.

removal achieved by coagulation using alum and FeCl_3 as coagulants for bakery wastewater under optimum conditions [12]. Possible explanations are the triazine manufacturing wastewater was more difficult to treat and the operating conditions were not optimized here.

3.2. Electrolysis

Fig. 3 shows the residual COD level in the wastewater during electrolysis at currents of 0.5 and 2.0 A. Significant variations in COD level were observed during electrolysis at 0.5 A, and the reasons were not clear. In contrast, under the higher current of 2 A, COD decreased gradually with time and reached 65,400 mg/L at 180 min. The wastewater turned greenish during treatment with the accumulation of greenish precipitate ($\text{Fe}(\text{OH})_2$), which gradually darkened and turned to brown color ($\text{Fe}(\text{OH})_3$). After complete settling of the precipitate, the wastewater became a clear, pink solution, similar to that after coagulation. These results indicate that coagulation by ferrous and ferric hydroxides (formed from the constantly released Fe^{2+} during electrolysis) played an important role in the observed COD removal.

Because the wastewater contained salts at relatively high levels, violent reactions occurred during electrolysis. Volatile organic contaminants with pungent smell were produced dur-

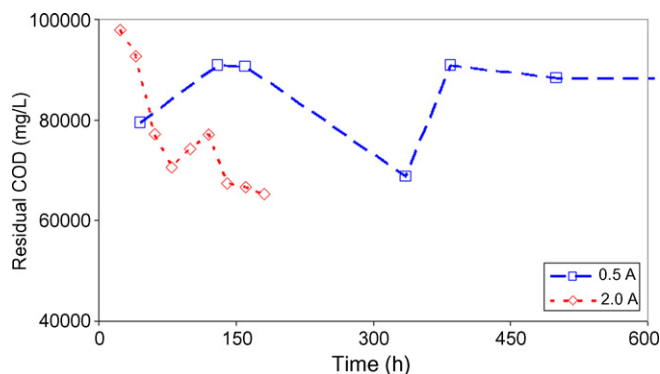


Fig. 3. Residual COD level in the wastewater as a function of reaction time under currents of 0.5 and 2.0 A during electrolysis pretreatment.

ing the electrolysis, probably due to cleavage of relatively large molecules in the electrolytic treatment processes. Oxidation of the organic contaminants by the radicals (OH^\bullet and O^\bullet) and oxidants (O_2 , O_3 , and H_2O_2) produced from electrolysis could also be responsible for COD reduction [16,21,25]. Overall, COD removal during electrolysis is postulated to be achieved through a combination of electrocoagulation and anodic oxidation of the organic contaminants in the wastewater.

After electrolysis at 2.0 A for 180 min, 33.2% COD was removed from the wastewater, almost twice that of coagulation (17.2%). Ferric iron is a good coagulant [7] and has been successfully used in COD removal [11,12]. The higher COD removal of electrolysis compared to coagulation was probably because the dosage (37 mmol/L at 2.0 A for 180 min) of coagulants (Fe^{2+} and Fe^{3+}) produced from electrolysis is much larger than that (3.7 mmol/L Al^{3+}) used in coagulation, besides the contribution from direct and indirect oxidation of the organic contaminants.

3.3. Internal microelectrolysis

Fig. 4 shows COD removal from the wastewater as a function of reaction time under the conditions of: $V_{\text{iron}}/V_{\text{GAC}}/V_{\text{wastewater}} = 1:1:490$, $2:2:490$, $2.5:2:490$, and $3:2:490$. Overall, residual COD in the wastewater exhibited similar patterns despite the significant variability. Appearance of brownish floc (precipitate) and gradual reduction in color of the wastewater during the treatment were observed. Little COD removal occurred before ~ 62 h, and the relatively small amounts of organic contaminants removed during the early stage were due to adsorption on GAC and volatilization of the relatively volatile organic contaminants, such as methanol, brought by air sparging. After that, COD dropped rapidly with time and reached the level of 45,300 to 64,500 mg/L at 75 h. Compared to electrolysis, rates of electrochemical reactions in internal microelectrolysis were very slow due to lack of external electricity supply. The half-cell reactions occurred initially at microscopic corroding surfaces, which progressed with time [44].

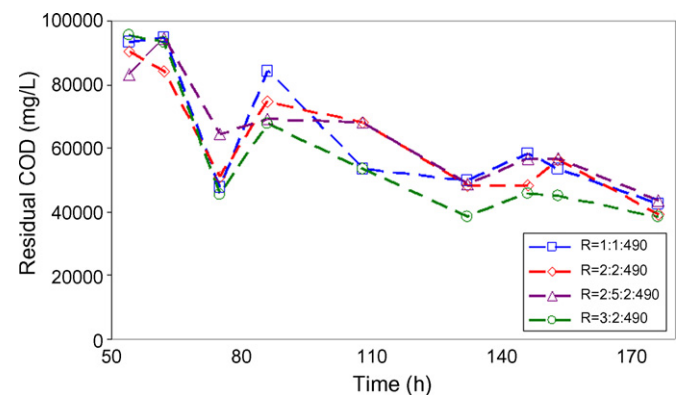


Fig. 4. Residual COD level in the wastewater as a function of reaction time under $R = V_{\text{iron}}/V_{\text{GAC}}/V_{\text{wastewater}} = 1:1:490$, $2:2:490$, $2.5:2:490$, and $3:2:490$ during internal microelectrolysis pretreatment.

Once the electrochemical processes occurred at significant rates, oxidation of the organic contaminants by the radicals (OH^\bullet and O^\bullet) and oxidants (O_2 , O_3 , and H_2O_2) could be responsible for COD reduction, similar to the case of electrolysis [16,21,25]. Furthermore, the continuous precipitation of ferrous and ferric hydroxides could also remove organic contaminants from the wastewater through adsorption, co-precipitation, and enmeshment. In particular, organic contaminants with carboxyl functional groups (e.g., benzoic acid) were expected to bind strongly to ferrous and ferric hydroxides. Increases in residual COD in the wastewater were observed between 75 and 85 h. This rebound in COD level was probably caused by releasing of organic contaminants associated with breaking of the floc by air sparging, as was observed in coagulation with high flocculation mixing rates and long flocculation times. Another possible explanation was back diffusion of organic contaminants associated with the hydroxide floc. Over time, organic contaminants, particularly those with high water solubilities, swept in the floc started to back diffuse into the solution phase. Back diffusion of dye materials trapped in alum sludge into the aqueous phase has been observed during coagulation of textile dye wastewater by alum, and addition of fresh alum was necessary to control this problem [9].

As the treatment time increased, more organic contaminants were oxidized by the radicals (OH^\bullet and O^\bullet) and oxidants (O_2 , O_3 , and H_2O_2) produced in the electrochemical reactions and more Fe^{2+} coagulant was produced. Consequently, apparent increases in COD removal occurred again between 85 and ~132 h. Over longer reaction time, formation of ferrous and ferric hydroxide coatings on the iron chip surfaces started to block electron transfer between iron and the wastewater and caused deactivation of iron surfaces. This gradually reduced the occurrence of electrochemical reactions and the production of Fe^{2+} . COD level started to rebound in the treatment system due to lack of sufficient production of fresh hydroxide floc to capture the organic contaminants released from floc breaking and back diffusion. These observations indicate that organic contaminants removed by coagulation can redistribute back into the wastewater, and long reaction time is not necessarily better for COD removal in the batch treatment system.

The fact that residual COD did not exhibit a clear trend under different iron/GAC/wastewater ratios suggests that COD removal by internal microelectrolysis is robust against variations in the amounts of iron chips and GAC present in the system. We also found that the COD removal was barely affected by pH (data not shown). This was expected because the presence of excess iron chips in the microelectrolysis system gradually reacted with H^+ and brought the pH to the neutral range, which is optimal for Fe^{3+} precipitation [41,42]. These results indicate that internal microelectrolysis is robust and can handle wastewater with a wide range of pH. It should be noted that removal of organic contaminants (and their degradation products) that are volatile to semi-volatile (i.e., with relatively high Henry's Law constants) could also be caused by volatilization during the constant air sparging, although its contribution is difficult to estimate at this point.

3.4. Applicability of internal microelectrolysis for pretreating concentrated wastewaters

The above results indicate that coagulation, electrolysis, and internal microelectrolysis could all be used for pretreating the wastewater from triazine manufacturing (Table 1). Different operating conditions were required for each of these pretreatment, and their performances also varied. Under the conditions studied, coagulation could remove 17.2% COD from the wastewater at 0.5 g/L PAC. COD removal of 33.2% could be achieved by electrolysis at 2.0 A for 180 min. Up to 60.5% of the COD in the wastewater was removed after internal microelectrolysis pretreatment for 132 h at iron/GAC/wastewater volumetric ratio of 3:2:490 and air sparge ratio of 2:490 min^{-1} . Significant reduction in the residual concentrations of the odor- and color-causing contaminants, and suspended solids was also achieved in all these pretreatment processes.

Results of this study suggest that internal microelectrolysis is an effective and economic pretreatment method for decontaminating highly concentrated wastewater from pesticide manufacturing. Because only iron chips are consumed in the pretreatment process and little external power is required (for air sparging), internal microelectrolysis pretreatment is low-cost and effective. It does not require chemical coagulant or high power consumption, as in the cases of coagulation and electrolysis, respectively. COD removal by internal microelectrolysis is also robust against variations of wastewater pH and the amounts of iron chips and GAC present. On the other hand, COD removal is relatively sensitive to reaction time due to releases of organic contaminants by floc breaking and back diffusion with development of hydroxide coatings on the iron chip surfaces. The deactivation problem can be solved by periodical rinsing of the iron/GAC mixture with a weak acid solution to dissolve the precipitated hydroxides. Oxidation by radicals and oxidants can break up the ring structure of aromatics, rendering the oxidized products more biodegradable. Significant increases in BOD/COD ratios of wastewater after internal microelectrolysis treatment has been reported [38]. Improvement in biodegradability of the wastewater after internal microelectrolysis pretreatment was also observed in our preliminary biological treatment experiments (data not shown). Therefore, it is expected that the pretreated wastewater will be able to be further treated using conventional biological treatment processes. Internal microelectrolysis can be used as a pretreatment step that complements biological treatment in dealing with concentrated toxic organic wastewaters.

4. Conclusion

Wastewater discharged from pesticide manufacturing usually contains a range of toxic organic chemicals at high concentrations and has poor biodegradability. Coagulation and electrolysis could only remove less than 35% of the COD for the triazine manufacturing wastewater under the conditions studied here. In contrast, 60.5% COD removal occurred in internal microelec-

tolysis pretreatment after 132 h under the operating conditions of iron/GAC/wastewater volumetric ratio of 3:2:490, air sparge ratio of 2:490 min⁻¹. The organic contaminants were removed by a combination of electrochemical and physical processes including oxidation, adsorption, co-precipitation, and enmeshment, and the residual organic contaminants were more amenable to biological treatment. Quality of the pretreated wastewater in terms of suspended solid, color, and odor was also significantly improved after the pretreatment. The results suggest that internal microelectrolysis using a mixture of iron chips and GAC is a promising pretreatment method for such hazardous wastewater. For a manufacturing plant capable of producing 200 t of triazine per year, concentrated manufacturing wastewater is produced as a rate of 3.7 m³/day. Therefore, an internal microelectrolysis reactor of 20.4 m³ will be able to pretreat the wastewater with a residence time of 132 h. This low-cost pretreatment method is environmentally friendly and does not form new toxic wastes. It is expected that internal microelectrolysis can also be applied in pretreating other types of industrial wastewater containing concentrated organic contaminants.

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