



## Decolorization and COD reduction of UASB pretreated poultry manure wastewater by electrocoagulation process: A post-treatment study

Kaan Yetilmezsoy\*, Fatih Ilhan, Zehra Sapci-Zengin, Suleyman Sakar, M. Talha Gonullu

Department of Environmental Engineering, Yildiz Technical University, 34349 Yildiz, Besiktas, Istanbul, Turkey

### ARTICLE INFO

#### Article history:

Received 8 January 2008

Received in revised form 16 April 2008

Accepted 5 May 2008

Available online 9 May 2008

#### Keywords:

Poultry manure wastewater  
Up-flow anaerobic sludge blanket  
Electrocoagulation  
Post-treatment  
Acute toxicity

### ABSTRACT

The performance of electrocoagulation (EC) technique for decolorization and chemical oxygen demand (COD) reduction of anaerobically pretreated poultry manure wastewater was investigated in a laboratory batch study. Two identical 15.7-L up-flow anaerobic sludge blanket (UASB) reactors were first run under various organic and hydraulic loading conditions for 216 days. Effects of operating parameters such as type of sacrificial electrode material, time of electrolysis, current density, initial pH, and electrolyte concentration were further studied to optimize conditions for the post-treatment of UASB pretreated poultry manure wastewater. Preliminary tests conducted with two types of sacrificial electrodes (Al and Fe) resulted that Al electrodes were found to be more effective for both COD and color removals than Fe electrodes. The subsequent EC tests performed with Al electrodes showed that optimal operating conditions were determined to be an initial pH of 5.0, a current density of 15 mA/cm<sup>2</sup>, and an electrolysis time of 20 min. The results indicated that under the optimal conditions, about 90% of COD and 92% of residual color could be effectively removed from the UASB effluent with the further contribution of the EC technology used as a post-treatment unit. In this study, the possible acute toxicity of the EC effluent was also evaluated by a static bioassay test procedure using guppy fish (*Lebistes reticulatus*). Findings of this study clearly indicated that incorporation of a toxicological test into conventional physicochemical analyses provided a better evaluation of final discharge characteristics.

© 2008 Elsevier B.V. All rights reserved.

### 1. Introduction

The tremendous amount of animal wastes produced by intensive poultry and livestock operations has become one of the most critical environmental problems facing both developed and developing countries in recent years. Kalyuzhnyi et al. [1] have reported that the yearly production of poultry and livestock waste on centralised farms (large pig farms up to 216,000 pigs per year, beef-breeding complexes up to 15,000 per year and industrial poultry farms up to 4 million chickens per year) in Russia exceeded 700 million m<sup>3</sup> in 1996 and has been currently one of the most urgent environmental problems existing in Russia. Similarly, the solid waste annually produced by poultry farm birds has been estimated at millions of tons in Nigeria in 2002 [2].

In recent years, anaerobic digestion technology has been chosen as an attractive option considering the dual benefits of environmental pollution control and meeting national energy needs [3]. This process has become a technology of growing importance, especially for highly polluted wastewater. Therefore,

anaerobic digestion has been regarded as one of the beneficial and advantageous processes in animal manure wastewater treatment [4]. In a comprehensive literature review, Sakar et al. [5] have reported that a number of studies have been conducted on the anaerobic treatment of animal manure wastewaters using different anaerobic process configurations.

Environmental preservation efforts and developments in the technology have resulted in stringent discharge standards. With environmental regulations becoming more stringent, regulatory compliance has also become a matter of increasing concern to the poultry industries. Therefore, there is a need to install effective post-treatment technologies, after undergoing anaerobic processes treating heavily contaminated waste streams, such as poultry manure wastewater. To meet strict laws on environmental protection, pollutant loads discharged from the poultry industries should be first reduced to a significant extent, and a proper post-treatment (polishing) step should be further applied to improve the quality of the final discharge in terms of residual pollutant contents [4,6].

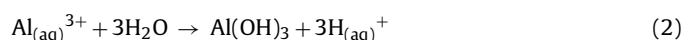
Although much attention has been given to both bio-chemistry and physical characteristics of the anaerobic digestion process in treatment of animal wastes, however, only a few information is available in the literature regarding the applicability of different advanced methods for the post-treatment of anaerobically pre-

\* Corresponding author. Tel.: +90 212 3833033; fax: +90 212 2619041.  
E-mail address: [yetilmez@yildiz.edu.tr](mailto:yetilmez@yildiz.edu.tr) (K. Yetilmezsoy).

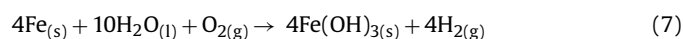
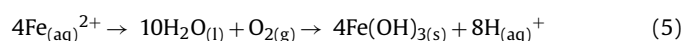
treated animal manure (mostly pig) wastewaters. Some of recent investigations specifically focused on the post-treatment of biologically pretreated animal manure wastewaters can be found in some studies, such as removal of remaining chemical oxygen demand (COD) and color from UASB pretreated poultry manure wastewater using Fenton's oxidation [4], anaerobic digestion and post-treatment of swine wastewater using IC-SBR (internal circulation anaerobic reactor and sequencing batch reactor) process [7], combination of biological and physicochemical methods for post-treatment of biologically pretreated livestock wastewater [8], combined biological and physicochemical treatment of filtered pig manure wastewater [9], removal of nutrients from UASB pretreated pig manure wastewaters using aerobic/anoxic biofilter [10], and ammonia removal from anaerobically pretreated piggery wastes by ion exchange [11].

Today, there is an urgent need to develop more efficient and cost-effective techniques for treatment of wastewaters. It is reported that the electrocoagulation (EC) technology provides a simple, reliable, cost-effective and promising technique for the treatment of various wastewaters without any need for additional chemicals [12]. In recent years, this technology has been conducted as an effective method to treat various types of wastewaters such as landfill leachate [13], rose processing wastewater [14], chemical mechanical polishing wastewater [15], oily bilgewater [16], textile wastewater [17,18], heavy metal contaminated groundwater [19], restaurant wastewater [20], dyeing wastewater [12,22,23], and olive oil mill wastewater [23,24].

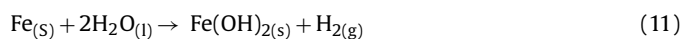
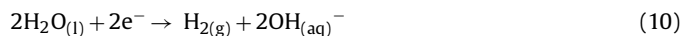
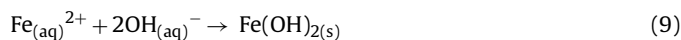
The EC process involves the generation of coagulants in situ by electrolytic oxidation of the sacrificial electrode materials. The materials employed in EC are usually Al or Fe. The electrodes can be made of Al or Fe plates or from scraps such as Fe or Al millings, cuttings, etc. Because there are a definite amount of metal ions required to remove a given amount of pollutants, it is usually to use Fe for wastewater treatment and Al for water treatment. The Al plates are also finding applications in wastewater treatment either alone or in combination with Fe plates due to the high coagulation efficiency of  $Al^{3+}$  [25]. Mollah et al. [26] have reported that the electrolytic dissolution of the Al anode produces the cationic monomeric species such as  $Al^{3+}$  and  $Al(OH)_2^+$  at acidic conditions. At appropriate pH values, they are transformed initially into  $Al(OH)_3$  and finally polymerized to  $Al_n(OH)_{3n}$  according to the following reactions [26]:



However, depending on the pH of the aqueous medium other ionic species, such as  $Al(OH)_2^+$ ,  $Al_2(OH)_2^{4+}$  and  $Al(OH)_4^-$  may also be present in the system. In addition, various forms of charged multimeric hydroxo  $Al^{3+}$  species may be formed under appropriate conditions. These gelatinous charged hydroxo cationic complexes can effectively remove pollutants by adsorption. The authors have also reported that Fe upon oxidation in an electrolytic system produces iron hydroxide,  $Fe(OH)_n$ , where  $n = 2$  or  $3$ . Two mechanisms have been proposed for the production of  $Fe(OH)_n$  [26]. The first mechanism for the production of  $Fe(OH)_3$  consists of Eqs. (4) and (5) for anode, Eq. (6) for cathode, and Eq. (7) for the overall reaction as follows:



The second mechanism for the production of  $Fe(OH)_2$  consists of Eqs. (8) and (9) for anode, Eq. (10) for cathode, and Eq. (11) for the overall reaction as follows:



The  $Fe(OH)_{n(s)}$  formed remains in the aqueous stream as a gelatinous suspension, which can remove the pollutants from wastewater either by complexation or by electrostatic attraction, followed by coagulation. In addition, the  $H_2$  produced as a result of the redox reaction may remove dissolved organics or any suspended materials by flotation [26]. The advantages of EC also include high particulate removal efficiency, compact treatment facility, relatively low cost and possibility of complete automation [25].

It is reported that the poultry manure wastewater can be successfully pretreated by means of high-rate anaerobic processes, however, compliance with the effluent discharge standards will not be met [27]. Therefore, a possible solution for sustainable treatment of such manure streams is the integration of biological and advanced treatment processes to achieve satisfactory final effluents. Because the EC process has wide-scale applicability in treatment of various types of wastewaters as mentioned above, this technique can be proposed as an effective post-treatment method for further removal of biorecalcitrant residues in the anaerobically pretreated poultry manure wastewater.

Although the integration of biological and advanced treatment processes usually yields satisfactory effluents, however, in some cases the final wastewater may cause harmful effects on the aquatic environment. Sponza [28] has reported that the chemical procedure alone cannot provide sufficient information on the potential toxic effects of various unknown and often undetermined substances in complex mixture. Therefore, toxicity tests should be incorporated into the existing receiving water discharge standards to assess the potential risks to organisms in the environment [29]. Although various countries such as the Netherlands, the United States and the United Kingdom are now using toxicity tests as part of their water quality monitoring program, in Turkey, chemical-specific monitoring is used, but toxicity testing has not been included in the regulations [28]. Only the fish toxicity test carried out with guppies (*Lebistes* sp.), based on the toxicity dilution factor (TDF) which indicates the degree of toxicity, has been included in the Turkish Water Pollution Control Regulation [30]. Although initial aquatic toxicity tests have been performed by using bacteria, invertebrates, such as *Cladocera* sp. and *Rotifera* sp., and other groups, they can in no way replace the actual test performed on fish, the last chain in the food web [31]. Therefore, in recent years, fish toxicity tests have been successfully conducted as promising techniques to evaluate the potential acute toxicity and hazardous impacts of various types of wastewaters such as textile, leather, and petrochemical industries wastewaters [32], dye production industry wastewater [29], stock temphos solution [33], asphalt and concrete production wastewaters [34], pharmaceutical wastewater [35] and pulp-paper industry wastewater [28].

The main objectives of this study were: (1) to investigate the performance of UASB reactors treating poultry manure wastewater under various organic and hydraulic loading conditions; (2) to investigate and to optimize the effects of operating parameters such as type of sacrificial electrode material, time of electrolysis, current density, initial pH, and electrolyte concentration on the EC of UASB pretreated poultry manure wastewater; (3) to demon-

strate the combination of a two-stage system on the treatability of poultry manure wastewater using an UASB process followed by EC technology; and (4) to evaluate the possible toxicity of the EC effluent according to the Turkish Water Pollution Control Regulation [30].

## 2. Materials and methods

### 2.1. Poultry manure source and feed preparation

Fresh poultry manure was collected from a moderate size commercial poultry farm (Hakan's Poultry Farm) located at Buyukkilici Village (41°9'25N, 28°10'14E) in Silivri, Istanbul. The collected manure was stowed in plastic boxes, and each box was wrapped with polyethylene bags. Then, they were stored in an industrial type refrigerator at 4 °C to minimize substrate decomposition and also odor from stacked manure before the experiment. The water content and density of the fresh poultry manure were determined to be 77.5 (±0.6)% and 1102 (±115) kg/m<sup>3</sup>, respectively. Prior to feeding, volatile solids (VS) was about 64.5 (±1.1)% of total solids (TS).

The feed for UASB reactors was prepared by diluting fresh poultry manure with the desired quantity of tap water. Four feed ratios (kg of fresh poultry manure to litre of tap water, respectively) of 1:8, 1:6, 1:4 and 1:2 were conducted to investigate the effects of different feed strengths on the digestion performance of the reactors, respectively. The diluted manure was mixed with a vertical stirrer (Makita HP1500) for 5–10 min to obtain a uniform environment in feeding material. The homogenized slurry was then filtered through a sieve having a mesh size of 1.18 mm (Endecotts Ltd.) to reduce potential clogging of the reactor tubing and also operational problems may be caused by broken egg shells, hair or feathers and inert bedding materials such as sand, sawdust and wood shavings which were present in the fresh manure. During the filtration of prepared slurry, a jet of tap water was applied occasionally to remove all scattered particles and impurities through the reverse side of the sieve. Prior to feeding, stored feed was warmed to the reactor operating temperature using Chiltern Hotplate Magnetic Stirrer, HS31.

Gungor-Demirci and Demirer [6] have reported that nutrients present in the manure can be sufficient for anaerobic microbial growth if sufficient amount of water is present to dissolve them. Therefore, addition of extra nutrient may not be necessary at low initial COD and TS concentrations. However, they observed an increase in the total methane production by nutrient and trace metal supplementation at relatively high substrate concentrations. This showed the positive effect of nutrient supplementation on digestion of manure at high initial COD and TS concentrations. In this study, a nutrient solution/basal media containing all necessary micro and macro nutrients for an optimum anaerobic microbial growth was prepared and added 1 mL/L of the daily fed substrate at relatively high initial COD and TS concentrations, as proposed by Ciler [36].

### 2.2. Seed sludge

Seeding is strongly recommended in order to increase the efficiency of the digestion process [6]. Amin [37] has reported that seeding with mature granules requires less time for start-up compared to reactors started with flocculent seed (biomass from a conventional anaerobic digester). Because granular biomass has higher settling velocity and higher specific activity than flocculent biomass, reactors were seeded with 4.5 L of actively digesting granular sludge (28.6% of the working volume) from an ongoing mesophilic UASB reactor of Pasabahce (Tekel) Distillery Inc. (Istanbul, Turkey).

The reactors were filled to their respective volumes of 15.7 L (79.1% of the total tank capacity) with poultry manure wastewater having a feed ratio of 1:10 (kg of fresh poultry manure to litre of tap water, respectively) to acclimate the anaerobic biomass to the feed. Prior to seeding, TS content of the granular sludge was determined about 90.8 g/L. The VS content of the sludge was found to be 82.3% of TS. Therefore, 15.7-L reactors contained about 336.3 g of VS. The contents of the reactors were maintained at respective temperatures (32 ± 2 °C) for a week to allow temperature equilibration and also utilization of the substrate by the anaerobic microorganisms.

The initial average diameter of the granules was found to be about 1.18 mm. The density of the granular sludge was measured to be 1075 kg/m<sup>3</sup>. The mean settling velocity and Reynolds number at terminal settling velocity of the granules having a diameter of 1.18 mm were determined to be 74.2 m/h and 24.3 for the viscosity of water at room temperature (10<sup>-3</sup> kg m/s or Pa s), respectively. The mean settling velocity was determined using the well-known force balance equation. In determination of terminal settling velocity, the drag coefficient being a function of Reynolds number at terminal settling velocity was obtained using Perry's and Green's equation. Results were found to be in accordance with the range of the granule diameters in a simulation analysis of a settling velocity model proposed by Liu et al. [38]. Detailed hydrodynamic calculations of terminal settling velocity and Reynolds number for sample granules can be found in the previous work of Yetilmesoy and Sakar [4].

In this study, scanning electron microscope (SEM) analysis of sample granule biomass was also done in a Jeol JSM-5910LV operated at an acceleration voltage of 20 kV, with Au sputtering-coated samples fixed in an Al stub. Prior to SEM analysis, the sample was placed in a Petri box for conservation, and then dried at room temperature for 2 days. SEM was used to obtain knowledge of both morphology and elemental composition of the original sample. SEM micrographs of original sample granule are shown in Fig. 1. It is clearly observed in Fig. 1(a and b) that the surface morphology of the sample granule shows a rough structure with an oval shape. Visual examination of granular biomass also revealed some slight irregular projections on the surface of the granule. According to Ahn's proposed model [39] for the anaerobic sludge granulation, SEM micrographs appear to represent the growth of a small granule in the diameter range of 1–2 mm. Detailed information on the anaerobic sludge granulation in UASB reactors can be found in the comprehensive review of Hulshoff Pol et al. [40]. A similar work on the morphological study of the granules in UASB and hybrid reactors has recently been elaborated by Gupta and Gupta [41].

The elemental composition of the granular biomass was analyzed by means of the SEM system equipped with an Oxford INCA EDS (Energy Dispersion Spectroscopy) software. On the basis of the procedure, amounts of Au and Al were not taken into account in determination of the elemental composition. As seen in Fig. 1(c), the elemental analysis of the sample indicated the following order of percentages: C > O > P > Mg > K > S > Ca. High percentage of carbon and oxygen found in the granular biomass indicates the high organic content of the sample. The elemental analysis also revealed that some trace elements such as calcium, magnesium, potassium and sulfur were present in the sample. In some studies, distillery wastewaters have been characterized for metal ions such as Ca<sup>2+</sup>, K<sup>+</sup> [42,43], and sulphates [44]. Therefore, the obtained results may be attributed to the presence of these minerals in the distillery wastewater fed to the previous mesophilic UASB reactor from which the granular biomass has been supplied. In an experimental study, Gupta and Gupta [41] have also reported similar observations for a determined mineral content of the granular sludge based on the characteristics of distillery spentwash used as a substrate in their study.

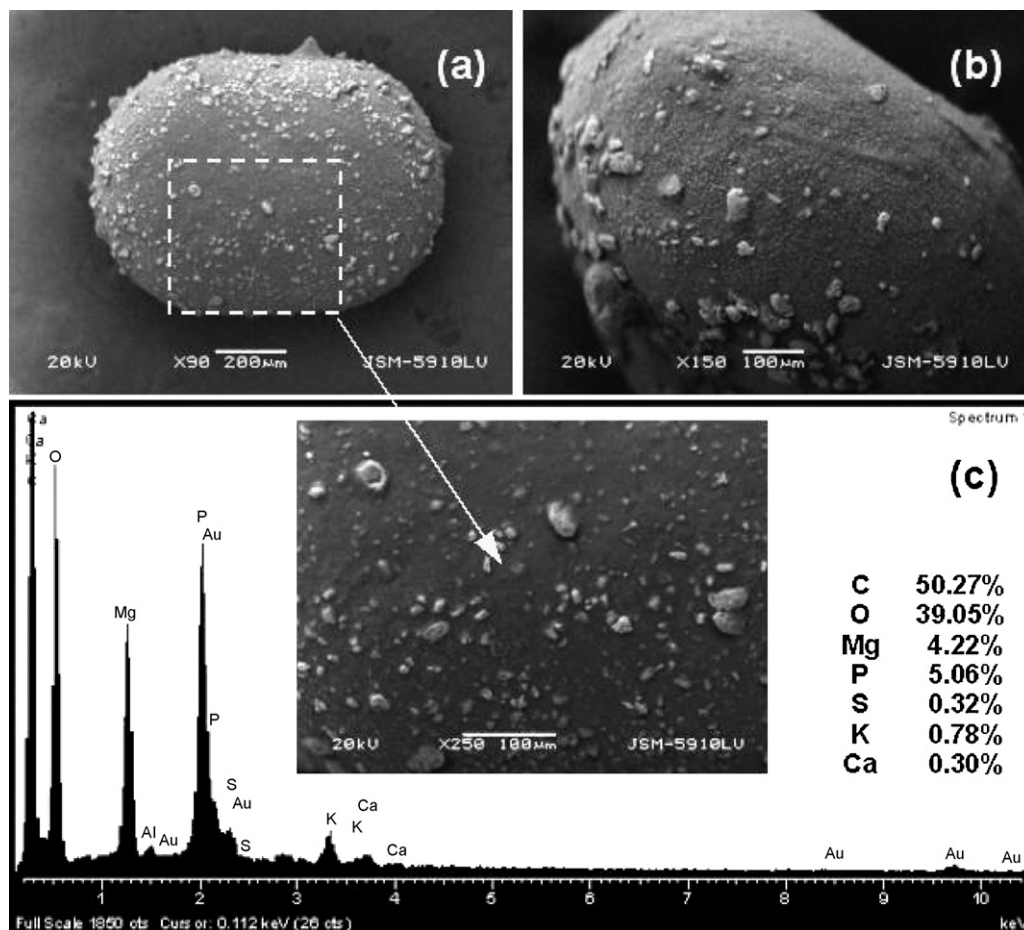


Fig. 1. SEM micrographs (a and b) and SEM/EDS spectrum (c) of an original sample granule, prior to start-up period.

### 2.3. UASB set-up and operation

Two identical 15.7-L UASB reactors (R1 and R2) were run to investigate the performance of reactors for treatment of poultry manure wastewater under different organic and hydraulic loading conditions. The external diameter, total height, total tank capacity of the reactors were 12 cm, 160 cm and 19.85 L, respectively. All parts of the reactors were made of transparent plexiglas material with a wall thickness of 5 mm. The reactors had a conical bottom of 20 cm length and a feed inlet pipe of 1.5 cm diameter to avoid choking during operation. An outlet weir was provided at the top (1.51 m), which was connected to an outlet gutter and outlet pipe to the effluent collection tank.

The reactors had ports for sampling, feeding, effluent and gas collecting. Gas was collected from the headspace on the top of the reactor and gas production was measured by the liquid displacement method. The gas collecting and measuring systems consisted of gas–solid–liquid (GSL) separators (made from inverted plastic funnels of 11 cm diameter), gas collecting pipes, glass water traps, graduated gas measuring tubes (3 L) and two water tank for keeping of gas measuring tubes. Both reactors were equipped with six sampling ports, localized at 0.35, 0.50, 0.65, 0.80, 0.90 and 1.10 m from the bottom of the reactors. The diameter of each sampling port was about 1.5 cm.

The reactors were started using poultry manure wastewater having a feed ratio of 1:10 (kg of fresh poultry manure to litre of tap water, respectively) as substrate for acclimatization of seed culture

and later the dilution was gradually decreased to increase organic loading rate and to study the effects of different feed strengths on the digestion performance of the reactors.

Both R1 and R2 were operated simultaneously in a daily-continuous mode feeding by pumping of the fresh feed into the reactors and collecting effluent samples daily. In feeding, different target HRTs were achieved using a peristaltic pump (FPU5-MT-220, OmegaFlex®). No recirculation of effluents or mixing were carried out in either reactor. During the feeding of the reactors, the feeding tank was continuously agitated with a glass rod to prevent the sedimentation of suspended solids (SS).

Sludge loading rates ( $F/M$  mass ratio) were conducted in the range of 0.01–0.11 kg COD/(kg VS day). The pH of the feed wastewater was adjusted between 6.6 and 7.8 by the gradual addition of  $H_2SO_4$  or NaOH reagents (Merck Chemical Corp.). Both reactors were operated at mesophilic conditions ( $32 \pm 2^\circ C$ ) in a temperature-controlled environment maintained by two adjustable radiators with thermostat (Demirdokum DEYR 7B CM).

The up-flow velocity is regarded as one of the main factors affecting the efficiency of up-flow reactors [45,46]. Wiegant [47] reported that the up-flow velocity could be a restrictive factor with respect to the required reactor volume when treating very low strength wastewater and wastewaters with high SS. The increasing up-flow velocity increases the rate of collisions between suspended particles and the sludge and thus might enhance the removal efficiency. In the mean time, increasing the up-flow velocity could also increase the hydraulic shear force, which counteracts the removal

mechanism through exceeding the settling velocity of more particles and detachment of the captured solids and consequently deteriorates the removal efficiency [46]. Therefore, the up-flow velocity should be sufficiently high to provide a good contact between substrate and biomass, and to disturb the gas pockets gathered in the sludge bed [48]. According to preliminary pumping tests and fluidity of the prepared slurry, an up-flow velocity of about 0.70 m/h was found to be appropriate for the present UASB reactors. Thus, feed wastewater samples were pumped to the reactors from the feeding tank with a stable up-flow velocity of 0.70 m/h by operating the peristaltic pump in a feeding mode of 50 rpm for the corresponding flow rate of 133 mL/min.

#### 2.4. Electrocoagulation process

EC experiments were conducted in a lab-scale EC cell having a total volume of 800 mL. The EC cell was made from 5-mm transparent plexiglas with the dimensions of 72 mm × 72 mm × 175 mm (width, length, height, respectively). A digital DC power supply (Good Will Instek, GPC-3060D, 0.0–30.0 V, 0.0–6.0 A) was used to give regulated electricity current to the EC cell.

Al and Fe are the most widely used materials as sacrificial anode for EC [24]. This is due to fact that they are cheap and their production is very simple [23]. For comparative purpose, preliminary EC tests were carried out with both materials used as sacrificial anode under the same conditions. In preliminary tests, two common use types of sacrificial electrodes (Al and Fe) were studied to select the most appropriate material for the present application. Both Al or Fe cathodes and anodes were made from rectangular-shaped plates with the dimensions of 50 mm × 180 mm × 5 mm (width, height, wall thickness, respectively). The total effective electrode area was 60 cm<sup>2</sup> and the distance between electrodes was 62 mm.

The pH has a considerable effect on the performance of the EC process [14,18,24]. In an experimental study conducted by Adhoum and Monser [24], the highest COD and color removal efficiencies have been obtained in acidic medium, at pH values in the limits of 4.0–6.0. However, very poor removals are found either at low (<2.0) or high (>10). This behaviour is attributed to the fact that the amphoteric character of Al(OH)<sub>3</sub> that does not precipitate at pH less than 2.0. In addition, it is reported that too high pH will increase Al(OH)<sub>3</sub> solubility and lead to the formation of soluble AlO<sub>2</sub><sup>-</sup> which is useless for water treatment. Similarly, Can et al. [22] have reported that especially at high pH values above 9.0, the quantity of Al(OH)<sub>3</sub> flocs diminishes and the decolorization efficiency and capacity fall. The authors have also suggested that an acidic or neutral initial medium is beneficial for low electrical energy consumption. Therefore, to examine the effects of pH on both COD and color removals, initial pH values were conducted in the range of 4.0–8.82 (original pH) for the present EC application. The pH of samples was adjusted by the gradual addition of 1 N H<sub>2</sub>SO<sub>4</sub> or 1 N NaOH solutions. To explore the effects of other parameters (types of sacrificial electrodes, current density and electrolysis time) on both COD and color removal efficiencies, the initial pH of wastewater samples was kept at original (8.82). Based on preliminary test results, subsequent experiments were then carried out at the best initial pH condition (as found in the previous step) to investigate the effect of selected electrolyte concentration on the EC of UASB pretreated poultry manure wastewater. All the runs were performed at a stable temperature of about 25 °C.

In the EC process, current density determines the coagulant production rate, adjusts the rate and size of the bubble production, and affects the growth of flocs within the reactor [12]. However, Chen [25] has reported when too large current is used, there is a high chance of wasting electrical energy in heating up the water. More

importantly, a too large current density would result in a significant decrease in current efficiency. In order to operate the electrocoagulation system for a long period of time without maintenance, the current density is suggested to be 20–25 A/m<sup>2</sup> unless there are measures taken for a periodical cleaning of the surface of electrodes. Therefore, to investigate the effect of current density on the both COD and color removals, the present EC process was carried out using various current densities ranging from 5 to 25 mA/cm<sup>2</sup>. In each EC run, 400 mL of UASB pretreated poultry wastewater sample was poured into the EC cell and various current densities were then applied. In the batch experiments, measured voltages and applied currents varied in the limits of 4.5–18 V and 0.3–1.5 A, respectively. With these experimental conditions, required energy consumptions were calculated in the range of 0.28–33.75 Wh/(L wastewater).

Kobyas et al. [18] have reported that the ionic strength generally causes an increase in current density at the same cell voltage, or the cell voltage decreases with increasing the electrolyte concentration at constant current density. Chen [25] has reported that table salt is usually employed as the electrolyte to increase the conductivity of the water or wastewater to be treated. Besides its ionic contribution in carrying the electric charge, it was found that chloride ions could significantly reduce the adverse effect of other anions such as HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>. The existence of the carbonate or sulfate ions was found to lead to the precipitation of Ca<sup>2+</sup> or Mg<sup>2+</sup> ions that forms an insulating layer on the surface of the electrodes. This insulating layer would sharply increase the potential between electrodes and result in a significant decrease in the current efficiency. Therefore, the author has recommended that among the anions present, there should be 20% Cl<sup>-</sup> to ensure a normal operation of EC in water treatment. The addition of NaCl would also lead to the decrease in power consumption because of the increase in conductivity. In addition, Wong et al. [49] concluded that the electrochemically generated chlorine was found to be effective in water disinfections. Similarly, Irdemez et al. [50] conducted experimental studies on the phosphate removal from wastewater by EC with four different types of chemicals (NaCl, NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub> and CaCl<sub>2</sub>) used as supporting electrolytes. They concluded that the optimum phosphate removal was obtained with 5 mM of NaCl. Taking into account its above-mentioned benefits, NaCl was selected as the supporting electrolyte in the present EC application. To investigate the influence of selected electrolyte concentration on the EC of UASB pretreated poultry manure wastewater, proper amounts of NaCl (Merck Chemical Corp., analytic quality) ranging from 0.2 to 1.2 g were added to the 400 mL of UASB effluent samples, giving electrolyte concentrations in the range of 0.5–3.0 g NaCl/L. Prior to applying the current, wastewater samples were gently mixed with a glass rod to dissolve the salt and to make the solution homogeneous.

In some of studies [18,22], mixing has been performed by an magnetic stirrer in a constant speed of 200 rpm. However, Ilhan et al. [13] have reported that mixing may cause the break up flocs and negatively affect electrolytic reactions in terms of COD removal efficiency. Therefore, the authors have suggested that a stable solution medium will be much more efficient for mobilization of ions by means of electricity applied. Taking into these considerations, no mixing was not included in the present EC treatment process to obtain higher removal efficiencies.

Samples from the EC cell were taken at predetermined electrolysis times (5, 10, 15, 20, 25, and 30 min). All samples were allowed to settle for about 25 min in a graduated glass vessel before any analysis. 50 mL of supernatant sample was then collected for COD and color analysis after the settling process. No centrifuging or filtration of samples were carried out in either EC run. The COD or color values of samples are in mg/L or Hazen color unit, respectively.

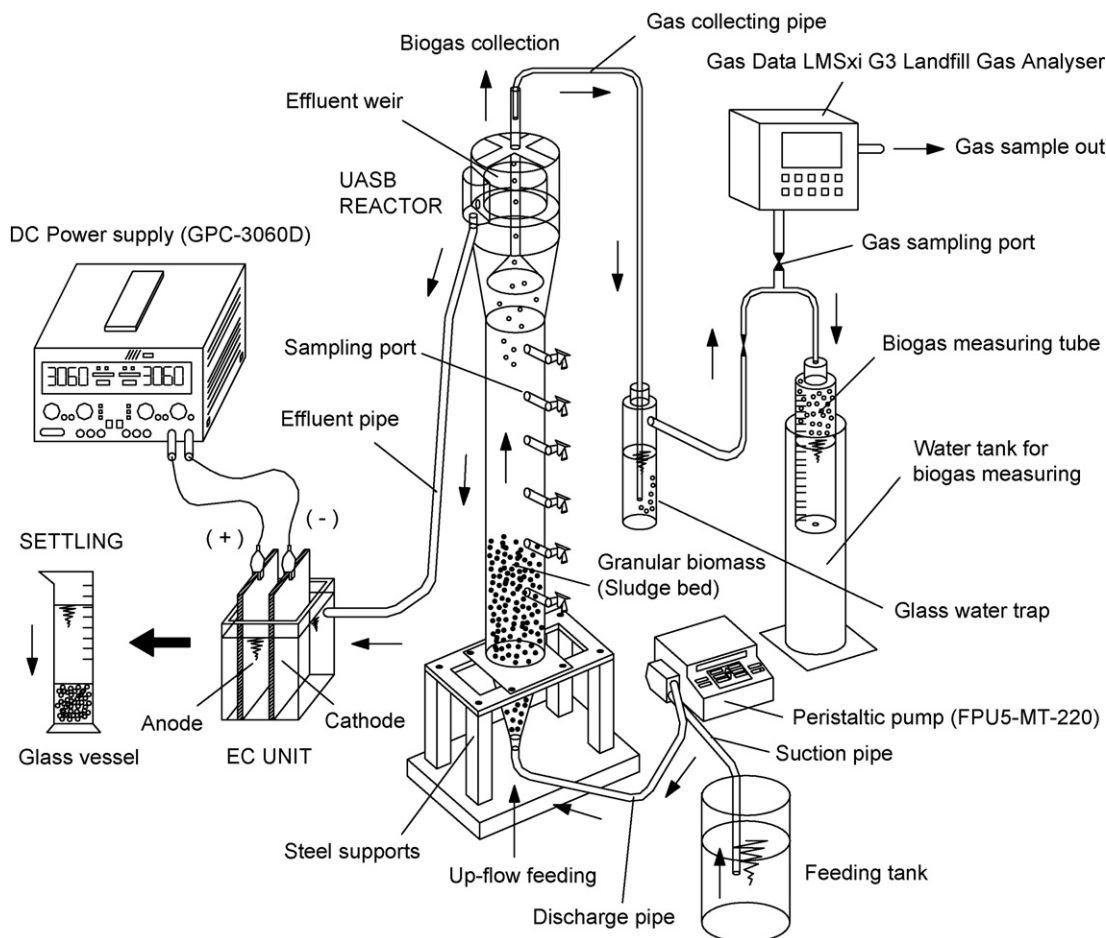


Fig. 2. A detailed schematic of the experimental set-up.

A detailed schematic of the experimental set-up is depicted in Fig. 2.

### 2.5. Fish toxicity test

The fish toxicity test was carried out based on the TDF which indicates the degree of toxicity [30]. Sponza [28] has reported that toxicity dilution volume indicates the volume of wastewater that is diluted with dilution water. In other words, toxic effects can be determined proportionally with the dilution volume in which the wastewater is diluted with a dilution liquid. According to the procedure, the minimum dilution volume in which all fishes remain alive is considered as the TDF value [29]. For example, TDF = 3 means that in wastewater which is diluted by the factor 1:2 and all fish survive a 48-h exposure [28].

Prior to the experimental period, a 10-L glass aquarium, which was also used as the control chamber, was filled only with sterilized dilution water. The sterilized dilution water served as the growth medium had a chemical composition as follows (amounts of constituents are given in parentheses as g for 5 L distilled water):  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  (2.41),  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  (0.616), and  $\text{NaHCO}_3$  (0.042). The prepared dilution water was continuously aerated for 24 h to remove chlorine before putting the fish in.

The acute toxicity potential of the EC effluent was determined using guppy fish (*Lebistes reticulatus*) as the test organism. Guppies were purchased from a local aquarium in Besiktas (Istanbul) and brought to the laboratory within about 15 min in a plastic bag with sufficient air. The plastic bag was first placed into the control aquar-

ium for about 45 min for acclimatization. Then, the plastic bag was cut open and the guppies were allowed to swim into the aquarium water for 48 h of adaptation to the new environment. During the last 24 h of adaptation, and throughout the duration of the experiment, guppies were not fed.

Meanwhile, six identical clean glass jars (each having an active volume of 1 L) were set up and filled with different predetermined volumes of aerated dilution water ranging from 750 to 910 mL. Six different predetermined volumes of EC effluents between 90 and 250 mL were then added to respective jars to obtain different dilution ratios (mL of EC effluent to mL of prepared dilution water, respectively) of 1:10, 1:8, 1:6, 1:5, 1:4 and 1:3, respectively. Although the dilution water was sufficiently aerated, dissolved oxygen levels in each test jar were periodically controlled, and always maintained above 4 mg/L by using an electronically adjustable air pump (Sera Air 275R) during the acute toxicity test. Depending on the dilution ratios, characteristics of obtained solutions were in the following ranges: Temperature  $25.2 \pm 0.2^\circ\text{C}$ , pH 7.1–7.35, dissolved oxygen 6.5–8.12 mg/L, conductivity 1.52–2.50 mS/cm, total dissolved solids (TDS) 545–999 mg/L, and salinity 0.06–0.12%.

After 48 h of adaptation, six guppies were gently netted from the control aquarium at random and immediately transferred into test jars containing different volumes of dilution water and the EC effluent. Behavioural changes of guppies exposed to different amounts of the EC effluent were closely observed for a test period of 48 h. At the end of 48 h, the dilution at which all fish remained alive (no mortality) was accepted as the appropriate dilution [30].

## 2.6. Analytical methods

Influent and effluent pH values were measured by a pH meter (Jenway 3040 Ion Analyser) and a pH probe (HI1230, Hanna Instruments). Soluble chemical oxygen demand (SCOD) was determined by filtering the sample through 0.45 µm Whatmann GF/C filter. Total COD, TS, total suspended solids (TSS), VS, 5-day biological oxygen demand (BOD<sub>5</sub>), alkalinity, ammonia nitrogen (NH<sub>3</sub>-N), total Kjeldahl nitrogen (TKN) and total phosphorus (TP) were conducted by the procedures described in the Standard Methods [51]. Samples were ignited at 550 °C by using an ashing furnace (Lenton) for VS and volatile suspended solids (VSS) analyses. Absorbance values were recorded at 690 nm by using a spectrophotometer (Pharmacia Biotech LKB Novaspec II) for TP analysis. Biogas composition was determined by using a portable multi-channel landfill gas analyser (Gas Data LMSxi G3 Landfill Gas Analyser). Color of wastewater samples was measured with a Merck photometer (SQ 118) and determined as Hazen color unit according to method number of 138 [52].

In the fish toxicity test, dissolved oxygen, TDS, salinity, conductivity, pH and temperature analyses were conducted by using a multiparameter instrument (WTW® Oxi 330i). Stability of the treatment process and components of wastewater samples were

monitored in Environmental Engineering Laboratory at Yildiz Technical University in Istanbul, Turkey.

## 2.7. Statistical analysis

All standard deviations reported in this study were calculated using the statistical functions in spreadsheets of Microsoft Excel and DataFit® scientific software (version 8.1.69, Copyright© 1995–2005 Oakdale Engineering) as ODBC (Open Database Connectivity) data sources.

## 3. Results and discussion

### 3.1. UASB process

Previous results of Yetilmezsoy and Sakar [27] regarding the anaerobic treatability of poultry manure wastewater under various organic and hydraulic loading conditions are summarized in Table 1. As seen in Table 1, the poultry manure wastewater was satisfactorily pretreated by means of high-rate anaerobic processes, specifically with the use of UASB reactors. The previous experiments were divided into three operational phases. The two of these (1:8 and 1:6) were consecutively performed in R1 and

**Table 1**  
Performance data of UASB reactors treating of poultry manure wastewater under various organic and hydraulic loading conditions [27]

Constituent	Reactor	Feed ratio	UASB influent (mean ± S.D.)	UASB effluent (mean ± S.D.)	Efficiency (%) (mean ± S.D.)
Total chemical oxygen demand, TCOD (mg/L)	R1	1:8	12100 ± 910	1750 ± 200	85 ± 2.0
	R1	1:6	19550 ± 730	1930 ± 170	90 ± 1.0
	R2	1:4	29970 ± 1560	3030 ± 600	90 ± 2.0
Biological oxygen demand, BOD <sub>5</sub> (mg/L)	R1	1:8	5900 ± 390	420 ± 50	93 ± 1.5
	R1	1:6	9100 ± 250	380 ± 40	96 ± 0.5
	R2	1:4	14800 ± 440	950 ± 150	94 ± 1.0
Soluble chemical oxygen demand, SCOD (mg/L)	R1	1:8	2090 ± 170	1110 ± 90	47 ± 6.5
	R1	1:6	3420 ± 140	1220 ± 100	65 ± 3.0
	R2	1:4	5220 ± 360	2490 ± 490	53 ± 9.0
Total solids, TS (mg/L)	R1	1:8	8280 ± 700	1980 ± 200	76 ± 3.5
	R1	1:6	12580 ± 500	1770 ± 150	87 ± 1.0
	R2	1:4	21110 ± 970	5550 ± 950	74 ± 5.0
Volatile solids, VS (mg/L)	R1	1:8	5370 ± 450	1380 ± 126	74 ± 3.5
	R1	1:6	8680 ± 260	1129 ± 100	87 ± 1.0
	R2	1:4	13210 ± 530	3940 ± 840	70 ± 6.5
Total suspended solids, TSS (mg/L)	R1	1:8	5020 ± 370	1130 ± 70	78 ± 2.5
	R1	1:6	8020 ± 300	1060 ± 100	87 ± 1.5
	R2	1:4	12300 ± 560	3150 ± 660	75 ± 5.5
Volatile suspended solids, VSS (mg/L)	R1	1:8	4020 ± 340	970 ± 120	76 ± 4.0
	R1	1:6	6760 ± 220	890 ± 70	87 ± 1.0
	R2	1:4	10060 ± 590	2730 ± 320	73 ± 4.0
Total Kjeldahl nitrogen, TKN (mg/L)	R1	1:8	1830 ± 130	1390 ± 120	23 ± 10.0
	R1	1:6	2980 ± 100	2310 ± 170	23 ± 6.0
	R2	1:4	4430 ± 210	3562 ± 320	20 ± 7.0
Ammonia nitrogen, NH <sub>3</sub> -N (mg/L)	R1	1:8	990 ± 70	1180 ± 70	-21 ± 12 <sup>a</sup>
	R1	1:6	1760 ± 70	1970 ± 90	-12 ± 6.0 <sup>a</sup>
	R2	1:4	2200 ± 90	2610 ± 170	-18 ± 7.0 <sup>a</sup>
Total phosphorus, TP (mg/L)	R1	1:8	450 ± 30	380 ± 30	14 ± 9.0
	R1	1:6	730 ± 30	460 ± 40	38 ± 5.0
	R2	1:4	1120 ± 60	890 ± 150	21 ± 13.5
pH	R1	1:8	7.30 ± 0.20	8.30 ± 0.20	-
	R1	1:6	7.20 ± 0.10	8.10 ± 0.20	-
	R2	1:4	7.10 ± 0.20	8.00 ± 0.10	-
Alkalinity (mg CaCO <sub>3</sub> /L)	R1	1:8	3210 ± 200	2690 ± 190	16 ± 9.0
	R1	1:6	5250 ± 200	3280 ± 270	38 ± 5.5
	R2	1:4	7550 ± 330	5920 ± 700	22 ± 9.0

<sup>a</sup> The negative value of ammonia corresponds to an increase in the reactor.

the other (1:4) in R2. On the basis of the cross-sectional area of the reactors (95 cm<sup>2</sup>) and applied feed flow rates from 1 to 2 L/day, hydraulic loading rates were controlled between 0.105 and 0.21 m<sup>3</sup>/(m<sup>2</sup> day). The UASB reactors were conducted with three different HRTs of 15.7, 12.0 and 8.0 days, and with OLR between 0.65 and 1.78 kg COD/(m<sup>3</sup> day). The pH of feed to the reactors ranged from 6.96 to 7.82, with an average value of 7.3 (±0.2). Both R1 and R2 showed a remarkable performance on total COD reductions with average treatment efficiencies between 85 and 90% under varying organic and hydraulic loading conditions.

During operational phases, TP and TKN removals ranged from 14 to 38%, and from 20 to 23% on average, respectively. These relatively low treatment efficiencies may be expected for TKN and TP, since anaerobic reactors are known to reduce negligible amounts of nutrients. Demirer and Chen [53] have observed similar results for the anaerobic digestion of dairy manure in a hybrid reactor with biogas recirculation. The removals in TP and TKN can be ascribed to both new biomass production, as well as settling in the reactor, as reported by Lyerly [54].

The NH<sub>3</sub>-N concentrations on average were increased between 12 and 21% during operational phases. This can be attributed to the anaerobic bioconversion of proteins contained in manure into amino acids and then to ammonia nitrogen, as reported by Demirer and Chen [53]. This also resulted in an increase of effluent pH, as seen in Table 1. The negative value of ammonia nitrogen removal in Table 1 corresponds to an increase in the reactors. These results agreed with the findings also reported by other researchers [53,55,56]. The reductions in the alkalinity can be ascribed to the buffering of the volatile fatty acids during the digestion process. The observed increases in COD, BOD<sub>5</sub>, SCOD and solids removals in R1, conducted with the feed ratio of 1:6, can be explained by acclimation of the granular biomass to operating conditions.

Depending on various organic and hydraulic loading conditions, daily biogas production rates ranged between 4.2 and 29.4 L/day, and over 73% of influent organic matters imposed to the systems were transformed to biogas on average, with a methane content over 70%. The volumetric COD removals were achieved between 0.55 and 3.78 kg COD<sub>removed</sub>/(m<sup>3</sup> day).

At the end of the third phase (1:4), a feed ratio of 1:2 was also employed as the highest substrate loading condition in R2. The daily-continuous operation was continued in R2 at relatively high COD concentrations ranging from 52,840 to 62,050 mg/L, with an average concentration of 57,820 (±3440) mg/L. The pH of the feed varied between 6.98 and 7.32, with an average value of 7.16 (±0.10). The last phase (1:2) was studied with same HRTs of 15.7, 12 and 8 days for a total operating time of 72 days. Although relatively high incoming COD concentrations were imposed to the system, R2 demonstrated a stable performance on the anaerobic treatability of poultry manure wastewater, and no process failure was recorded. This should be due to acclimatization of both acidogens and methanogens to the gradual flow regime and OLR after a longer adaptation stage. Results showed that rounded COD removal percentages in the last phase (1:2) ranged from 75 to 81%, with an average value of 78.5 (±2.5)%.

During operational phases, UASB effluents were periodically collected in a 15-L plastic container for further analyses. Remaining volumes of effluent wastewaters were used for other experimental analyses. Because the mixed wastewater contained different volumes of effluents from all operating phases, COD and color analyses were performed on the mixed wastewater to determine final organic pollutant contents after undergoing biological treatment. Experimental results showed that the mixed UASB effluent had a high COD concentration of 4120 mg/L and was dark in color (3390 Hazen units). Initial pH and conductivity of the mixed effluent were about 8.22 and 4.48 mS/cm at 25 °C, respectively. High

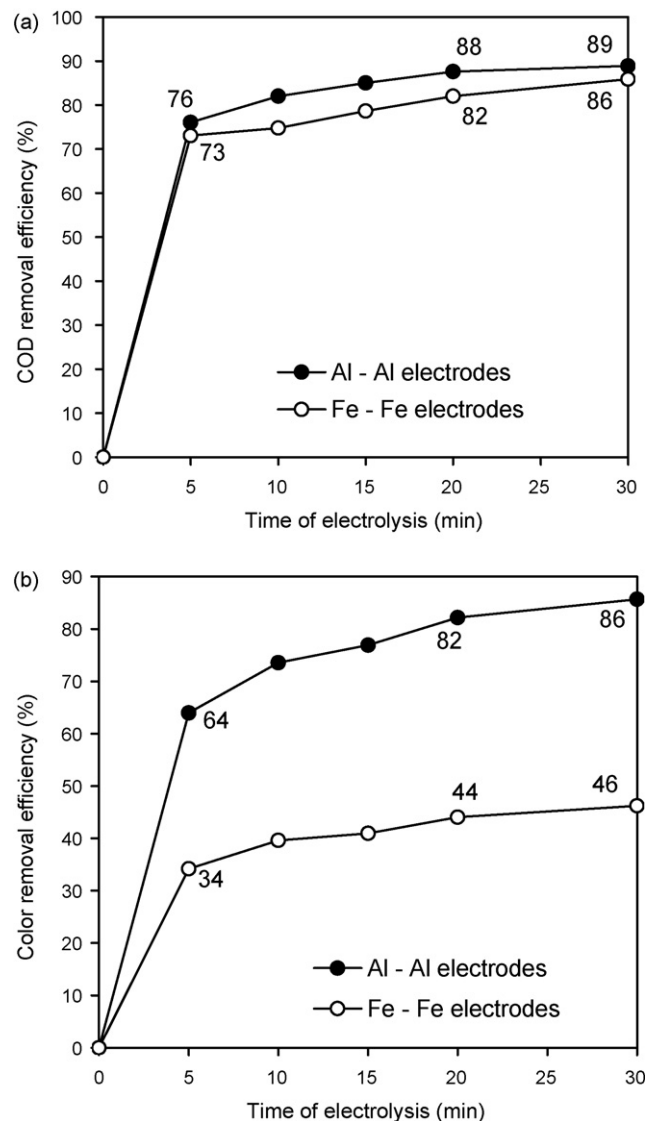


Fig. 3. Effects of electrode materials on COD and color removal efficiencies (current density: 15 mA/cm<sup>2</sup>, initial pH: 8.22, electrolyte concentration: 1 g NaCl/L, electrolysis time: 5–30 min).

COD concentration and dark brown color of the mixed wastewater can be attributed to the contribution of the effluent of the last phase (1:2) conducted as the highest substrate loading condition in R2. Although high removals were obtained even at relatively higher organic loading conditions such as (1:4) and (1:2), the effluent quality particularly in terms of the residual COD indicated that compliance with the effluent discharge standards would not be met.

### 3.2. Electrocoagulation process

#### 3.2.1. Selection of the electrode material

COD and color removals as a function of electrode material are depicted in Fig. 3(a and b). Results showed that both materials are almost equally effective in terms of COD removals. In preliminary tests, COD removal efficiencies ranged from 76 to 89% and 73 to 86% for Al and Fe electrodes, respectively. Although high COD removals were achieved with both materials, the performance of Al electrodes were superior than Fe electrodes in terms of the color removal. Preliminary test results indicated that color removal



efficiencies ranged from 64 to 86% and 34 to 46% for Al and Fe electrodes, respectively. This phenomenon may be ascribed to the excess of  $\text{Fe}^{2+}$  and/or  $\text{Fe}^{3+}$  species generated during the electrolysis and characterized by their yellow-brown color. Adhoum and Monser [24] have reported similar results for decolorization and removal of phenolic compounds from olive mill wastewater by EC process.

To conclude, Al electrodes were found to be more effective for both COD and color removals than Fe electrodes in this study. Due to the fact that the costs of both types of electrodes are almost same, it will be a good choice for higher treatment efficiencies to select Al electrodes. Therefore, subsequent batch experiments were conducted with Al electrodes to investigate the effects of other operational parameters on the removal efficiencies of COD and color, respectively.

The previous studies [12–14,18,21–24] conducted with Al, Fe and stainless steel (SS) electrode materials reveal that total effective area of electrodes and the distance between electrodes have been studied in the limits of 35–80  $\text{cm}^2$  and 3–65 mm, respectively. On the basis of maximum COD and color removals obtained for different types of electrode materials, the present data seems to be comparable with those reported by others. However, it is noted that differences are due to the characteristics of studied wastewaters and main operating conditions such as applied current, initial pH, electrolysis time, and also different types of electrode materials (Al, Fe and SS). Low COD [21,23] and color [21] removals may be attributed to the presence of several recalcitrant inorganic compounds, complex components, and other undesirable impurities in the wastewaters.

### 3.2.2. Effect of current density

Fig. 4(a and b) represent the effects of the electrolysis time on COD and color removal efficiencies for various current densities using Al electrode materials. As the current density increased, the electrolysis time needed to achieve similar efficiencies decreased.

As seen in Fig. 4(a and b), about 80.8% of COD removal was obtained at the current density of 5  $\text{mA}/\text{cm}^2$  in 30 min. However, 81 and 82% of COD removals were reached at current densities of 10 and 15  $\text{mA}/\text{cm}^2$  in 20 and 10 min, respectively. At the current density of 25  $\text{mA}/\text{cm}^2$ , 80% of COD removal was achieved in a relatively short electrolysis time of 5 min. Likewise, almost 69% of color removal was attained at the current density of 5  $\text{mA}/\text{cm}^2$  in 30 min. Similar color removal efficiencies of about 70% and 69% were obtained at current densities of 10 and 25  $\text{mA}/\text{cm}^2$  in 15 and 5 min, respectively. This expected behaviour can be explained by the fact that the treatment efficiency was mainly affected by charge loading, as reported by others [20,24]. This phenomenon may also be ascribed to increasing bubble density at high current, resulting in a greater flux and faster removal of pollutants. In an experimental study, Khosla et al. [57] have reported similar observations on the pulsed electrogeneration of bubbles for electroflotation.

In general, the graphs of COD and color removals versus electrolysis time demonstrated an increasing trend with the increase of current density. However, on the basis of present discharge standards for livestock and poultry industries stated in the Turkish Water Pollution Control Regulation [30], acceptable final discharge levels in terms of COD concentration were achieved at current densities of 15, 20 and 25  $\text{mA}/\text{cm}^2$  for the corresponding electrolysis times of 20, 15 and about 14 min, respectively. Although high COD removals up to about 83% were achieved at current densities below 15  $\text{mA}/\text{cm}^2$ , however, desired effluent quality was not found to be sufficient to meet current discharge requirements even in a relatively long electrolysis time of 30 min.

The electrical energy consumptions in electrolysis times of 20, 15 and about 14 min were determined to be about 2.6, 3.17 and

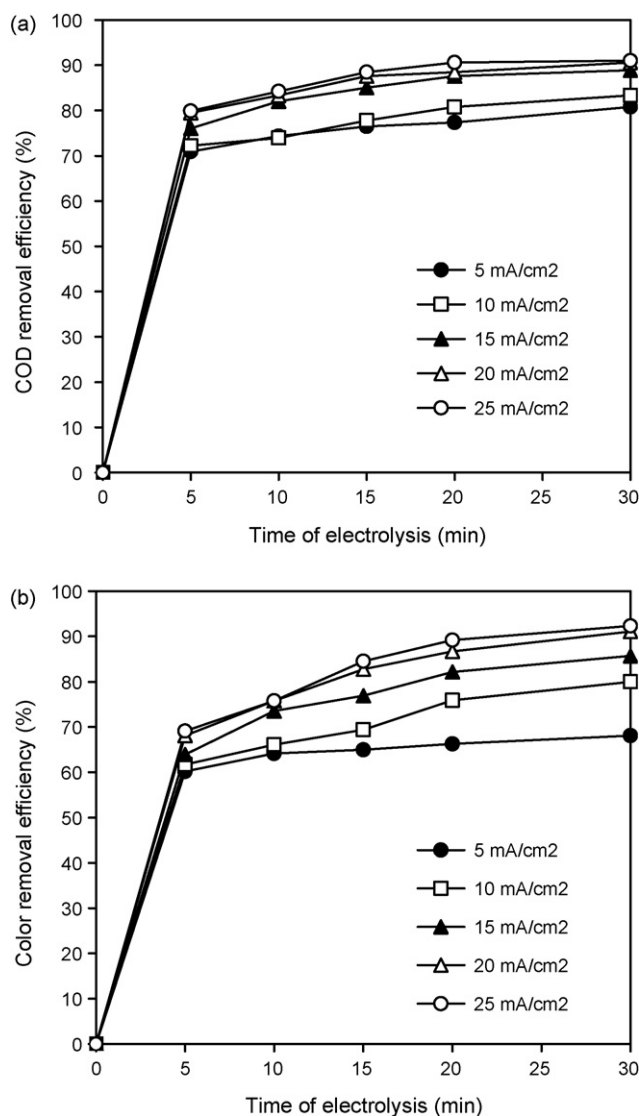


Fig. 4. Effects of electrolysis time on COD and color removal efficiencies (current density: 5–25  $\text{mA}/\text{cm}^2$ , initial pH: 8.22, electrolyte concentration: 1 g NaCl/L).

4.35  $\text{Wh}/\text{g COD}_{\text{removed}}$  for the corresponding current densities of 15, 20 and 25  $\text{mA}/\text{cm}^2$ , respectively. From the economical point of view, the optimal operating condition to guarantee acceptable discharge standards was determined to be a current density of 15  $\text{mA}/\text{cm}^2$  with an electrolysis time of 20 min. Results also showed that after an electrolysis time of 20 min, both COD and color removal efficiencies were generally not found to be changed significantly. To summarize, longer electrolysis times (>20 min) unnecessarily prolonged the process to obtain similar result. Therefore, taking into account both cost of energy consumed and imposed discharge standards, an electrolysis time of 20 min was considered to be optimal for further batch experiments.

Findings of batch experiments showed that both COD and color removal efficiencies increased with the increase of current density. However, it also increases the electrical energy consumption. From the economical point of view, removal efficiencies and the corresponding energy consumptions should be evaluated to achieve an optimized current density. Therefore, Fig. 5 was developed as a graph with removal efficiencies and energy consumptions according to required electrical energy quantities to remove per g COD and color units.

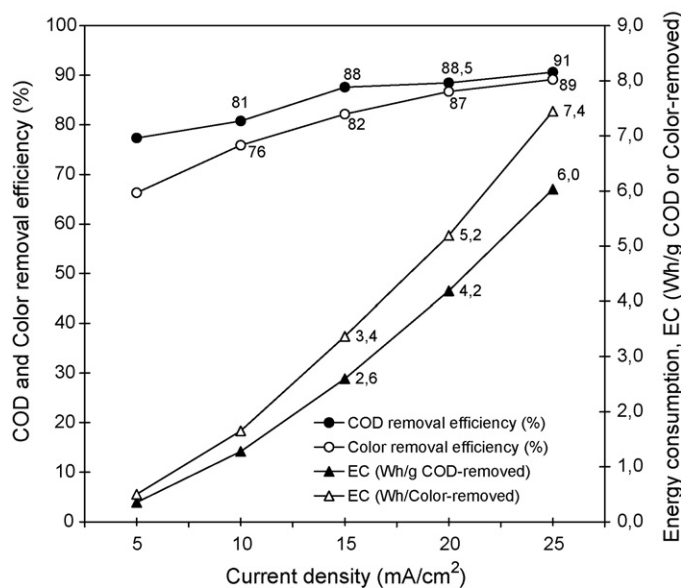


Fig. 5. Effects of current density on COD and color removal efficiencies (initial pH: 8.22, electrolyte concentration: 1 g NaCl/L, electrolysis time: 20 min).

With these experimental conditions, high percentages of COD and color removals (>80%) were obtained from the point of 15 mA/cm<sup>2</sup>, as seen in Fig. 5. A further increase in current density from 15 to 25 mA/cm<sup>2</sup> resulted a small increase from 88 to 91% in the efficiency of COD removal. For the same increase in current density, color removal efficiency increased from 82 to 89%. However, as shown in Fig. 5, electrical energy consumptions in term of Wh/Color<sub>removed</sub> and Wh/g COD<sub>removed</sub> were determined to be about 2.2 and 2.3 times higher in this case, respectively. Daneshvar et al. [12] reported similar results for the decolorization of basic dye solutions by the EC process. Taking into account the cost of electrical energy consumed in the EC process, the optimal current density was determined to be 15 mA/cm<sup>2</sup> for high COD and color removals with reasonable energy consumptions.

### 3.2.3. Effect of initial pH

COD and color removals as a function of initial pH are depicted in Fig. 6. As shown in Fig. 6, high removals of COD (88.6–89.4%) and color (90.6–92%) were achieved in acidic medium, at initial pH

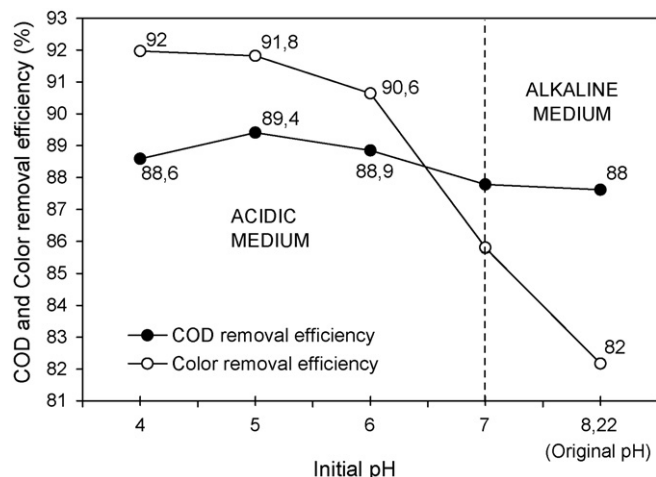


Fig. 6. Effects of initial pH on COD and color removal efficiencies (current density: 15 mA/cm<sup>2</sup>, electrolyte concentration: 1 g NaCl/L, electrolysis time: 20 min).

values in the range of 4.0–6.0. When the initial pH was kept original at 8.22, removal efficiencies of COD and color were obtained to be 88% and 82%, respectively. Although high removals of COD and color were attained by the EC without further pH adjustment, experimental results at pH 5.0 indicated that performance of the EC process in terms of COD and color removal efficiencies can be improved up to about 90 and 92%, respectively.

Batch experiments clearly demonstrated that the highest removal efficiencies were obtained in acidic medium with pH < 7.0. Results also indicated that decolorization performance decreased slowly from 4 to 6 but rapidly from 6 to 8.22. This can be attributed to the fact that acidic or alkaline medium affects the mechanism of coagulation and leads to the formation of different chemical species in the bulk wastewater. Similar results have been reported in other studies using Al electrodes [21,22].

It can be concluded that an acidic initial medium was found to be beneficial to achieve the highest COD and color removals. Final effluents under these conditions were observed to be transparent and very pale yellow in color. However, it is noted that acceptable final discharge levels in terms of COD concentration can also be achieved at original pH. Thus, a further pH adjustment may not be necessary. On the other hand, when the initial pH was kept original, lower color removal efficiency was obtained compared to color removals achieved in acidic medium. From an aesthetic point of view, results indicated that acidic medium was more suitable to achieve highest efficiencies in terms of both COD and color removals. Considering the highest removal efficiencies, particularly for COD, pH 5.0 was selected as the best initial pH condition for the present application. However, it can also be noted that neutral or original pH conditions can be conducted for the post-treatment of UASB pretreated poultry manure wastewater, depending on the desired effluent quality at the time of discharge.

### 3.2.4. Effect of electrolyte concentration

Fig. 7 depicts the effect of electrolyte concentration on the performance of the present EC process. Voltages between electrodes were also measured and plotted against the electrolyte concentration of related wastewater samples (Fig. 7). Increasing the electrolyte concentration resulted in the reduction of cell voltages that caused a decrease in electrical energy consumption. Results showed that high COD and color removals can be achieved with low cell voltages. With the addition of NaCl to the medium, following reactions take place in the wastewater [25,58]:

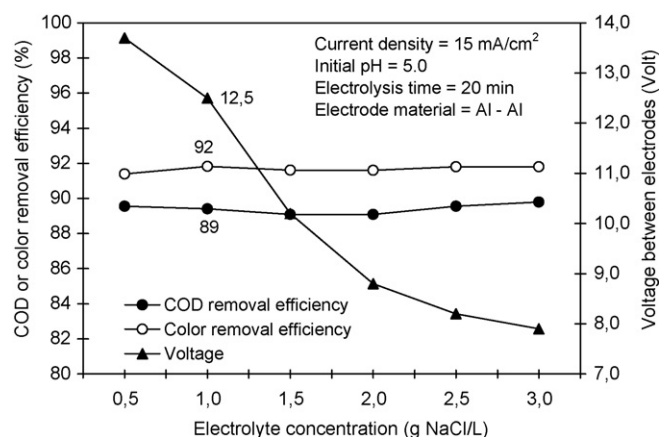


Fig. 7. Effects of electrolyte concentration on COD and color removal efficiencies (current density: 15 mA/cm<sup>2</sup>, initial pH: 5.0, electrolysis time: 20 min).



As shown in above reactions, the electrochemically generated  $\text{Cl}_2$  served as a strong oxidant that could oxidize some organic compounds remaining in the bulk wastewater. However, it was found that with the addition of more NaCl to the wastewater samples, COD and color removal efficiencies remained almost unchanged in the investigated electrolyte concentration range of 0.5–3.0 g NaCl/L. Based on the experimental results, it can be concluded that electrolyte concentration did not show a considerable effect on both COD and color removal from the UASB effluent as much as other parameters.

In the previous studies, conductivity or electrolyte concentration have been adjusted by adding an appropriate amount of NaCl, and similar results have been expressed as either mS/cm [12–14,18,22,23] or g NaCl/L [21]. Based on these units, previous findings show that conductivity or electrolyte concentration have been conducted in the range of 0.25–21.1 mS/cm or up to 2 g NaCl/L, respectively.

### 3.3. Fish toxicity test

The maximum permissible TDF value (for composite samples taken in both 2 and 24 h) for the present type of discharge was set at 10 according to the Turkish Water Pollution Control Regulation [30]. Therefore, to evaluate the toxicity of the EC effluent, guppies were exposed to different media having TDF values both below and above this limit. The survival of guppies (*L. reticulatus*) was monitored after 48 h of incubation period at ambient temperature. It was observed that all guppies were alive and showed normal behaviour at the end of 48-h exposure. Toxicity test results indicated that guppies survived even in more concentrated solutions having TDF values lower than the national permissible TDF limit of 10. After 48 h of test period, guppies were not netted from test jars and behavioural changes of individuals were monitored for an additional 120 h of incubation. Results indicated that all guppies were still alive and showed normal behaviour even at the end of the additional 120 h of exposure.

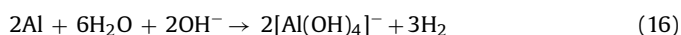
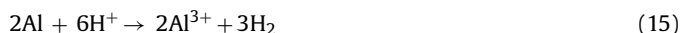
The present toxicity test clearly proved that the EC effluent did not cause any acute toxicity symptoms or mortality in guppies. This can be attributed to the fact that residual biorecalcitrant compounds, which may have adverse effects on the aquatic environment, have been effectively eliminated from the UASB effluent by the EC process. On the basis of the toxicity test results, it can be concluded that the use of EC process as a post-treatment technology has successfully detoxified the UASB effluent and removed its undesirable compounds. This result has opened promising and encouraging perspectives on the post-treatment of anaerobically pretreated animal manure wastewaters by the EC, which can be proposed as a reliable, safe and cost-effective method.

### 3.4. Final disposal of the EC sludge

The handling and disposal of the sludge resulting from chemical precipitation (CP) is one of the greatest difficulties associated with chemical treatment. Sludge is produced in large volumes from most CP operations, and the total sludge generated by CP contains almost 50% of added coagulant. In addition, CP usually generates sludge in the caustic pH range above 10. The metals precipitate as hydroxides, a hazardous form because the metals will become soluble again at the natural pH range around 7. Therefore, when CP is used, anaerobic digestion for sludge stabilization and also land application may not be possible because of the toxicity of the precipitated

heavy metals. On the other hand, EC can produce an environmentally friendly sludge at a pH range from 6 to 7. The metals in the EC sludge at this pH range are stabilized in a non-hazardous form as oxides [59]. However, taking into account the increasing public health problems, Al content of the sludge becomes an important issue. Since this metal has been pointed out to be a potential hazard in a leaching event and also a primary cause of the Alzheimer disease, the disposal of alum sludge needs to be given a particular focus for investigation.

Chen et al. [20] have reported that electrochemical reactions in the bulk wastewater, in most cases, make the wastewater acidic at anode surfaces and alkali at cathode surface. As a result, the actual electrode consumption can be expected to be greater than the theoretical value. According to several authors [20,22,58,60], the dissolution of Al occurs at the anode and cathode vicinities through the following reactions, respectively [20,60]:



With the optimum conditions determined in this study, Al contents in the supernatant and in the EC sludge were found to be about 2.3 and 405.2 mg/L, respectively. Results showed that almost 99.5% of the amount of the released Al precipitated in the form of alum sludge. The amount of Al generated during the EC exceeded the theoretical value (250 mg/L) calculated from Faraday's law. The current efficiency of aluminum dissolution was in our case about 163%. This was similar to the value reported by Mouedhen et al. [60]. These results also indicated that the Al content in the supernatant was found to be less than 3 mg/L, which was considered the only acceptable Al level for composite samples taken in 2 h [30].

Alum sludge from commercial or industrial wastewater treatment plants is regulated waste and its disposal, incineration, recycling or reprocessing, transportation, storage and treatment must be carried out under a licence or development approval issued in accordance with the provisions of the Environmental Protection Act in force [61]. However, land disposal of alum sludge requires at least 10–20% solids content. Currently, the most effective means of sufficiently dewatering alum sludge for disposal is mechanical filter pressing. Although this method yields dewatered alum sludge possessing at least 30–50% solids, the initial equipment cost and subsequent operational costs are high [62]. In any case, the disposal of alum sludge in a landfill results in the loss of a valuable asset and at the same time depletes the capacity of the landfill [63]. In addition, alum sludge is generally considered unsuitable for use as a soil conditioner due to its potential to reduce fertility by soil phosphates binding with Al [61].

The cost of alum sludge disposal is related to its solids content and dewatering characteristics. It is well known that recovery of alum in the form of the alum sludge improves the dewatering characteristics of the remaining solids and reduces the overall quantity of solids which require disposal. Therefore, recovery of alum in the form of the alum sludge reduces the overall disposal cost [62,63]. This process is a viable method of reducing sludge-handling requirements. Furthermore, the recovered alum can be used at the water and at the wastewater treatment plants [63]. In recent years, recycled alum sludge has been used in various types of treatment processes such as lead metal removal [64] and dye removal from textile wastewater [65]. Consequently, acceptance of recovered alum as a sustainable, low-cost, and environmentally friendly by-product will contribute to its universal appeal for disposal of alum sludge, particularly for the needs of developing countries.

#### 4. Conclusions

The UASB process showed a remarkable performance for the pretreatment of highly concentrated poultry manure wastewaters under various organic and hydraulic loading conditions. During all phases, total COD removal efficiencies ranged between 75 and 94%, and volumetric COD removal rates ranging from 0.55 to 6.10 kg COD<sub>removed</sub>/(m<sup>3</sup> day) were achieved. Under the highest substrate loading phase (1:2) conducted with a HRT of 8 days, the maximum OLR and the maximum total COD reduction were about 7.9 kg COD/(m<sup>3</sup> day) and 81%, respectively. Although relatively high substrate loadings were imposed to the system, noticeable difficulties in the reactor performance such as excessive foaming or sludge flotation were not observed. However, pretreated effluents obtained in this step still contained relatively high COD and color levels, which were not suitable to meet receiving water discharge standards. Therefore, an important objective was to explore the applicability of the EC as an advanced treatment technique for removal of residual COD and color from anaerobically pretreated poultry manure wastewater.

Effect of various operational parameters on the EC of UASB pretreated poultry manure wastewater were investigated and optimized. Preliminary tests conducted with two types of sacrificial electrodes indicated that Al electrodes were found to be more effective for both COD and color removals than Fe electrodes for the present application. Batch experimental results showed that optimal operating conditions were found to be an initial pH of 5.0, a current density of 15 mA/cm<sup>2</sup>, and an electrolysis time of 20 min. The electrolyte concentration was not found to have a considerable influence on both COD and color removal from the UASB effluent as much as other parameters. Findings of this experimental study clearly showed that under the optimal conditions, about 90% of COD and 92% of residual color could be successfully removed from the UASB effluent with the further contribution of the EC technology used as a post-treatment unit. Consequently, the EC can be considered as an appropriate alternative to existing techniques or applied as a post-treatment step after an undergoing biological process to improve the quality of the final discharge in terms of residual COD and color removal.

In order to evaluate the possible toxicity of the EC effluent according to the Turkish Water Pollution Control Regulation, a toxicological test was also performed using guppy fish (*L. reticulatus*) as the test organism. All guppies survived and exhibited normal visual responses at the end of 48-h exposure. The present toxicity test proved that the EC effluent did not cause any acute toxicity symptoms or mortality in guppies. Findings of this study also showed that incorporation of a toxicological test into conventional physicochemical analyses provided a better evaluation of discharge characteristics of a specific effluent for its possible hazardous impacts on the aquatic ecosystem.

#### Acknowledgements

The authors wish to thank to Mr. Hasan Mutlu who is the owner of Hakan's Poultry Farm for providing the poultry manure used as feed material in the experiments. The authors would like to thank to Pasabahce (Tekel) Distillery Inc. for supplying the granular biomass used in this study. The authors also appreciate Dr. Bulent I. Goncaloglu for providing information regarding the fish toxicity test.

#### References

- [1] S. Kalyuzhnyi, V. Fedorovich, A. Nozhevnikova, Anaerobic treatment of liquid fraction of hen manure in UASB reactors, *Bioresour. Technol.* 65 (1998) 221–225.
- [2] E.I. Atuanya, M. Aigbirior, Mesophilic biomethanation and treatment of poultry wastewater using pilot scale UASB reactor, *Environ. Monit. Assess.* 77 (2002) 139–147.
- [3] S. Harikishan, S. Sung, Cattle waste treatment and Class A biosolid production using temperature-phased anaerobic digester, *Adv. Environ. Res.* 7 (2003) 701–706.
- [4] K. Yetilmezsoy, S. Sakar, Improvement of COD and color removal from UASB treated poultry manure wastewater using Fenton's oxidation, *J. Hazard. Mater.* 151 (2008) 547–558.
- [5] S. Sakar, K. Yetilmezsoy, E. Kocak-Enturk, Anaerobic digestion technology in poultry and livestock waste treatment—a literature review, *Waste Manage. Res.* (in press).
- [6] G. Gungor-Demirci, G.N. Demirer, Effect of initial COD concentration, nutrient addition, temperature and microbial acclimation on anaerobic treatability of broiler and cattle manure, *Bioresour. Technol.* 93 (2004) 109–117.
- [7] L.-W. Deng, P. Zheng, Z.-A. Chen, Anaerobic digestion and post-treatment of swine wastewater using IC-SBR process with bypass of raw wastewater, *Process Biochem.* 4 (2006) 965–969.
- [8] S.W. Hong, Y.S. Choi, G. Kwon, K.Y. Park, Performance evaluation of physicochemical processes for biologically pre-treated livestock wastewater, *Water Sci. Technol.* 52 (2005) 107–115.
- [9] S. Kalyuzhnyi, V. Sklyar, A.E.I. Arkhipchenko, I. Barboulina, O. Orlova, A. Klapwijk, Combined biological and physico-chemical treatment of filtered pig manure wastewater: pilot investigations, *Water Sci. Technol.* 45 (2002) 79–87.
- [10] S. Kalyuzhnyi, V. Sklyar, A.E.I. Arkhipchenko, I. Barboulina, O. Orlova, A. Kovalev, A. Nozhevnikova, A. Klapwijk, Sustainable treatment and reuse of diluted pig manure streams in Russia, *Appl. Biochem. Biotechnol.* 109 (2003) 77–94.
- [11] Z. Milan, E. Sanchez, P. Weiland, C. de Las Pozas, R. Borja, R. Mayari, N. Roviroso, Ammonia removal from anaerobically treated piggery manure by ion exchange in columns packed with homoionic zeolite, *Chem. Eng. J.* 66 (1997) 65–71.
- [12] N. Daneshvar, A. Oladegaragoze, N. Djafarzadeh, Decolorization of basic dye solutions by electrocoagulation: an investigation of the effect of operational parameters, *J. Hazard. Mater.* 129 (2006) 116–122.
- [13] F. Ilhan, U. Kurt, O. Apaydin, M.T. Gonullu, Treatment of leachate by electrocoagulation using aluminum and iron electrodes, *J. Hazard. Mater.* 154 (2008) 381–389.
- [14] Y. Avsar, U. Kurt, T. Gonullu, Comparison of classical chemical and electrochemical processes for treating rose processing wastewater, *J. Hazard. Mater.* 148 (2007) 340–345.
- [15] N. Drouiche, N. Ghaffour, H. Lounici, M. Mameri, Electrocoagulation of chemical mechanical polishing wastewater, *Desalination* 214 (2007) 31–37.
- [16] M. Asselin, P. Drogui, S.K. Brar, H. Benmoussa, J.-F. Blais, Organics removal in oily bilgewater by electrocoagulation process, *J. Hazard. Mater.* 151 (2008) 446–455.
- [17] Z. Zaroual, M. Azzi, N. Saib, E. Chainet, Contribution to the study of electrocoagulation mechanism in basic textile effluent, *J. Hazard. Mater.* 131 (2006) 73–78.
- [18] M. Kobya, O.T. Can, M. Bayramoglu, Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes, *J. Hazard. Mater.* B100 (2003) 163–178.
- [19] J.R. Parga, D.L. Cocke, J.L. Valenzuela, J.A. Gomes, M. Kesmez, G. Irwin, H. Moreno, M. Weir, Arsenic removal via electrocoagulation from heavy metal contaminated groundwater in La Comarca Lagunera México, *J. Hazard. Mater.* 124 (2005) 247–254.
- [20] X. Chen, G. Chen, P.L. Yue, Separation of pollutants from restaurant wastewater by electrocoagulation, *Sep. Purif. Technol.* 19 (2000) 65–76.
- [21] T.-H. Kim, C. Park, E.-B. Shin, S. Kim, Decolorization of disperse and reactive dyes by continuous electrocoagulation process, *Desalination* 150 (2002) 165–175.
- [22] O.T. Can, M. Bayramoglu, M. Kobya, Decolorization of reactive dye solutions by electrocoagulation using aluminum electrodes, *Ind. Eng. Chem. Res.* 42 (2003) 3391–3396.
- [23] H. Inan, A. Dimiglo, H. Simsek, M. Karpuzcu, Olive oil mill wastewater treatment by means of electro-coagulation, *Sep. Purif. Technol.* 36 (2004) 23–31.
- [24] N. Adhoum, L. Monser, Decolourization and removal of phenolic compounds from olive mill wastewater by electrocoagulation, *Chem. Eng. Process.* 43 (2004) 1281–1287.
- [25] G. Chen, Electrochemical technologies in wastewater treatment, *Sep. Purif. Technol.* 38 (2004) 11–41.
- [26] M.Y.A. Mollah, R. Schennach, J.R. Parga, D.L. Cocke, Electrocoagulation (EC)—science and application, *J. Hazard. Mater.* B84 (2001) 29–41.
- [27] K. Yetilmezsoy, S. Sakar, Development of empirical models for performance evaluation of UASB reactors treating poultry manure wastewater under different operational conditions, *J. Hazard. Mater.* 153 (2008) 532–543.
- [28] D.T. Sponza, Toxicity studies in a chemical dye production industry in Turkey, *J. Hazard. Mater.* A138 (2006) 438–447.
- [29] D.T. Sponza, Application of toxicity tests into discharges of the pulp-paper industry in Turkey, *Ecotoxicol. Environ. Saf.* 54 (2003) 74–86.
- [30] TWPCR (Turkish Water Pollution Control Regulation), Official Gazette No. 25687 dated December 31, 2004.
- [31] A. Castano, M.J. Cantarino, P. Castillo, J.V. Tarazona, Correlation between the RTG-2 cytotoxicity test EC50 and in vivo LC50 rainbow trout bioassay, *Chemosphere* 32 (1996) 2141–2157.
- [32] D. Sponza, Toxicity survey in the effluents of leather, textile and petrochemical industry treatment plants, *Su Kirlenmesi Kontrolu Dergisi* 11 (2001) 17–30.

- [33] M. Selvi, R. Sarikaya, F. Erkok, Acute behavioral changes in the guppy (*Poecilia reticulata*) exposed to temephos, *G.U. J. Sci.* 17 (2004) 15–19.
- [34] M. Boran, H. Karacam, A. Sayin, Investigation of the characteristics of waste water from some industrial establishments located in Değirmendere Basin (Trabzon, Türkiye) and determination of level and distribution of pollutants, *E.U. J. Fish. Aquat. Sci.* 21 (2004) 17–21.
- [35] H. Tekin, O. Bilkay, S.S. Ataberk, T.H. Balta, I.H. Ceribasi, F.D. Sanin, F.B. Dilek, U. Yetis, Use of Fenton oxidation to improve the biodegradability of a pharmaceutical wastewater, *J. Hazard. Mater.* 136 (2006) 258–265.
- [36] M. Ciler, Design principles for the treatment of high-strength wastewaters in a UASB system, PhD Thesis, Istanbul Technical University, Istanbul, 1985.
- [37] M.M. Amin, Performance evaluation of three anaerobic bioreactors: ASBR, HAIS, and UASB, Ph.D. Thesis, Department of Civil and Environmental Engineering University of Illinois at Urbana-Champaign (UIUC) Illinois, USA, 2004.
- [38] Y.-H. Liu, Y.-L. He, S.-C. Yang, C.-J. An, Studies on the expansion characteristics of the granular bed present in EGSB bioreactors, *Water SA* 32 (2006) 555–560.
- [39] Y.-H. Ahn, Physicochemical and microbial aspects of anaerobic granular pellets, *J. Environ. Sci. Health A35* (2000) 1617–1635.
- [40] L.W. Hulshoff Pol, S.I. de Castro Lopes, G. Lettinga, P.N.L. Lens, Anaerobic sludge granulation, *Water Res.* 38 (2004) 1376–1389.
- [41] S.K. Gupta, S.K. Gupta, Morphological study of the granules in UASB and hybrid reactors, *Clean Technol. Environ. Policy* 7 (2005) 203–212.
- [42] H. Harada, S. Uemura, A.C. Chen, J. Jayadevan, Anaerobic treatment of a recalcitrant distillery wastewater by a thermophilic UASB reactor, *Bioresour. Technol.* 55 (1996) 215–221.
- [43] N. Musee, M.A. Trerise, L. Lorenzen, Post-treatment of distillery wastewater after UASB using aerobic techniques, *S. Afr. J. Enol. Viticulture* 28 (2007) 50–55.
- [44] S. Ramana, A.K. Biswas, S. Kundu, J.K. Saha, R.B.R. Yadava, Effect of distillery effluent on seed germination in some vegetable crops, *Bioresour. Technol.* 82 (2002) 273–275.
- [45] Metcalf, Eddy, *Wastewater Engineering—Treatment, Disposal, Reuse*, third ed., McGraw Hill, New York, USA, 1991.
- [46] N.J.A.-H. Mahmoud, Anaerobic pre-treatment of sewage under low temperature (15 °C) conditions in an integrated UASB-digester system, PhD Thesis, Wageningen University, Wageningen, The Netherlands, 2002.
- [47] W.M. Wiegant, Experiences and potential of anaerobic wastewater treatment in tropical regions, *Water Sci. Technol.* 44 (2001) 107–113.
- [48] S.S. Hang, C.P. Byeong, Improved performance of upflow anaerobic sludge blanket (UASB) reactors by operating alternatives, *Biotechnol. Lett.* 12 (1990) 469–474.
- [49] H.M. Wong, C. Shang, Y.K. Cheung, G. Chen, Chloride assisted electrochemical disinfection, in: Proceedings of the Eighth Mainland-Taiwan Environmental Protection Conference, Tsing Chi, Taiwan, 2002.
- [50] S. Irdemez, Y.S. Yildiz, V. Tosunoglu, Optimization of phosphate removal from wastewater by electrocoagulation with aluminum plate electrodes, *Separat. Purif. Technol.* 52 (2006) 394–401.
- [51] APHA (American Public Health Association), Standard Methods for the Examination of Water and Wastewater, 19th ed., Washington, DC, 1995.
- [52] Merck Corp., Manual for photometer SQ 118, Method list with measuring range, Spectroquant® Küvettestests, 138 Hazen colour, Merck KGaA, Darmstadt, Germany, 2003, pp. 1–28.
- [53] G.N. Demirel, S. Chen, Anaerobic digestion of dairy manure in a hybrid reactor with biogas recirculation, *World J. Microbiol. Biotechnol.* 21 (2005) 1509–1514.
- [54] C.N. Iyerly, Swine wastewater treatment in an integrated system of anaerobic digestion and duckweed nutrient removal: pilot study, M.Sc. Thesis, Graduate Faculty of North Carolina State University, Raleigh, 2004.
- [55] J. Cheng, B. Liu, Swine wastewater treatment in anaerobic digesters with floating medium, *Trans. Am. Soc. Agricult. Eng.* 45 (2002) 799–805.
- [56] J.H. Martin Jr., P.E. Wright, S.F. Inglis, K.F. Roos, Evaluation of the performance of a 550 cow plug-flow anaerobic digester under steady-state conditions, in: Ninth International Animal Agricultural and Food Processing Wastes Proceedings, Research Triangle Park, NC, USA, October 12–15, ASAE, St. Joseph, MI, 2003, pp. 350–359.
- [57] N.K. Khosla, S. Venkachalam, P. Sonrasundaram, Pulsed electrogeneration of bubbles for electroflotation, *J. Appl. Electrochem.* 21 (1991) 986–990.
- [58] M. Kobya, H. Hiz, E. Senturk, C. Aydinler, E. Demirbas, Treatment of potato chips manufacturing wastewater by electrocoagulation, *Desalination* 190 (2006) 201–211.
- [59] Powell Water Systems Inc., Powell electrocoagulation, Sustainable technology for the future, New times demand more effective technology, Technical Manual 02-26-02, Centennial, CO, 2002.
- [60] G. Mouedhen, M. Feki, M. De Petris Wery, H.F. Ayedi, Behavior of aluminum electrodes in electrocoagulation process, *J. Hazard. Mater.* 150 (2008) 124–135.
- [61] Queensland Government, Environmental Protection Agency, Queensland Parks and Wildlife Service, Determinations for the management of regulated wastes, Operational policy: Waste management, Version 3, 051006, 2007.
- [62] A.R. White, Jr., Process for recovering and recycling coagulant present in water treatment sludges, United States Patent 4448696, US Environmental Products, Inc., Boca Raton, Fla., May 15, 1984.
- [63] The North Carolina Department of Natural Resources and Community Development, Division of Environmental Management, Pollution Prevention Pays Program, Pollution Prevention Challenge Grant, Project Summaries, Raleigh, North Carolina April 1986.
- [64] W. Chu, Lead metal removal by recycled alum sludge, *Water Res.* 33 (1999) 3019–3025.
- [65] W. Chu, Dye removal from textile dye wastewater using recycled alum sludge, *Water Res.* 35 (2001) 3147–3152.