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Treatment of ink wastewater via heterogeneous photocatalytic oxidation

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ABSTRACT

This article is mainly concerned with the treatment of wastewater from an ink production plant. The wastewater is highly contaminated with organic and inorganic matter. The chemical oxygen demand (COD) ranged from 5200 to 27458 mgO_2/l. The end-of-pipe has been treated using two alternatives namely, the first treatment alternative chemical coagulation using ferric chloride ($FeCl_3$) aided with lime, followed by photocatalytic oxidation. The second treatment alternative was direct via heterogeneous photocatalytic oxidation using titanium dioxide/ultraviolet (TiO_2/UV) and hydrogen peroxide (H_2O_2). The optimum operating conditions required for photocatalytic oxidation such as contact time, doses of H_2O_2 and TiO_2 were investigated. The results indicated that the direct treatment of raw wastewater using photocatalytic oxidation reduced the COD, total suspended solids (TSS) and turbidity up to 81%, 95% and 90%, respectively, while the corresponding residual values were 1700 mgO_2/l, 82 mg/l and 100 nephelometric turbidity units (NTU). However, pretreatment of raw wastewater with chemical coagulation followed by photocatalytic oxidation improved the quality of the effluent produced. Residual COD, TSS and turbidity were 420 mgO_2/l, 50 mg/l and 80 NTU, respectively. Also, complete removal of color was achieved. The quality of the treated effluent complies with the National Regulatory Standards for wastewater discharge into a public sewage network.

Keywords: Ink wastewater; Photocatalytic oxidation; TiO_2; UV; Chemical coagulation

1. Introduction

Over the last two decades, implementation and enforcement of stringent environmental regulations have created opportunities to reduce and reuse wastewater from their manufacturing processes. Even though the cost benefits of reusing wastewater may not be realized immediately, the intangible benefits of preventing contamination of the environment on either a short or long term basis can be significant [1]. Ink manufacturing industries generate both wastewater and rinse water. Such water contains both organic and inorganic matter as well as various proportions of biodegradable constituents. This causes the complexity in ink effluent characterization for water quality assessment. It is uncommon for many public sewer treatment facilities to set limits on water quality parameters for industrial wastewater discharged into the public sewer system. In Egypt, for example, discharge of such treated ink wastes into the public sewer is subjected to compliance with the Environmental laws stated by the Egyptian Environmental Affair Agency (EEAA) [1–3]. In order to quantify the extent of ink wastewater treatment, the selection of appropriate on-site water quality indicators is vital. Thus, the ink-making industries are constantly striving to search for effective water quality monitoring criteria and better treatment options to discharge such waste. Similarly, ink manufacturing industries generate large volumes of rinse water that must be

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disposed. The elimination of chemicals found in ink wastewater is presently of great concern since their complete biodegradation is usually very slow and requires several days or weeks [4].

There are many technologies which may be applied for the treatment of wastewater from paint and ink manufacturing industries. These technologies include coagulation and precipitation, centrifugation, electrophoresis, evaporation and ultrafilteration. Recently, Fenton's oxidation reaction and photocatalytic oxidation have been used for the degradation of organic materials [5].

Photocatalytic oxidation by irradiated semiconductors is a relatively new technique of pollution abatement. The vast majority of current studies employ TiO_2 as the semiconductor due to its stability and relatively low price. Titanium dioxide has been extensively employed as photocatalytic material for eliminating toxic chemicals from wastewater [6,7]. Also, a TiO_2/UV system has been widely investigated in the heterogeneous photocatalytic process, during which UV irradiation upon the semiconductor can photoactivate TiO_2 generating electron/hole couples with strong redox properties [7].

The efficiency of these systems is based on the production of strong oxidant species, such as hydroxyl radicals, which are able to oxidize almost all organic pollutants. The photo-assisted catalysis involves the irradiation of a semiconductor like TiO_2 with UV light at λ below 387 nm, generating an electron-hole pair on the catalyst surface and inducing the formation of radical reduced oxygen species. These radicals are produced and are highly reactive and unselective oxidants. Such reactions have usually been carried out using suspensions of powdered TiO_2 [8].

The most commonly used oxidants are H_2O_2, O_3 or O_2. The combined systems TiO_2/UV/H_2O_2 and UV/Fe^{3+}/H_2O_2 are considered as the most promising for the treatment of wastewater.

Mechanisms of removal — The photocatalytic degradation of organic compounds occurs on the surface of TiO_2, primarily in trapped holes. •OH and $O_2{\bullet}^{2-}$ are considered as primary reactive species and O_2 and H_2O are necessary for photocatalytic degradation. Oxygen adsorbed on the TiO_2 surface prevents the recombination of electron-hole pairs by trapping electrons and super oxide ions are thus formed. •OH radicals are formed from holes reacting with either H_2O or $\bullet OH^-$ adsorbed on the TiO_2 surface. •OH and $O_2{\bullet}^{2-}$ are also formed from H_2O. In this process, H_2O_2, O_2 and $HO{\bullet}_2$, which are suitable for trapping electrons, and •OH and O_2^{2-} are the most important oxidants. The oxidizing power of the •OH radicals is strong enough to break bonds of the compound molecule adsorbed on the surface of the TiO_2 leading to the formation of CO_2 and inorganic ions. When the intensity of light is constant, the number of •OH and $O_2{\bullet}^{2-}$ radicals increases with increasing irradiation period, resulting in the complete photodegradation of organic molecules to smaller fragments like CO_2 and H_2O, while the other elements bonded to the organic compounds are converted to anions such as nitrate sulfate or chloride [9–13]. It is worth noting that the hydrogen peroxide absorbs only the UV light with a wavelength <300 nm.

$$H_2O_2 + h\upsilon_{(\lambda < 300\ \mathrm{nm})} \longrightarrow 2^{\bullet}OH \qquad (1)$$

In heterogeneous photocatalysis, the band-gap model has proven to be very useful for explaining the mechanism of the semiconductor-catalyzed oxidative degradation of organic compounds in aqueous systems [10]. Some of the many events taking place subsequent to the near-UV light absorption by TiO_2 particles (λ <385 nm) are summarized in Eqs. (2)–(9); generation and separation of electron (e) and proton (h) [Eq. (2)]; electron transfer from adsorbed substrate RX [Eq. (3)]; electron transfer from adsorbed solvent molecules (H_2O and −OH) [Eqs. (4) and (5)]; electron-transfer reaction from the conduction band of the photocatalyst to the oxygen [Eq. (6)].

$$TiO_2\ h\upsilon \longrightarrow TiO_2\ (e^- + h^+) \qquad (2)$$

$$TiO_2\ (h^+) + RX_{ad} \longrightarrow TiO_2 + RX^{\bullet}{}_{ad}{}^{+} \qquad (3)$$

$$TiO_2\ (h^+) + H_2O_{ad} \longrightarrow TiO_2\ {}^{\bullet}OH_{ad} + H^+ \qquad (4)$$

$$TiO_2\ (h^+) + {}^-OH_{ad} \longrightarrow TiO_2 + {}^{\bullet}OH_{ad} \qquad (5)$$

$$TiO_2\ (e^-) + O_2 \longrightarrow TiO_2 + O^{\bullet}{}_2{}^- \qquad (6)$$

$$O^{\bullet}{}_2{}^- + HO^{\bullet}{}_2 \longrightarrow {}^{\bullet}OH + O_2 + H_2O_2 \qquad (7)$$

$$2HO^{\bullet}{}_2 \longrightarrow O_2 + H_2O_2 \qquad (8)$$

$$TiO_2\ (e^-) + H_2O_2 \longrightarrow TiO_2 + {}^{\bullet}OH + {}^-OH \qquad (9)$$

It has also been shown that the addition of hydrogen peroxide enhances the rate of photodegradation, probably via reaction [9]. Organic pollutants adsorbed onto the surface of the titanium dioxide particles will then be oxidized by OH radicals. Addition of H_2O_2 in the last step makes the process even more effective, since H_2O_2 is an efficient electron scavenger and generates additional OH radicals [Eq. (10)] [9–13]. A wide range of applications has been reported for different compounds using these systems [9]. Therefore, the aim of this study is to investigate the capability of using heterogeneous photocatalytic oxidation process (TiO_2/UV/H_2O_2) as a tool for the treatment of ink wastewater.

2. Material and methods

2.1. Wastewater sampling and analysis

Composite wastewater samples were collected from an ink production plant located in Sadat City, northeast of Cairo, Egypt. The wastewaters are generated mainly from the rinsing of the mixing reaction tanks used for the production of ink. Wastewater was analysed for chemical oxygen demand total (COD_{tot}) and soluble (COD_{sol}), total suspended solids (TSS) and turbidity. COD analysis is carried out using closed reflux coloremeteric method. COD_{tot} is the total COD measured, while COD_{sol} measured after filtration of the samples using 0.45 μm membrane filter paper. Turbidity is that of raw wastewater and treated samples were carried out using the nephelometric method. The analyses were carried out according to the American Public Health Association for water and wastewater analysis [14].

2.2. Treatability study

Two treatment approaches were investigated. The first approach is the pre-treatment of wastewater using chemical coagulation–sedimentation followed by photocatalytic oxidation, while the second treatment alternative was direct photocatalytic oxidation of the raw wastewater. The treatment train is described in Fig. 1.

2.3. Chemical coagulation–sedimentation

A bench-scale chemical coagulation process was carried out using the Jar test procedure. This was intended to obtain the pH value and coagulant dosage required for the best removal of the pollutants. $FeCl_3$ aided with lime was chosen as an efficient coagulant for this type of wastewater. The pH was raised to 11.5 with lime followed by addition of $FeCl_3$ to pH 8.5. Flash mix (200 rpm) for 2 min was carried out after which slow mixing was applied (40 rpm) for 15 min. The resulting flocs were allowed to settle for 1 h.

2.4. Photocatalytic degradation

The $TiO_2/UV/H_2O_2$ process is used to oxidize the high organic content present in the raw wastewater as well as the pre-treated effluent using coagulation-sedimentation. The initial pH of raw wastewater was adjusted to pH 3.0 ±0.1 using concentrated sulphuric acid (H_2SO_4). The reaction vessel used was a glass vessel with a volume of 250 ml. The samples were subjected to UV source using medium pressure mercury lamp acted as a UV source generating output between 320–400 nm. This lamp was located above the reaction vessel. Hydrogen peroxide was used as an oxidant aided with activated TiO_2 as a catalyst. Titanium dioxide used was rutile type (Merck) with a surface area of 230±10 m^2/g and particle size ranged from 0.2 to 0.4 μm. The reaction media were supplied by oxygen using an aquarium air pump to ensure good mixing of the reactants. The optimum operating conditions which produce the best oxidation, such as the doses of TiO_2, H_2O_2 and contact time were investigated. All the experiments were carried out at a bench-scale batch mode. The study flow diagram is presented in Fig. 1.

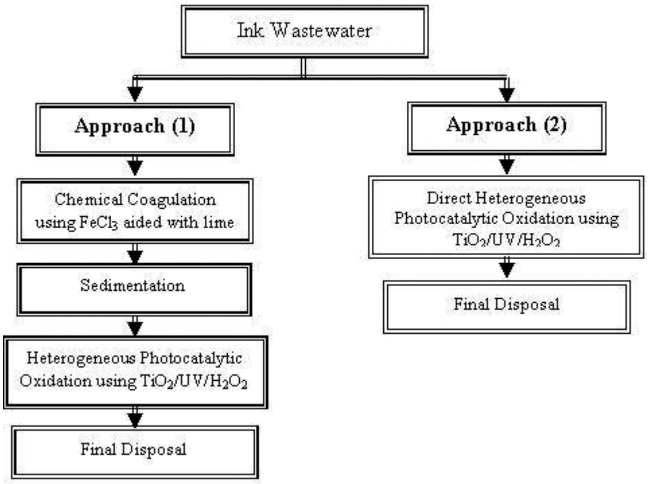

Fig. 1. Schematic diagram of the treatment sequences.

3. Results and discussion

3.1. Characterization of wastewater

Analysis of wastewater indicated that it was highly contaminated with organic and inorganic pollutants. The COD_{tot} concentration varied from 5200 to 27458 mgO_2/l with an average value of 9120 mgO_2/l. Also, the TSS and turbidity were as high as 5421 mg/l and 4850 NTU, respectively. The waste has different colors according to the production schedule. The COD level of the ink wastewater was found to be much higher than that examined by Zhang et al. [15]. They found the COD level ranged from 3000 to 8000 mg/l.

3.2. Alternative 1: Chemical coagulation followed by photocatalytic oxidation

Chemical coagulation–sedimentation as a pretreatment prior to photocatalytic oxidation was carried out. The chemicals used are 0.41 g/l $FeCl_3$ aided with 0.3 g/l lime at a pH value 8.5±0.2. The results shown in Fig. 2 indicate that a great portion of the colloidal as well as the suspended solids was removed.

The total COD removal value reached 81% with a residual of 1770 mgO_2/l, 85%, mostly in soluble form

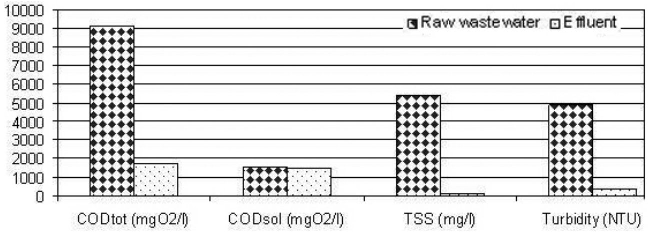

Fig. 2. Efficiency of chemical treatment process.

(1500 mgO_2/l). These results are in a good agreement with that obtained by Metes et al. [10]. They studied the effect of using $AlCl_3.6H_2O$ and $FeCl_3.6H_2O$ on the treatment of ink wastewater. Both coagulants were found to be efficient for the treatment of wastewater. Although the organic removal rate reached 88% (reflected by TOC); however, the treated effluent required further treatment. Nandy et al. [15] examined different coagulants (i.e. ferrous sulsulphate, ferric chloride, aluminium sulphate and polyaluminium chloride). They found that polyaluminium chloride (PAC) proved to be the most efficient coagulant, which achieved removal rate of color, TSS, BOD and COD of 95.9–96.5%, 96.5–97.0%, 61.3–65.8% and 54.8–61.8%, respectively at an optimum concentration of PAC 1.5 g/l.

In order to degrade the residual soluble organic matter, the pre-treated effluent was subjected to photocatalytic oxidation using $TiO_2/UV/H_2O_2$. To accomplish that the optimum operating conditions such as the doses of TiO_2, H_2O_2 and contact time which produce the high quality effluent with minimum residual values of the concerned parameters were investigated.

3.2.1. Determination of the optimum dose of H_2O_2

Preliminary investigation using different concentrations of H_2O_2 less than 150 mg/l at fixed doses of TiO_2 (0.5 mg/l) and UV (320–400 nm) did not achieve any significant improvement in the quality of the treated effluent. Therefore, different doses of H_2O_2, namely 150, 300 and 600 mg/l, were investigated for the pre-treated wastewater and under the pre-mentioned dose of TiO_2 and UV. The results obtained in Fig. 3 show that increasing the dose of H_2O_2 from 150 to 600 mg/l and at a contact time of 4 h improved the quality of treated effluent. The COD_{tot} removal values reached 95.4%, 95.5% and 95.9%, respectively. Since there is no great variation in the removal efficiencies the COD_{tot}, the use of 150 mg/l H_2O_2 was taken as an optimal dose.

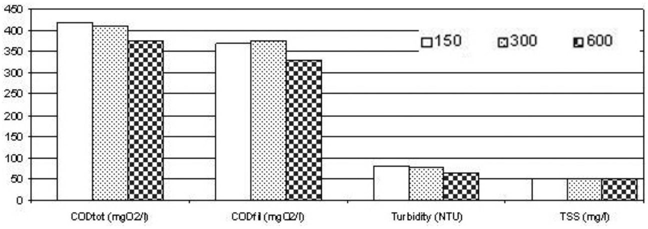

Fig. 3. Effect of different doses of H_2O_2.

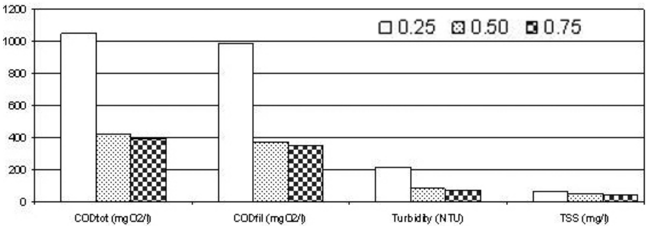

Fig. 4. Effect of different doses of TiO_2 on the treatment process.

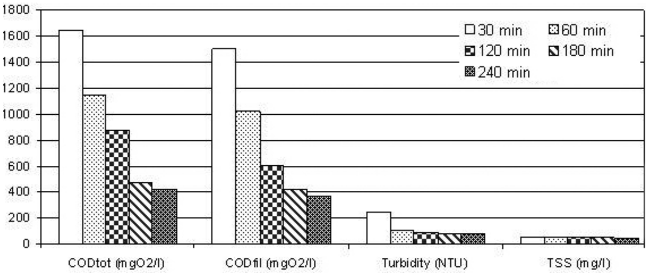

Fig. 5. Effect of contact time on the treatment process.

3.2.2. Determination of the optimum TiO_2 dose

Different doses of TiO_2, namely 0.25, 0.5 and 0.75 mg/l, were used at the pre-determined optimal dose of H_2O_2. Doses less than 0.25 mg/l were found to be ineffective for the removal of COD. The results depicted in Fig. 4 show that the use of 0.5 mg/l TiO_2 removed up to 76% of the pre-treated wastewater at a contact time of 4 h. However, increasing the TiO_2 dose from 0.5 to 0.75 mg/l improved the removal rate of COD by only 1.3%. From an economic point of view, the optimum dose of TiO_2 (0.5 mg/l) was selected.

3.2.3. Determination of the optimum contact time

One of the most important parameters in this oxidation process is the contact time. Different contact times ranging from 0.5 to 4 h were investigated. The results depicted in Fig. 5 show that increasing the contact time to 4 h removed 76% of the soluble organic matter. The residual COD_{sol} did not exceed 370 mgO_2/l.

The overall treatment process at the pre-determined optimum operating conditions is shown in Table 1. It is obvious that the combination of coagulation–sedimentation followed by photocatalytic oxidation proved to be an efficient technique for removing COD_{tot}, TSS and turbidity. Their corresponding removal values were 95.4, 98.9 and 96%, respectively. Swarnalatha and Anjaneyulu [5] concluded that TiO_2 is found to be an efficient photocatalyst for degradation of organic wastewater.

Table 1
Efficiency of the treatment process at the optimum operating conditions

Parameter	Raw wastewater	Treated effluent	%*R*	Parameter	*T* %*R*
COD_{tot}	9120	1770	81.0	420	95.4
COD_{sol}	1530	1500	2.0	369	98.9
TSS	1650	95	94.2	50	97.0
Turbidity	988	351	64.5	40	96.0

Table 2
Efficiency of direct treatment of ink wastewater

Parameter	Raw wastewater	Treated effluent	% *R*
COD_{tot}	9120	1700	81.4
BOD_{sol}	1530	1440	6
TSS	1650	82	95
Turbidity	988	100	90

3.3. Alternative 2: Direct treatment of raw wastewater using photocatalytic oxidation

In this part of the study, direct treatment of wastewater was carried out using $TiO_2/UV/H_2O_2$ oxidation at the pre-determined optimum operating conditions, namely 150 mg/l H_2O_2, 0.5 mg/l TiO_2 and 4 h reaction detention time. Table 2 shows that 81.4% of COD has been removed, 95% of TSS disappeared and 90% of turbidity was almost removed. However, their corresponding residual values were still high for wastewater discharge into a public sewage network. The residual COD_{tot} values were almost 1700 mgO_2/l with a soluble value of 1440 mgO_2/l. Therefore, the wastewater requires pre-treatment prior to photocatalytic oxidation.

A comparison of the two treatment approaches applied in this study revealed that the presence of a high concentration of suspended and colloidal particulates retarded the direct oxidation process of the raw wastewater using $TiO_2/UV/H_2O_2$. The removal of these particulates with chemical coagulation–sedimentation as a pre-treatment step prior to photocatalytic oxidation enhanced the penetration of UV and consequently the oxidation process.

4. Conclusions

Direct treatment of highly contaminated wastewater using photocatalytic oxidation was not enough to satisfy the National Regulatory Standards for wastewater discharge into public sewage network. The removal rate of COD and TSS was 81.4% and 95% with residual values of 1700 mgO_2/l and 82 mg/l.

Pre-treatment of wastewater using ferric chloride aided with lime prior to photocatalytic oxidation proved to be very efficient. Removal rates of COD and TSS were 81% and 94% with residual values of 1770 mgO_2/l and 95 mg/l.

The quality of the treated effluent complying with the National Regulatory Standards for wastewater discharge into a public sewage network.

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