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Treatment of paper mill effluents in a batch-stirred electrochemical tank reactor

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ABSTRACT

Electrochemical treatment of organic pollutants is a promising treatment technique for substances which are resistant to biodegradation. In this study an electrochemical treatment based on the principle of anodic oxidation was used to treat paper mill effluent from Rakta's Pulp and Paper Company where rice straw is used to produce paper pulp. Experiments were carried out in a cylindrical agitated vessel lined with lead sheet as anode while a concentric cylindrical stainless steel sheet screen was placed as a cathode. The effect of current density, pH, NaCl concentration, impeller rotational speed and temperature on the rate of color and COD removal was studied. The results showed that the use of electrochemical technique reduces the COD from an average value of 5500 to 160. The percentage color removal ranged from 53% to 100% depending on the operating conditions. Energy consumption calculation shows that energy consumption ranges from 4 to 29 kWh/m^3 of effluent depending on the operating conditions. The experimental results proved that the electrochemical oxidation is a powerful tool for treating paper mill effluents where rice straw is used as a raw material.

1. Introduction

The manufacture of paper generates significant quantities of wastewater containing high concentration of lignin causing brown color and COD [1]. This effluent has adverse effect on aquatic life, as well as the aesthetic values of the environment. The dark color, in discharged pulp mill effluents, limits the amount of sunlight that penetrates the water surface. This prevents submerged aquatic vegetation from getting the necessary light to carry on photosynthesis [2].

Pulp and paper wastewater treatment systems have been the subject of many research projects [3–12] in which different techniques including physical, chemical and biological methods have been applied with variety of shortcomings. Physical and chemical processes are quite expensive and remove high molecular weight chlorinated lignins, color, toxicants, suspended solids and chemical oxygen demand. But BOD and low molecular weight compounds are not removed efficiently [13]. Examples of the methods which are used for wastewater treatment from pulp and paper mills are adsorption [14], wet oxidation [15], ozone treatment [16], ion exchange [17], chromophores removal via hydrogenation–biological batch reactors [18], color, TOC and AOX (adsorbable organic halogens) removals by advanced oxidation processes [19]. In general, several methods have been attempted for removal of color from the pulp and paper mill effluents. Lignin is difficult to degrade by microorganisms. Therefore, the effluent from the wastewater treatment system, which is a biological process, still contains a high content of color, lignin and COD [1].

In recent years, electrochemical technologies such as electrooxidation, electrocoagulation and electrofloatation have been widely used and several applications have been recently reviewed by Chen [20]. Electrooxidation on anodes made of graphite, Pt, TiO_2, IrO_2, PbO_2, several Ti-based alloys and, more recently, boron-doped diamond electrodes in the presence of chloride ions (typically NaCl) has been employed for the decontamination of various organic containing effluents [21]. Electrochemical oxidation assisted by transition-metal-modified kaolin [22], photoelectrochemical degradation of lignin [23], photoassisted electrochemical degradation of organic pollutants on a DSA type oxide electrode: process test for a phenol synthetic solution and its application for the E1 bleach kraft mill effluent [24] and electrochemical decolorization either by circulating the liquor in electrolytic cell [25], or by using carbon fiber reactor [26] are also studied. Although the electrochemical oxidation of various synthetic and actual industrial effluents has received considerable attention, relatively few studies reported the use of this technology to treat paper mill

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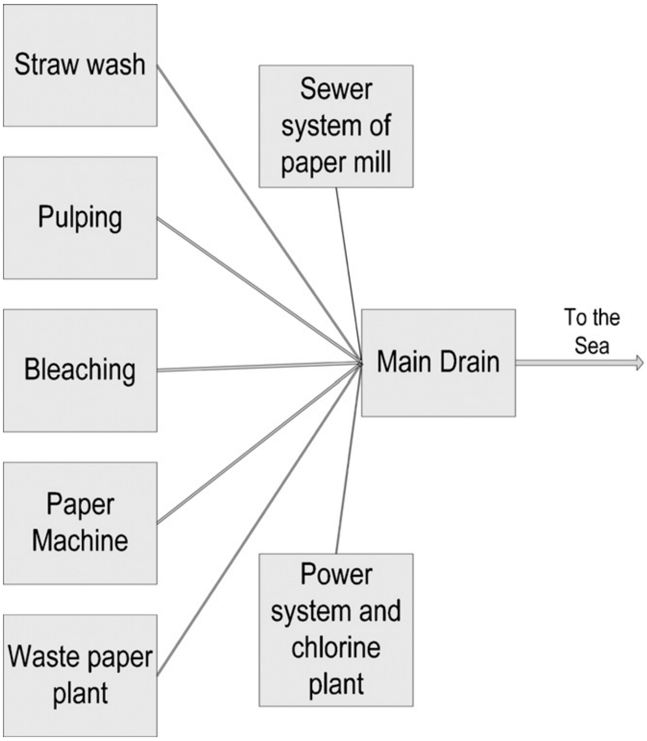

Fig. 1. Sources that contribute in the effluent from paper mill.

effluents on industrial scale, probably because the technique needs further improvement. The present work differs from previous electrochemical studies of paper mill effluents in two respects, namely:

(i) The majority of previous studies have concentrated on effluents resulting from the production of paper pulp from wood chips while the present work is concerned with the black liquor resulting from Rakta's plant (Egypt) where paper pulp is obtained from rice straw.

(ii) The present work uses a new cell with improved hydrodynamic conditions to enhance the rate of electrochemical decolorization which is a diffusion-controlled process [26,27]. The cell consists of an agitated cylindrical vessel provided with a rotating impeller, the vessel was lined with a cylindrical lead anode, a concentric stainless steel screen cylindrical cathode was placed at a short distance from the anode. The stainless steel screen acted also as a turbulence promoter [28,29] to enhance the diffusion-controlled anodic oxidation. The present cell performance in decolorizing paper mill effluents was studied under different current densities, impeller rotation speed, pH, temperature and sodium chloride concentration.

2. Materials and methods

2.1. Characterization of wastewater

The wastewater used in this study was collected from the effluent of Rakta's Pulp and Paper Company, located in Alexandria, Egypt, which produces writing and printing paper from soda pulping of rice straw, and hypochlorite bleaching of the produced pulp. The paper mill effluent was taken from the main drain as shown in Fig. 1. The wastewater was characterized for BOD, COD, pH, dissolved solids, suspended solids and color using the standard methods [30] and the data are presented in Table 1. The effluent was filtered using a screen filter to remove suspended solids and small fibers before used for the subsequent studies.

Table 1
Characteristics of wastewater used for electrochemical treatment

Characteristics	Value
Temperature	40 °C
pH	≈8
Color	Brown
BOD (mg/l)	300–400
COD (mg/l)	5000–6000
Dissolved solids (mg/l)	4000–4500
Suspended solids (mg/l)	1200–1300

2.2. Experimental set-up and measurements

The experimental set-up used in the present study is schematically shown in Fig. 2. It consists mainly of a plexiglass cylindrical agitated vessel having a diameter of 13.8 cm and a height of 24 cm. The vessel was equipped with four plexiglass rectangular baffles, fixed to the container wall 90° from one another. The agitated vessel was fitted with four-blade 45° pitched turbine (axial flow impeller) of 7 cm diameter; it was isolated with epoxy and connected to a digital variable speed motor. The rotational speed of the motor ranged from 200 to 1000 rpm. A cylindrical lead sheet lining the inner wall of the vessel was used as anode, while a cylindrical stainless steel screen cathode made of 304 stainless steel (18% Cr, 8% Ni, balance Fe, 0.02 C, mesh no. 10, area = 682 cm^2) was placed at a distance of 1 cm in front of the anode. Lead was used as anode in view of its stability, low cost and high O_2 overpotential [31] which delays O_2 evolution in favour of Cl_2 evolution. The electrodes were connected to a dc power supply (20 V, 10 A) with a voltage regulator and a multi-range ammeter connected in series. In each run, 2 l of the paper mill effluent was placed into the electrochemical-agitated reactor; after mixing with the appropriate amount of sodium chloride, the current density was adjusted to the desirable value and the electrochemical oxidation was started. The temperature of the effluent was controlled by thermostatically controlled water bath. The experiments were carried out at different current densities (2.2, 4.4, 6.6, 8.8 and 10 mA/cm^2), pH (6.7 and 8.0), NaCl concentration (0.5, 1.0, 1.5, 2.0 and 2.5 g/l), impeller rotational speed (200, 400, 600, 800 and 1000 rpm) and temperature (25, 30, 40, 50 and 60 °C). Samples were drawn at regular intervals of 10 min for analysis. Color intensity and COD were measured using spectrophotometer (Labomed, USA) at 450 nm wavelength and an open reflux system respectively as per standard methods [30].

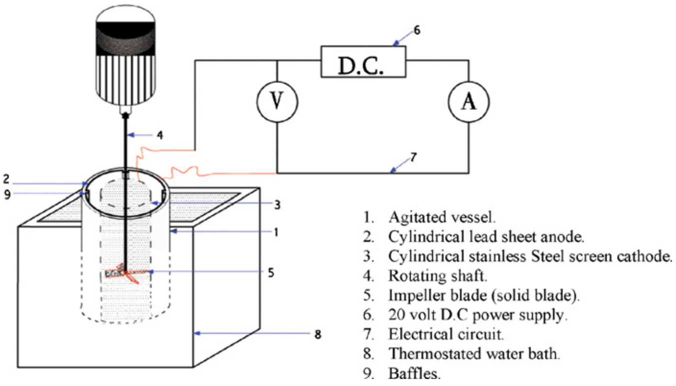

Fig. 2. Schematic diagram of the experimental set-up.

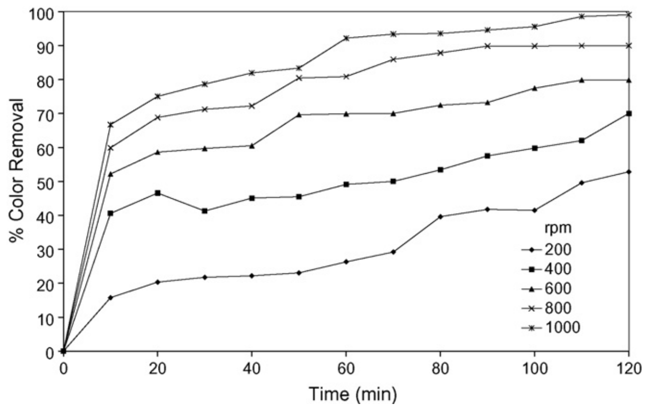

Fig. 3. Effect of rotational speed (rpm) on percentage color removal (c.d. = 2.2 mA/cm^2, pH 8, temperature = 25 °C, NaCl = 1 g/l).

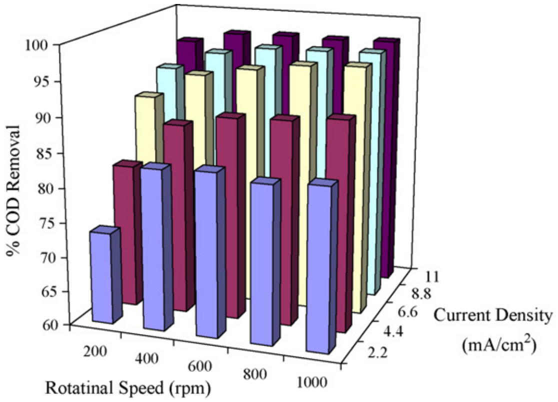

Fig. 4. Effect of rotational speed (rpm) on percentage COD removal at different current densities (pH 8, temperature = 25 °C, NaCl = 1 g/l, time = 120 min).

3. Results and discussion

In order to shed some light on the mechanism of color removal by anodic oxidation electrolysis was conducted using two different electrolytes Na_2SO_4 and NaCl. Anodic oxidation using Na_2SO_4 as electrolyte failed to decolorize the solution; the anodic reaction was O_2 evolution. Color removal was possible when NaCl was used as electrolyte where Cl_2 is the main anodic reaction. Thus, decolorization occurs indirectly in the solution bulk due to the reaction between the generated chlorine/hypochlorite and the coloring material. The main reactions at the electrodes are [32,33]

$$\text{Anode}: \quad 2Cl^- \rightarrow Cl_2 + 2e^- \tag{1}$$

$$\text{Cathode}: \quad 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2}$$

In the solution bulk Cl_2 hydrolysis takes place as follows.

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \tag{3}$$

$$HOCl \rightarrow H^+ + OCl^- \tag{4}$$

Some of the useful hypochlorite ion (OCl^-) is lost via the diffusion-controlled cathodic reduction to Cl^- and anodic oxidation to chlorate [33].

Hypochlorite loss reactions:

$$\text{At the cathode}: \quad ClO^- + H_2O + 2e \rightarrow Cl^- + 2OH^- \tag{5}$$

At the anode :

$$6ClO^- + 3H_2O \rightarrow 2ClO_3{}^- + 4Cl^- + 6H^+ + (3/2)O_2 + 6e \tag{6}$$

At the anode O_2 evolution competes with Cl_2 evolution according to the reaction

$$H_2O \rightarrow 2H^+ + (1/2)O_2 + 2e \tag{7}$$

3.1. Effect of impeller rotational speed

Fig. 3 shows that the percentage color removal increases from 53% to 99% as the impeller rotational speed increases from 200 to 1000 rpm. This confirms the fact that the color removal reaction is diffusion controlled, the increase in rotational speed leads to increase in the intensity of turbulence and reduces the diffusion layer thickness at the electrode surface and improves the mixing conditions in the electrolyte bulk. This enhances the rate of transfer of reactants and products to and from the anode surface [27]. However Fig. 3 shows that the enhancing effect of rotation speed on the rate of color removal becomes less pronounced at high rotation speeds (e.g. >800 rpm) probably because the diffusion-controlled cathodic reduction of hypochlorite and its anodic oxidation reaction are favoured at high rotation speed. Also by increasing rotation speed, COD removal is increased up to 400 rpm beyond that, there is no significance increase in COD removal by increasing rpm as shown in Fig. 4.

3.2. Effect of current density

Fig. 5 shows that the rate of color removal increases with increasing current density. This is consistent with Faraday's law according to which the hypochlorite content increases with c.d. The removal of color was increased with increasing current density up to 6.6 mA/cm^2; beyond that, the color removal is little affected by c.d. This may be attributed to the following: (i) The discharge potential of Cl_2 increases with current density [34] and becomes close to the discharge potential of O_2. Under such conditions simultaneous evolution of O_2 along with Cl_2 takes place with a consequent reduction in the current efficiency and the rate of Cl_2 generation. (ii) The increased loss of hypochlorite via cathodic reduction and anodic oxidation of hypochlorite to Cl^- and $ClO_3{}^-$ respectively [32] owing to the enhanced mass transfer conditions at the cathode and anode as a result of the increased formation of H_2, Cl_2 and O_2 bubbles which generate turbulence in the electrode vicinity during their detachment and rise in the solution [35]. Moreover, the effect of current density on the percentage COD removal is the same as its effect on the percentage color removal as seen from Fig. 4 and this proves that electrochemical degradation by-products are easily oxidized as the original material.

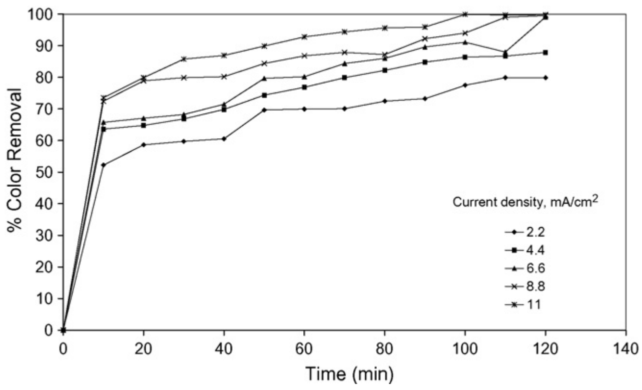

Fig. 5. Effect of current density on percentage color removal (rpm = 600, pH 8, temperature = 25 °C, NaCl = 1 g/l).

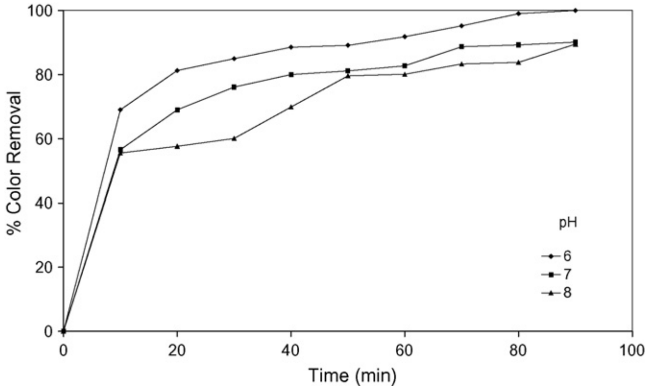

Fig. 6. Effect of pH on percentage color removal (rpm = 400, c.d. = 6.6 mA/cm^2, temperature = 25 °C, NaCl = 1 g/l).

3.3. *Effect of pH*

Fig. 6 shows that the percentage color removal increases with the decrease in pH of the solution (% color removal reaches 100% at pH 6), while it decreases in the alkaline solutions. Probably because of the decrease in the current efficiency of Cl_2 evolution in view of the fact that as the pH increases the discharge potential of O_2 decreases according to Nernst equation and the amount of O_2 which evolves simultaneously with Cl_2 increases at the expense of Cl_2 current efficiency [34].

3.4. *Effect of sodium chloride concentration*

The presence of NaCl in the effluent is essential not only to generate hypochlorite but also to render the solution electrically conducting. Fig. 7 shows the effect of varying NaCl concentration on effluent decolorization as a function of treatment time. Color removal increased from 78% to 99% as NaCl concentration increased from 0.5 to 2.5 g/l. This is due to the increase in current efficiency of Cl_2 generation at the anode where O_2 evolution competes with Cl_2 evolution. Increasing NaCl concentration lowers the discharge potential of Cl_2 according to Nernst equation [34].

As the discharge potential of Cl_2 decreases with increasing NaCl concentration more current is consumed in Cl_2 and hypochlorite generation at the expense of O_2 evolution. Hence, the rate of color removal increases. The presence of NaCl has a considerable effect on the percentage COD removal in the range of 0.5–1.0 g/l NaCl, while there is a slight increase in COD removal (from 96.66% to 97.3%) as NaCl increase from 1.0 to 2.5 g/l as shown in Fig. 8.

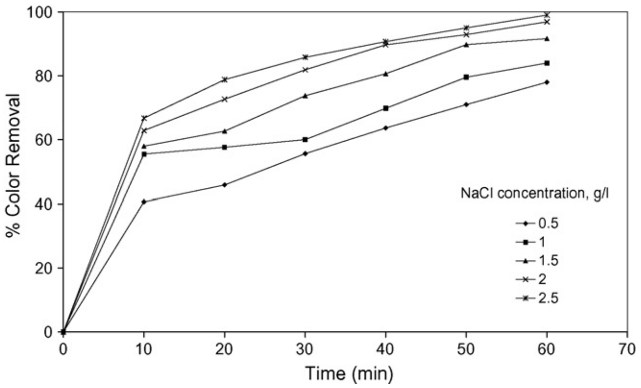

Fig. 7. Effect of NaCl concentration on percentage color removal (rpm = 400, c.d. = 6.6 mA/cm^2, pH 8, temperature = 25 °C).

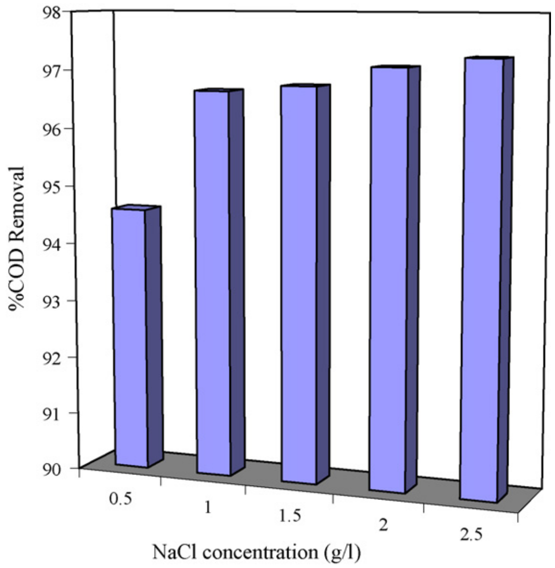

Fig. 8. Effect of NaCl concentration on percentage COD removal (rpm = 400, pH 8, time = 60 min, temperature = 25 °C, c.d. = 6.6 mA/cm^2).

3.5. *Effect of temperature*

Color removal increases from 80% to 99.6% as temperature increases from 25 to 40 °C respectively; beyond this temperature there is no significant effect on color removal as shown in Fig. 9. Furthermore, there is no significant effect on COD removal as temperature increases (Fig. 10). The effect of temperature is complex in view of the fact that increasing temperature has opposing effects on the present process. According to Arrhenius equation the increase of temperature should increase the rate of all reactions involved in the process such as lignin degradation and hypochlorite loss through cathodic reduction and anodic oxidation. At sufficiency high temperature O_2 over potential on the anode decreases, accordingly the discharge of O_2 at the anode increases with a consequent decrease in the current efficiency of Cl_2 generation. Also, when temperature increases sufficiently, the solubility of Cl_2 in the solution decreases with a consequent reduction in the hypochlorite content of the solution [32]. In view of the present results it seems that within the temperature range 25–40 °C, the beneficial effects of temperature prevail over the adverse effects. For temperatures higher than 40 °C it seems that the beneficial effects balance the adverse effects.

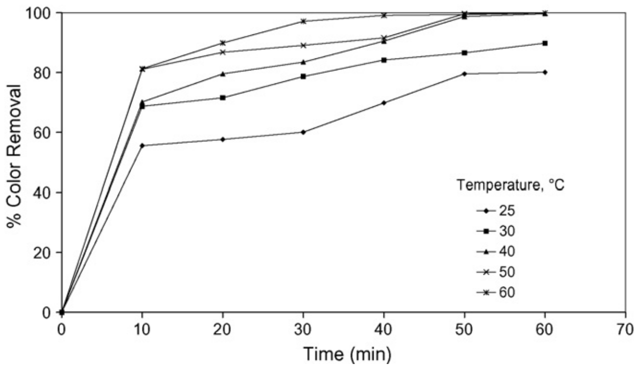

Fig. 9. Effect of temperature on percentage color removal (rpm = 400, c.d. = 6.6 mA/cm^2, pH 8, NaCl = 1 g/l).

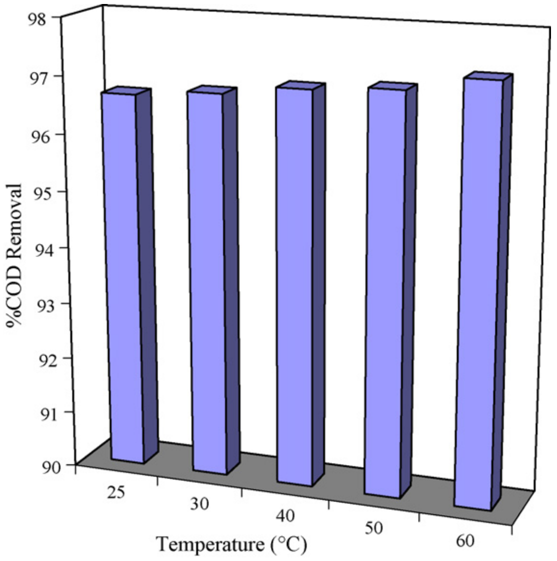

Fig. 10. Effect of temperature on percentage COD removal (rpm = 400, pH 8, time = 60 min, temperature = 25 °C, c.d. = 6.6 mA/cm^2).

3.6. *Energy consumption*

In order to assist in the economic evaluation of the present technique in comparison with other techniques, electrical energy consumption was calculated under different operating conditions using the equation [36]:

$$\text{Energy consumption (kWh/m}^3) = \frac{VIt}{\text{Treated volume (l)}} \quad (8)$$

where V is the cell voltage in volt, I the current in ampere (A) and t the treatment time (h). Figs. 11 and 12 show that energy consumption ranges from 4 to 29 kWh/m^3 of effluent depending on the operating conditions. It is clear from these figures that energy consumption decreases with increasing rotational speed and NaCl concentration. This is consistent with the enhancing effect of both increasing rotational speed and NaCl on the rate of color removal. Besides, increasing NaCl decreases the cell voltage as a result of improving solution conductivity. It should be also added that increasing the degree of stirring tends to reduce energy consumption via reducing the cell voltage by assisting in the early release of gas bubbles adhering to the electrode surface. Adhering gas bubbles increase the cell resistance appreciably [35].

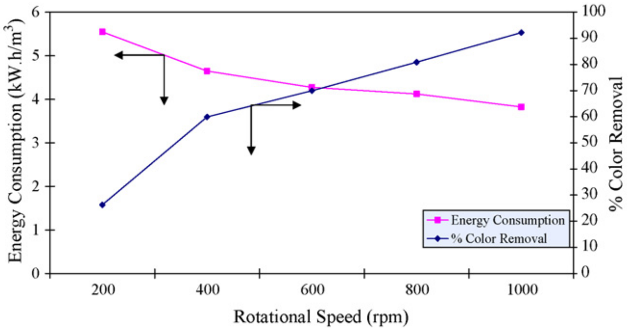

Fig. 11. Effect of rotational speed on percentage color removal and energy consumption (c.d. = 2.2 mA/cm^2, NaCl = 1 g/l, temperature = 25 °C, pH 8, time = 60 min).

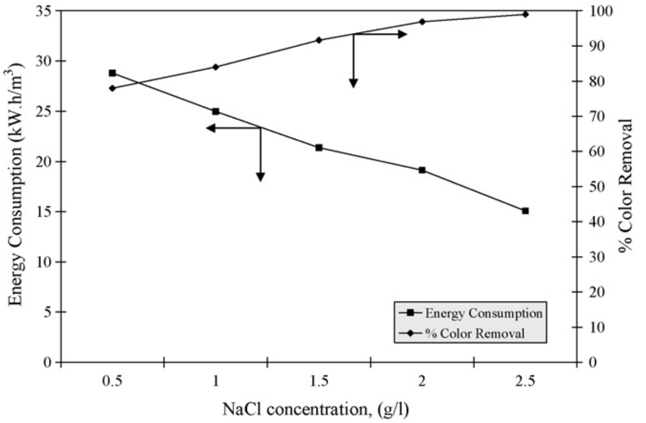

Fig. 12. Effect of NaCl concentration on percentage color removal and energy consumption (c.d. = 6.6 mA/cm^2, rpm = 400, time = 60 min, pH 8, temperature = 25 °C).

4. Conclusions

Electrochemical decolorization of Rakta's paper mill effluent was investigated using a batch-stirred tank electrochemical reactor with lead sheet anode and a stainless steel screen as a cathode. The effects of various operating parameters were studied. Experiments were conducted at initial pH (pH 8). The decolorization and COD percentage removal were found to increase with the increase in sodium chloride concentration, current density, impeller rotational speed and temperature. Energy consumption was found to decrease with increasing impeller rotational speed and NaCl concentration while it increases with increasing current density.

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