

Combined Performance of Electrocoagulation and Magnetic Separation Processes for Treatment of Dye Wastewater

Su-Hee Shin, Yong-Ha Kim[†], Su-Kyong Jung, Kuen-Hack Suh, Shin-Gyung Kang*,
Sun-Kwang Jeong** and Hang-Goo Kim**

Department of Chemical Engineering, Pukyong National University, Pusan 608-739, Korea

*Environmental Conservation Research Team, Research Institute of Industrial Science and Technology,
Kwangyang 545-090, Korea

**Fluidized-bed Reduction Team, FINEX R&D Project Dept. POSCO, Pohang 790-330, Korea

(Received 31 March 2003 • accepted 5 January 2004)

Abstract—In this study, a combined system of electrocoagulation (EC) and magnetic separation (MS) has been applied to the treatment of dye wastewater, and its performance has been evaluated. The flocs formed in the electrocoagulation using Fe anode are magnetized and thus they could be removed by magnetic separation. The removal of suspended solids, color and COD was improved with an increase in electric current up to about 15 A and with a decrease in liquid velocities in EC. While the remaining suspended solids in the treated water were reduced to a few ppm and the color was removed almost perfectly (Max. 96%), that of COD was relatively low and only 81%. A further powerful operation can be expected from the present system if it is combined with an additional process, such as electrolysis or oxidation, to reduce COD more efficiently.

Key words: Electrocoagulation, Magnetic Separation, Wastewater, Flocs, Magnetization

INTRODUCTION

In recent years, the treatment of wastewater has been the subject of much research and discussion as the environmental contamination by dye wastewater has become more and more of a concern. At present, inorganic coagulants such as aluminum salts and iron salts are usually used for the pretreatment of colored dye wastewater from dyeing works before an activated sludge process. In this method, however, there are limitations in removing of organic matters and color. Therefore, these materials are poorly removed by the above mentioned method. Furthermore, because of the overflow of aeration tanks and bulking phenomena, the concentration of contaminants in treated water sometimes exceeds the maximum permissible limits. If the environmental wastewater regulation becomes more severe, a second facility of wastewater treatment or an improvement of existing facility may be necessary to meet the regulation, especially when a high concentration of coagulants is used.

Electrocoagulation (EC) has been recognized as an alternative to the above-mentioned chemical coagulation. The coagulant in this method is generated by dissolution of a sacrificial anode such as Fe and Al. It has a wide application field and it can be also effective for complicated dye wastewater which contains heavy metals, oils, and bacteria. Many research works for the effective use of these advantages are underway in the world, and several test plants have come into being for the treatment of wastewater [Mills, 2000; Mollah et al., 2001]. Basically, the electrocoagulated flocs are removed by flotation and precipitation. Small sized flocs can be easily floated by gas bubbles of H₂ and O₂. On the other hand, large flocs cannot be floated due to their gravitational forces. This will result in their

settling down. A long settling time of 30-60 min required for precipitation hinders the reduction of treating time in wastewater treatment. Therefore, a new consecutive process which can overcome the existing inherent problems needs to be developed in order to make the electrocoagulation effective for the treatment of wastewater. For this purpose, in some studies, a magnetic separation (MS) has been applied based on the fact that the electrocoagulated flocs can be attracted by magnets if these flocs are magnetized when they are dispersed in a solution [Kim et al., 2000b; Tsouris et al., 2001]. The magnetic separation is one of most effective and simple methods for removing suspended solids from the wastewater. This method is possible because the magnetized flocs formed by attractive force between suspended solids and magnetic fine powders are moved to and finally captured by the magnets. Applications of the magnetic separation in industrial wastewater treatment include the removal of phosphate from water [Shaikh and Dixit, 1992], the recovery of hematite and chromite fines and their ultrafines [Wang and Forssberg, 1994], and the removal of oil and suspended solids from municipal sewage.

In this study, a combined system of electrocoagulation and magnetic separation has been presented as a new technology for treating wastewater, and its application to the dye wastewater has been examined. In addition, the effects of operating parameters, such as electric current and influent linear velocity into the electrocoagulation, on the removal of the flocs have also been investigated.

EXPERIMENTAL

An experimental apparatus used in this study for electrocoagulation and magnetic separation is shown in Fig. 1.

1. Electrocoagulation System

For the electrocoagulation, a two-pass system was used in which

[†]To whom correspondence should be addressed.

E-mail: yhkim@pknu.ac.kr

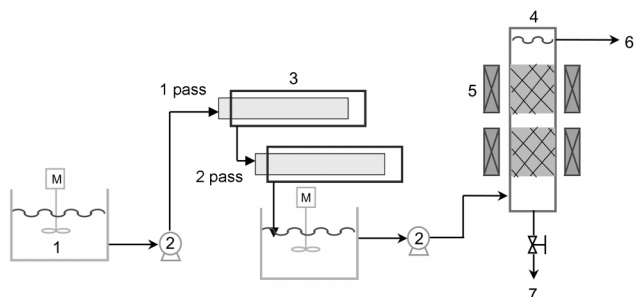


Fig. 1. Schematic diagram of experimental apparatus.

- | | |
|-----------------------|------------------|
| 1. Dye wastewater | 5. Magnet |
| 2. Peristaltic pump | 6. Treated water |
| 3. Electrocoagulator | 7. Sludge |
| 4. Magnetic separator | |

the two electrodes were connected in series. Two tube-type electrodes were arranged so that a direct current could be constantly charged to the wastewater passing through the annular space between anode and cathode. The inner and the outer diameters of anode are 1.2 cm and 1.7 cm, respectively, those of cathode are 2.1 cm and 2.7 cm, respectively, and the length of electrodes is 33 cm. The anode is made of carbon steel (soluble) and the cathode of stainless steel. A direct current as an electric power for electrocoagulation was constantly supplied by a rectifier (cf. maximum capacity: 150 A and 26 V), and a periodic polar inversion between the inner and the outer tubes was stably achieved.

2. Magnetic Separation System

A magnetic separating system was composed of a magnetic separator, a tank for mixing wastewater, a peristaltic pump, and on/off-type electromagnet sets. The magnetic separator was made of transparent acrylic and had the dimension of 5 cm diameter $\times$ 100 cm height. Magnet sets were electromagnetic ones of which the magnetic force at the surface was about 1,500 Gauss. The magnet sets were installed along the circle of the outer wall of the magnetic separator in two steps, the length of each step was 150 mm, and the distance between the two steps was 20.5 cm. The treating efficiency of wastewater has been further improved by the installation of wire gauzes (filters) at each magnet set in the magnetic separator.

3. Test Procedure

The wastewater from dye works in Pusan, Korea was used as a raw sample and its characteristics are as follows: SS (28-146 ppm), turbidity (33.2-78.1 NTU), pH (7.7-10.8), conductivity (1,551-2,052 μ S/cm), TCOD (450-766 ppm) and color (670-875 ADMI (: American Dye Manufacturers Institute)). The dye wastewater was introduced into the electrocoagulator by a peristaltic pump. The dye wastewater was first fed into the inner anode (+) tube and then discharged through the annular space between the inner anode (+) and the outer cathode (-) tubes, and the influent linear velocity $U_{l,EC}$ into the electrocoagulator was ranged at 1.20-2.77 cm/s (i.e., residence time: 0.8-1.7 min.). The electric current was changed in the range of 5-15 A, and the voltage was changed according to the variation of electric current. In order to prevent the electrocoagulated flocs from rising to the surface of wastewater by gas bubbles of H_2 and O_2 , the wastewater was kept agitated. Afterward, the electrocoagulated wastewater was introduced into the lower part of the magnetic separator and flowed toward the upper part by the per-

istaltic pump. At this moment, the wastewater was cleaned by the removal of the flocs which were captured and accumulated in the wire gauzes of the magnetic separator. As the wire gauzes were saturated with the captured flocs, the flocs were hardly removed and remained in the treated water. When this phenomenon happened, the electric power was cut off from the magnet and the peristaltic pump, and then the valve installed at the bottom of separator was opened to discharge the captured flocs by gravity settling. The flocs inside the magnetic separator were discharged in a slurry state. The magnetic separator was then restarted. Once the floc concentration in the treated water increases distinctly, it can be judged that a breakthrough begins. Before the breakthrough, there was no particular change in the floc concentration when the superficial flow velocity $U_{l,MS}$ of wastewater in the magnetic separator was in the range of 0.31-1.23 cm/s (i.e., residence time: 1.4-5.4 min). In this experiment, therefore, it was fixed at the value of 0.42 cm/s (i.e., residence time: 4.0 min).

4. Sample Analysis

The sampling of treated water was done when the cumulative treated volume reached 3 liters, which corresponds to 1.5 times of the magnetic separator volume. There was no pretreatment and special care was taken so that air could not infiltrate during the introduction into the magnetic separator. Samples were taken twice at each condition, and the samples of raw wastewater and treated water were analyzed for suspended solids (SS) contents according to a Standard Method, turbidity using a turbidimeter (HACH 2100 N, USA), chemical oxygen demand (COD) by an open reflux method ($K_2Cr_2O_7$ method), and a color by the ADMI Tristimulus Filter Method using a spectrophotometer (HACH DR/4000U, USA). The removal efficiencies of color and COD were calculated according to the difference in values between raw wastewater and treated water.

RESULTS AND DISCUSSION

1. Characteristics of Electrocoagulated Flocs

The combined system of electrocoagulation and magnetic separation is established based on the characteristics of the flocs that are produced from the Fe electrode and magnetized during a phase transformation into iron oxides. The feasibility of the present process depends mainly on how much the Fe oxides are magnetically attractive.

Fig. 2 shows the pictures of the dye wastewaters after electrocoagulation at the electric current of 5 A, 10 A, and 15 A (current density: 142 A/m², 284 A/m², and 426 A/m², respectively), and the treated water after magnetic separation.

As can be seen in the pictures, the electrocoagulated flocs formed at 15 A and 10 A were gathered to permanent magnets. The size of flocs gathered at 15 A was found to be smaller than that at 10 A. It seems that the flocs at 15 A are more strongly attracted. Those at 5 A were so weakly attracted by the magnetic force from the magnet that some flocs were deposited at the bottom. It is, therefore, considered that the degree of magnetization of the flocs produced from Fe electrode increases with electric current [Tsouris et al., 2001], and it can be expected that the magnetic separation becomes more favorable as the electric current increases. The degree of magnetization of the flocs produced from Fe electrode was compared with that of flocs from Al electrode and also with that of Fe_3O_4 powder

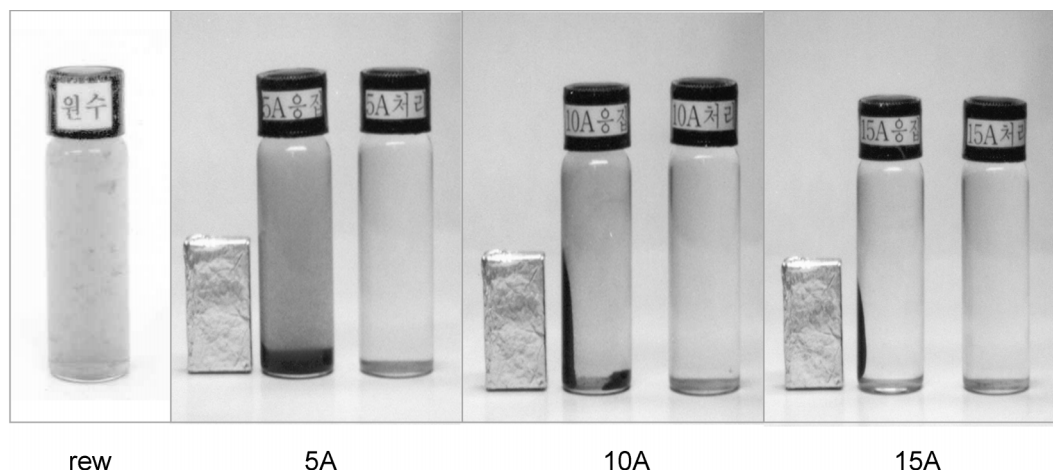


Fig. 2. Comparison of the magnetic susceptibilities of flocs formed at different electric currents.

which is a magnetic substance [Kim et al., 2000b]. The flocs produced at the Al electrode had magnetization close to 'zero', whereas those at the Fe electrode had about 70 emu/g, which is similar to that of Fe_3O_4 powder. This means that the flocs produced at the Fe electrode have a high degree of magnetization similar to permanent magnetic substance. It is seen that the flocs produced during electrocoagulation can be removed by a method of magnetic separation.

2. Removal of Suspended Solids

Fig. 3 shows the effects of the electric current and the influent linear velocity into electrocoagulator on the concentration of SS in the treated water. The superficial liquid velocity in the magnetic separator was kept at 0.42 cm/s. During the electrocoagulation, the SS in wastewater becomes much higher to the range of 400–2,800 ppm in comparison with an average value of 87 ppm in raw wastewater. It increased with an increase in electric current and with a decrease in the influent linear velocity. The SS in the treated water decreased considerably after magnetic separation. When the elec-

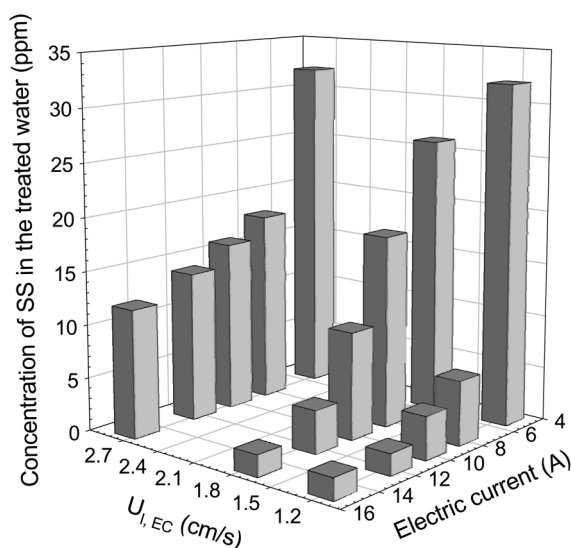


Fig. 3. Effect of electric current and linear velocity in EC on the concentration of SS in the treated water.

trocoagulation was carried out at 1.20 cm/s and 15 A, the SS in the treated water was very low (i.e., below 5 ppm). However, as the influent linear velocity increased (1.75 cm/s and 2.77 cm/s) and as the electric current decreased (10 A, 8 A, and 5 A), the SS in the treated water increased up to 32 ppm. In case of 5 A, the SS in the treated water increased sharply irrespective of influent linear velocities. This is because the electrocoagulated flocs were less magnetized at 5 A. Therefore, it can be concluded that a high removal of electrocoagulated flocs is obtained if the flocs are sufficiently magnetized.

3. Removal of Color

One of the most important characteristics of dye wastewater is a deep color, and the dye components which bring out the color can cause environmental pollution as well as spoil the appearance of the surroundings. The removal, therefore, of the color from dye wastewater is regarded to be more important than many other things.

The removal efficiency of color in dye wastewater is shown in Fig. 4. The removal efficiency was not significant to the electric current except for the low influent velocity, in which the removal efficiency increased slightly with the increase of the electric current. For the effect of influent linear velocity, the highest removal

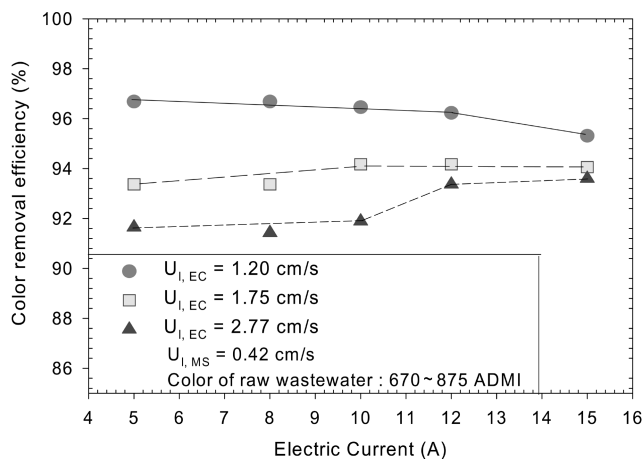


Fig. 4. Effect of electric current on color removal efficiency.

efficiency of color, 96%, was obtained at a low influent linear velocity of 1.20 cm/s, and the efficiency decreased down to 92-93% as the velocity increased. In other words, the removal efficiency of color was somewhat affected by electric current when the influent linear velocity was high, but a nearly constant value was obtained regardless of electric current when it was low. The reason for the less effect of electric current on the removal of color at a low influent linear velocity seems to be similar to that of the SS as above mentioned. The dye molecules in wastewater are reduced into small organic matters at the cathode during electrocoagulation and then removed after being adsorbed by coagulants which are produced during electrocoagulation. As the residence time in the electrocoagulator increases, the dye molecules can be reduced further, and thus the removal efficiency is not affected strongly by electric current. On the other hand, if the influent linear velocity is high, there is no time to be sufficiently reduced. Therefore, in this case, the removal efficiency of color can be improved, even if so low as 1-2%, with an increase in electric current.

4. Removal of COD

Fig. 5 shows the effect of electric current on the removal efficiency of COD. When the influent linear velocity was as low as 1.20 cm/s, the removal efficiency of COD was 69% at 5 A, 78% at 10 A, and 81% at 15 A. However, when the influent linear velocity increased to 1.75 cm/s, the removal efficiency decreased slightly and it was 64% at 5 A, 72% at 10 A, and 73% at 15 A. Furthermore, when the influent linear velocity increased up to 2.77 cm/s, it was 63% at 5 A, 68% at 10 A, and 69% at 15 A. When an electric current was kept above 10 A, a further increase of electric current had little effect on the additional removal of COD. This aspect became more clear at a higher influent linear velocity.

In the present study, the removal efficiency of COD ranged from 65-81%, which is considerably low compared to those of SS and color. It can be estimated that in the case for the raw wastewater having COD of 608 ppm, the COD in the treated water should be reduced to about 115 ppm, at most, even at the COD removal efficiency of 81%. This value is far from 40 ppm which is the maximum permissible limit notified by the Ministry of Environment for industrial complex wastewater from terminal treatment stations. The reason for this low efficiency is that there is a limit in removing soluble materials from wastewater only by electrocoagulation

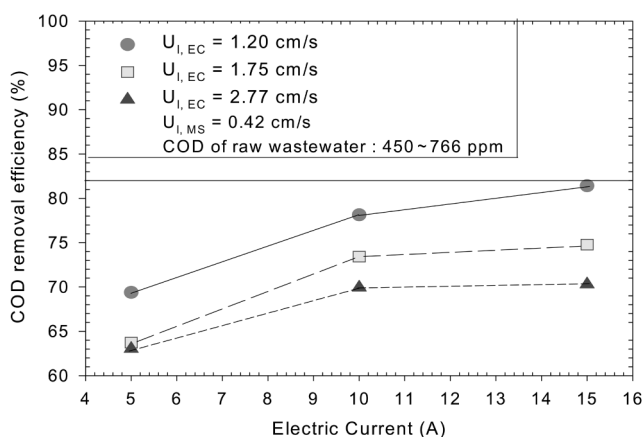


Fig. 5. Effect of electric current on COD removal efficiency.

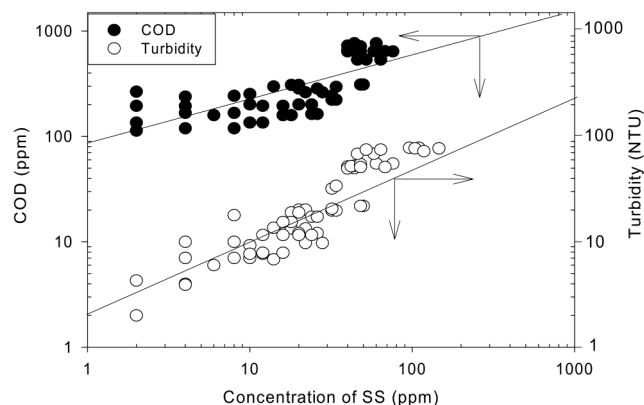


Fig. 6. Relationships between concentration of SS and COD and between concentration of SS and turbidity for the treated water.

[Chen et al., 2000]. This can be also seen by a mutual relation among SS, turbidity, and COD, as shown in Fig. 6. As the SS decreases to 1 ppm, the turbidity decreases down to about 1 NTU, but the COD does not decrease below 100 ppm. This is because insoluble solids are removed during electrocoagulation and magnetic separation while the soluble ones are not. Some electrocoagulated flocs are formed by the combination of Fe ions dissolved during electrocoagulation with OH^- or Cl^- ions in the wastewater. They are non-magnetic and thus still remain without being removed after magnetic separation. In the present system, which combines electrocoagulation and magnetic separation, an additional process, such as electrolysis or oxidation [Barrera-Díaz et al., 2003; Bejankiwar, 2002; Kim et al., 2000a, 2002; Wu et al., 2002] is necessary to reduce COD more efficiently.

CONCLUSIONS

A combined system of electrocoagulation (EC) and magnetic separation (MS) has been applied to the treatment of dye wastewater, and its performance has been investigated. The results can be summarized as follows:

1. In the magnetic separation of the flocs produced during electrocoagulation, the degree of magnetization of the flocs increased with an increase in electric current in an electrocoagulator. This aspect is expected to be favorably operated for magnetic separation.
2. The removal of suspended solids, color, and COD was improved with an increase in electric current in an electrocoagulator and a decrease in influent linear velocity into an electrocoagulator.
3. While the remaining suspended solids in the treated water were reduced to a few ppm and the color was removed almost perfectly (Max. 96%), that of COD was relatively low and only 81%. This can be ascribed to the fact that soluble solids contained in dye wastewater and non-magnetic flocs can still remain after the treatment.

The present system in which an electrocoagulator and a magnetic separator are combined showed a high removal of suspended solids and color. A further powerful operation can be expected from the present system if it is combined with an additional process, such as electrolysis or oxidation to reduce COD more efficiently.

ACKNOWLEDGMENT

We acknowledge a grant-in-aid for research from Pukyong National University.

NOMENCLATURE

$U_{1,EC}$: influent linear velocity of wastewater into the electrocoagulator [cm s^{-1}]

$U_{1,MS}$: superficial flow velocity of wastewater in the magnetic separator [cm s^{-1}]

REFERENCES

- Barrera-Díaz, C., Ureña-Núñez, F., Campos, E., Palomar-Pardave, M. and Romero-Romo, M., "A Combined Electrochemical-irradiation Treatment of Highly Colored and Polluted Industrial Wastewater," *Radiat. Phys. Chem.*, **67**, 657 (2003).
- Bejankiwar, R. S., "Electrochemical Treatment of Cigarette Industry Wastewater: Feasibility Study," *Water Res.*, **36**, 4386 (2002).
- Chen, X., Chen, G. and Yue, P. L., "Separation of Pollutants from Restaurant Wastewater by Electrocoagulation," *Separation and Purification Technol.*, **19**, 65 (2000).
- Kim, T.-H., Park, C., Lee, G., Lee, J., Shin, E.-B. and Kim, S., "Pilot-scale Treatment of Textile Wastewater by Combined Biological Pretreatment-Chemical Coagulation-Electrocoagulation-Electrochemical Oxidation," *Theories and Applications of Chem. Eng.*, **6**, 3909 (2000a).
- Kim, T.-H., Park, C., Lee, J., Shin, E.-B. and Kim, S., "Pilot Scale Treatment of Textile Wastewater by Combined Process (Fluidized Bio-film Process-Chemical Coagulation-Electrochemical Oxidation)," *Water Res.*, **36**, 3979 (2002).
- Kim, Y. H., Shin, S. H., Suh, K. H. and Kim, H. G., "Combined Process of Electrocoagulation and Magnetic Fluid Separation: Application to the Removal of Contaminants from Dye Wastewater," in Proceedings of the 7th Asian Conference on Fluidized-Bed and Three-Phase Reactors, Hamanako, Shizuoka-Ken, Japan, 373 (2000b).
- Mills, D., "A New Process for Electrocoagulation," *J. Am. Water Works Assoc.*, **92**, 34 (2000).
- Mollah, M. Y. A., Schennach, R., Parga, J. R. and Cocke, D. L., "Electrocoagulation (EC) Science and Applications," *J. Hazard. Mater.*, **B84**, 29 (2001).
- Shaikh, A. M. H. and Dixit, S. G., "Removal of Phosphate from waters by Precipitation and High Gradient Magnetic Separation," *Water Res.*, **26**, 845 (1992).
- Tsouris, C., DePaoli, D. W., Shor, J. T., Hu, M. Z.-C. and Ying, T.-Y., "Electrocoagulation for Magnetic Seeding of Colloidal Particles," *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **177**, 223 (2001).
- Wang, Y. and Forssberg, E., "The Recovery of Hematite and Chromite Fines and Ultrafines by Wet Magnetic Methods," *Minerals and Metallurgical Processing*, **11**, 87 (1994).
- Wu, Z., Cong, Y., Zhou, M., Ye, Q. and Tan, T., "Removal of Phenolic Compounds by Electro-assisted Advanced Process for Wastewater Purification," *Korean J. Chem. Eng.*, **19**, 866 (2002).