

Electro-chemical removal effects for the pollutants with K-ACFs

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A study of the treatment of wastewater using K-activated carbon fiber (ACF) system followed electrochemical removal was carried out at laboratory scale. Various different types of ACF treated with potassium salts as K sources have been used in this study to investigate the catalytic removal efficiency of pollutants from the wastewater. The electro-chemical removal capacities of K-ACF electrodes were associated with their adsorption properties and were related to physico-chemical properties such as surface area and kind of treated potassium salts, and to reaction time. And, surface morphologies and elemental analysis for the K-ACFs after ECR as a function of time are investigated by SEM and EDX to explain the changes in removal capacities. The K-ACFs were electrochemically reacted with wastewater to investigate the removal efficiencies for the COD, BOD, T-N and T-P. A satisfactory removal performance except results for the T-P removal performance was achieved.

Key words: K-ACF, Adsorption, SEM/EDX, ECR, Pollutant.

Introduction

Removal of pollutants is currently a strategic issue using activated carbon fiber (ACF) [1, 2], which is grounded in environmental regulations combined searchers for new clean sources. The prime objective of environmental control in the industrial setting is to prevent or reduce the generation of contaminants at waste source. In general, ACF processes have been attracted interest for municipal wastewater treatments with most of the academic researches into these fields concentrating on the removal of low concentrations of low molecular weight contaminants. Among various methods used to removal of pollutants, adsorption on activated carbon fiber is considered as a very efficient and cost effective approach. This is the result of unique surface properties of carbonaceous adsorbents such as large surface area, and high pore volume, along with particular surface chemistry [3], which promotes catalytic oxidation of pollutants in the presence of even small amounts of air and/or electrical source [4]. To enhance the catalytic properties of ACF, various methods have been used of which the most common is impregnation of activated carbon and its fiber with sodium or potassium hydroxide or salts containing potassium such as potassium carbonate [2, 5, 6]. Doing this leads to a good performance with only increase in

the cost of materials. Recent research on the performance of sewage sludge-based carbonaceous materials as pollutants removal media showed the significant role of inorganic phase [7]. It is also well known that impregnation of carbon with transition metals such as copper, silver or manganese is the best way to lead to a good performance of activated carbons in the removal of pollutants [8]. The industrial applications of ACFs showed that when these materials was in contact with metal ions (Ag^+ , Cu^{2+} , Ni^{2+} , Pd^+ etc.) solutions its chemical properties changed, as a consequence of spontaneous metal ions adsorption [9]. Such metal modified carbons can also used as a catalysts [10, 11], or electro-catalysts [4, 12]. K-ACFs electrode for the removal of pollutants can also be used as catalyst and catalyst support in the electro-chemical removal (ECR) reaction. Because these pollutants in solution have difference ionization tendency, Coulomb force and electrochemical behavior, the electrical characterization of K-ACFs is very important for electro-chemical and -catalytic removal reactions. The sorption capacity for electro-chemical behavior of ACF pre-adsorbed with potassium is strongly influenced by the chemical surface structure of the potassium supported activated carbon fiber.

The objectives of this research it to study the electro-catalytic effect of activated carbon fibers (ACFs) containing potassium in the interlayer spaces on the electrical performance of adsorbents in the process of pollutants removal in the wastewater. In this study, the electro-chemical removal of various pollutants by K-ACF electrodes from wastewater was investigated.

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After ECR, the surface properties of the metal-ACFs reacted with pollutants were investigated as a function of ECR time. The ECR capacities of K-ACF electrodes were proportional to physical properties such as adsorption isotherm, surface area and porosity and to reaction time. The morphologies on carbon surfaces were observed by SEM to explain the changes in removal properties. And, quantitative properties in the ACFs were also studied by EDX. Finally, the K-ACFs were electrochemically reacted to waste water to investigate the removal efficiency for the COD, T-N and T-P.

Experimental Procedure

Raw materials

Self-made ACFs used as a raw material were prepared from commercial PAN fibers (T-300 Amoco, USA). The carbonized PAN fiber was heated first at 823 K for burn off, and the carbon fibers were activated by steam diluted with nitrogen in a cylinder quartz glass tube in the temperature range of 1053-1073 K for 30 min. These activated carbon fibers were washed with deionized water and dried for 24 h at ambient temperature. The 0.01 M diluted sulfuric acid at boiling temperature was used in the oxidation treatment to increase the formation of functional groups without the damage of the ACF surface. The oxidation was carried out at the boiling temperature for 1 h. The oxidized ACFs were washed and dried at 323 K for 24 h. We prepared to K-ACF series in solutions of 0.1 M of KNO_3 , KCl , KOH and KMnO_4 for the potassium loading. The K-ACFs prepared also dried at 323 K for 24 h at nitrogen atmosphere. For the effluent characterization, the work involves the treatment of aqueous piggery urine effluent with chemical oxygen demand (COD) and biological oxygen demand (BOD) levels approaching 5000 mg/L from the piggery farm. The analytical results for the primitive piggery waste were listed in Table 1. The levels can be dropped under 365-450 mg/L by physico-chemical primary treatment step (coagulation). The samples of under 450 mg/L leveled were used for characterization for the ECR of K-ACFs. Figure 1 was shown the procedure for characterization from piggery waste.

Preparation of ECR system

The K-ACFs of test electrodes was consist of the size

Table 1. The Analytical Results for the Primitive and Primary Treated Piggery Waste

Step	CDO (mg/L)	BOD (mg/L)	T-N (mg/L)	T-P (mg/L)
Primitive Waste (Over)	50,000	50,000	426	512
Primary (ca.)	450	365	90.6	135

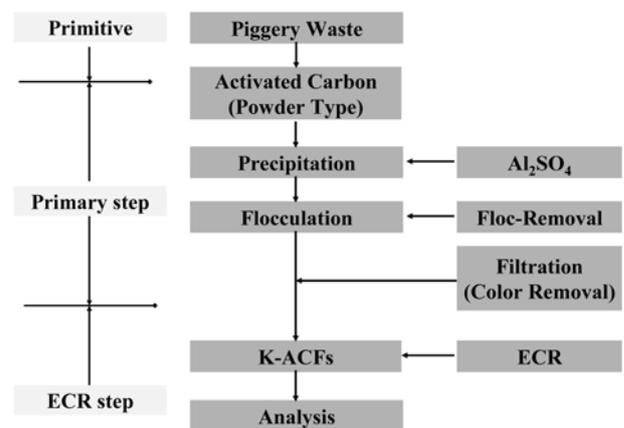


Fig. 1. The procedure of characterization for the piggery waste.

of 40×15×3 mm hexagonal felt typed ACFs. The counter electrode of same size was artificial graphite rod (TCK, Korea). The electrolyte was samples of piggery waste under 450 mg/L COD leveled. The condition of ECR for the measurements of contents of organic and inorganic pollutants was 0.5 mAcm^{-2} at room temperature. The measured voltage was set to 4.5V. The trial examples for the ECR of K-ACF and nomenclature are listed in Table 2.

Instrumental analysis for K-ACFs

Nitrogen adsorption isotherms of dried K-ACFs after ECR were measured using an ASAP 2010 (Micrometrics,

Table 2. The Trial Examples for the ECR of K-ACF and their Nomenclature

Sample		
Preparation of Electrode (K-ACFs)	Operation Time (min.)	Nomenclature
0.1 M KNO_3 + ACF	1	A-1
0.1 M KNO_3 + ACF	30	A-30
0.1 M KNO_3 + ACF	60	A-60
0.1 M KNO_3 + ACF	90	A-90
0.1 M KNO_3 + ACF	120	A-120
0.1 M KCl + ACF	1	B-1
0.1 M KCl + ACF	30	B-30
0.1 M KCl + ACF	60	B-60
0.1 M KCl + ACF	90	B-90
0.1 M KCl + ACF	120	B-120
0.1 M KOH + ACF	1	C-1
0.1 M KOH + ACF	30	C-30
0.1 M KOH + ACF	60	C-60
0.1 M KOH + ACF	90	C-90
0.1 M KOH + ACF	120	C-120
0.1 M KMnO_4 + ACF	1	D-1
0.1 M KMnO_4 + ACF	30	D-30
0.1 M KMnO_4 + ACF	60	D-60
0.1 M KMnO_4 + ACF	90	D-90
0.1 M KMnO_4 + ACF	120	D-120

USA) at 77 K. Before the experiment the samples were heated at 473 K and then outgassed at this temperature under a high vacuum of 1.33×10^{-5} torr to constant pressure. The isotherms were used to calculate the specific surface area and pore volume. Scanning electron microscopy (SEM, JSM-5200 JOEL, Japan) was used to observe the surface state and pore structure of K-ACFs polluted from ECR. The chemical composition of the pollutant contaminated K-ACFs after ECR was determined by analyzing fiber surfaces by EDX connected to the JSM-5200 JOEL.

COD, BOD, N and P contents analysis

The chemical oxygen demand (COD) is an indication of the overall oxygen load that a wastewater will impose on an effluent stream. COD is equal to the amount of dissolved oxygen that sample will absorb from a hot acidic solution containing potassium permanganate. The samples were then analyzed using standard COD analysis method (potassium permanganate titration method). Biological oxygen demand (BOD) was carried out by general method. BOD removal values were measured by using 300 mL BOD bottle occupied with effluent after incubation in dark incubator

at 20 °C during 5 days [13]. In considering the total nitrogen (T-N) balance in the treatment process, nitrogen removal was measured as UV absorbance spectrometric method [13]. The primary purified effluents by coagulation could be prepared to samples for the T-N measurement by chemicals treatment. T-N removal values were measured by UV spectrophotometer at 220 nm wavelengths. For the analysis of $\text{NH}_4\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$, Spectrophotometer (PhotoLab S6, WTW) was also used. The measurements of total phosphorous (T-P) of these samples were carried out via Vis spectrophotometer at 880 nm wavelengths using ascorbic acid reduction method [13]. These analyses were carried out according to standard methods for the examination of water and wastewater [14].

Results and Discussion

Figure 2 shows the representative adsorption isotherm of K-ACFs after ECR as a function of time. Almost adsorption isotherms are type I according to the IUPAC classification [15]. Note that at low values of operation time the isotherm exhibit a high adsorption volume. The isotherms presented in this figure show

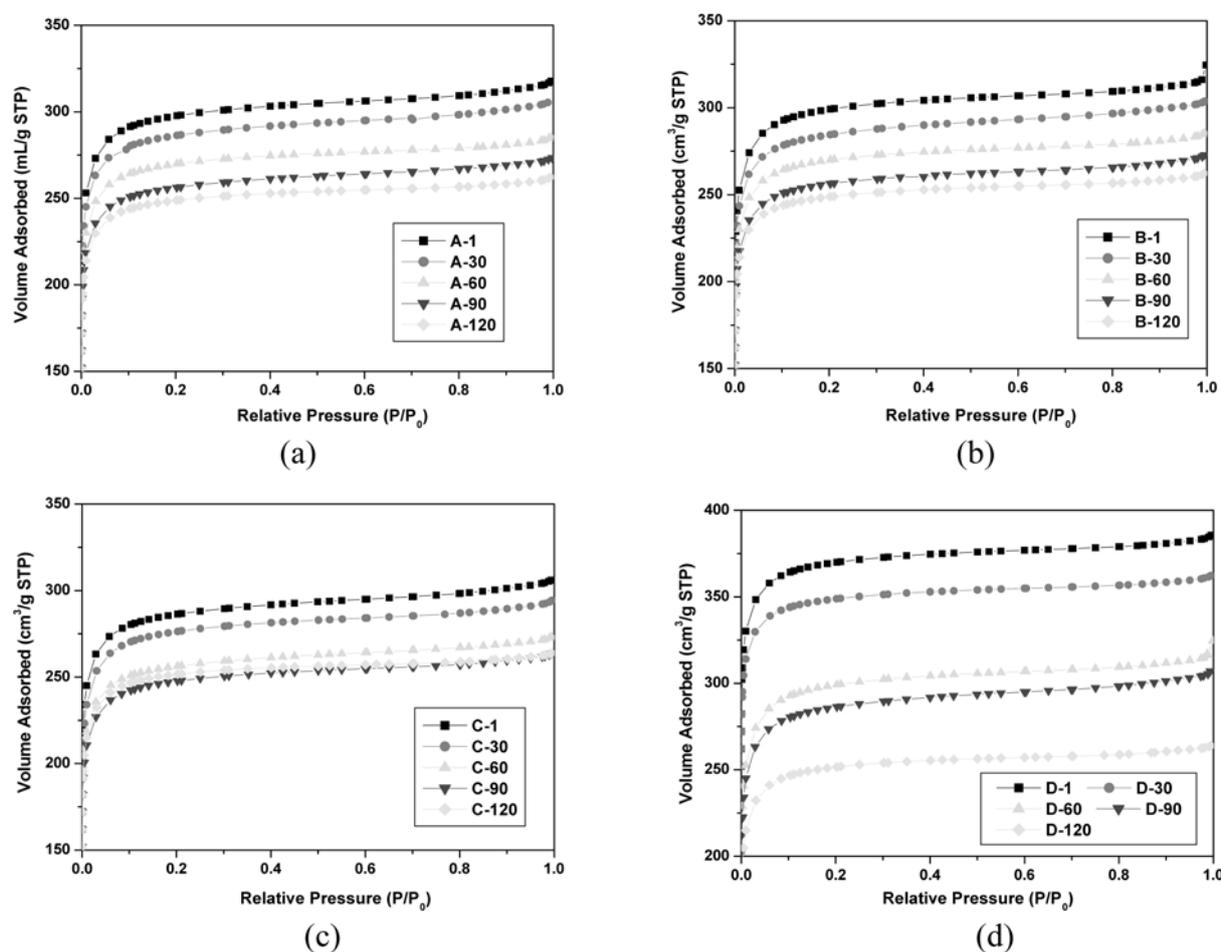
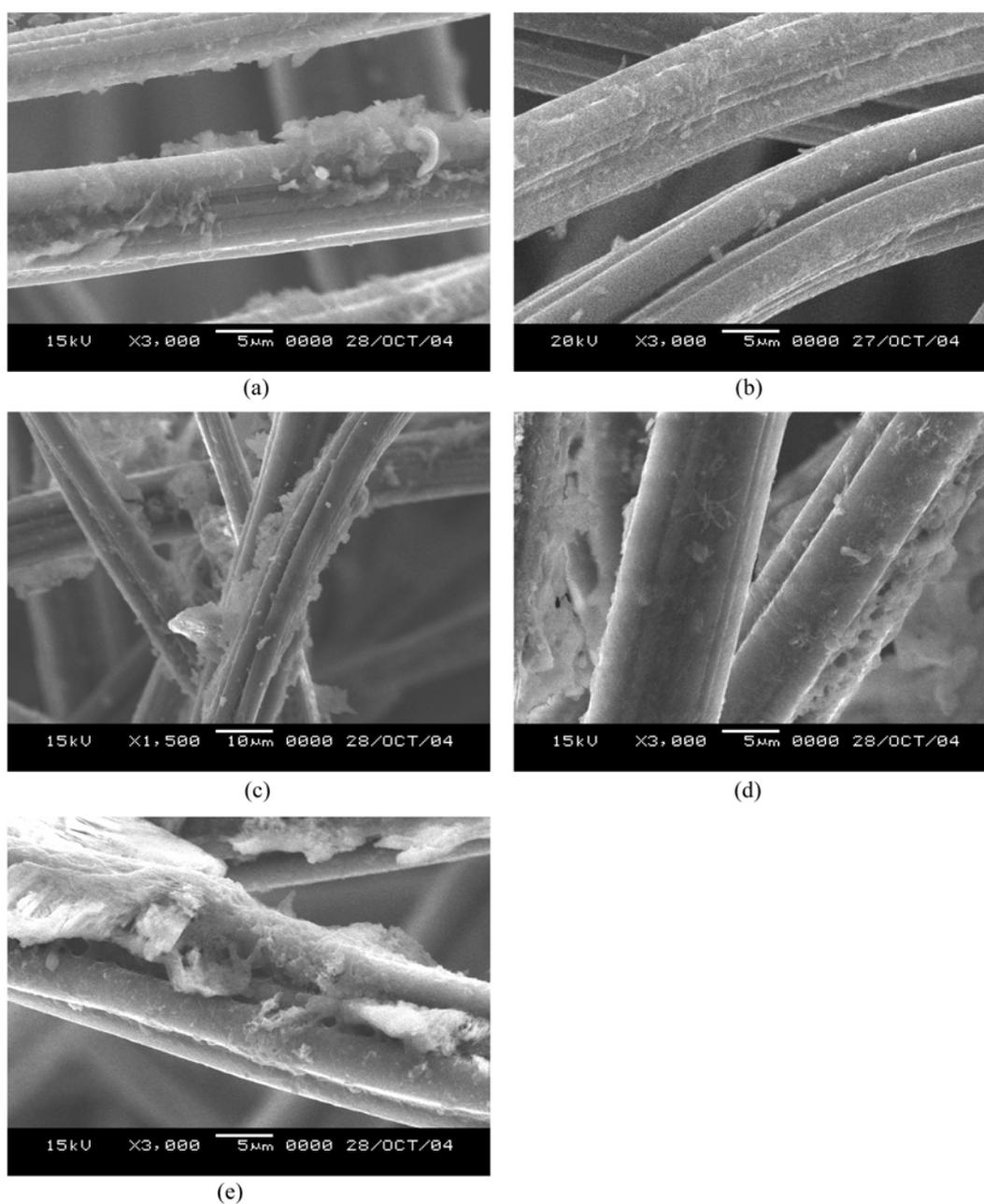


Fig. 2. Adsorption isotherms for K-ACFs after ECR as a function of time; (a) A- series, (b) B- series, (c) C- series and (d) D- series.

Table 3. Comparison of physical parameters of K-ACFs after ECR

Sample	S_{BET} (m^2/g)	Micropore Volume (cm^3/g)	Adsorption Average Pore Diameter (\AA)	Micropore Surface Area (m^2/g)	Sample	S_{BET} (m^2/g)	Micropore Volume (cm^3/g)	Adsorption Average Pore Diameter (\AA)	Micropore Surface Area (m^2/g)
A-1	1105	0.38	15.54	1068	C-1	1003	0.39	15.43	976.4
A-30	1003	0.35	15.52	989.2	C-30	987.1	0.34	15.37	956.3
A-60	973.9	0.33	15.54	937.1	C-60	957.7	0.33	15.13	921.7
A-90	893.2	0.33	15.28	846.5	C-90	833.5	0.30	15.13	779.3
A-120	823.7	0.31	15.21	801.2	C-120	821.5	0.29	15.11	765.4
B-1	1011	0.39	15.33	1091	D-1	984.2	0.38	15.71	934.6
B-30	1001	0.34	15.37	966.3	D-30	918.2	0.35	15.85	862.5
B-60	967.7	0.33	15.23	931.7	D-60	899.6	0.34	15.62	815.9
B-90	843.5	0.30	15.13	789.3	D-90	894.8	0.34	15.39	809.5
B-120	798.4	0.30	14.98	755.4	D-120	823.5	0.31	15.25	777.8

**Fig. 3.** SEM images obtained from A-series; (a) A-1, (b) A-30, (c) A-60, (d) A-90 and (e) A-120.

that the total sorption uptake decreases with increasing ECR time and exhibit a sharp knee bands followed by a horizontal plateau. Above relative pressure of 0.9 occurs a steep increase in adsorbed volume, which may be assigned to the filling of some mesopores. The information on the relative amount of micropore and mesopore can be obtained by analyzing adsorption isotherm over a whole range of relative pressures. Adsorption of low relative pressure is normally result-

ed in the pore filling of micropores. However, at moderate low relative pressure the amount of N_2 adsorption for K-ACFs of low values of operation time was greater than that for the K-ACFs of high values of operation time. Adsorption in this range of relative pressure can be contributed to monolayer coverage formation on the surfaces of micropores. As previously mentioned, adsorption isotherms were analyzed by BET method to obtain the specific surface area (S_{BET}).

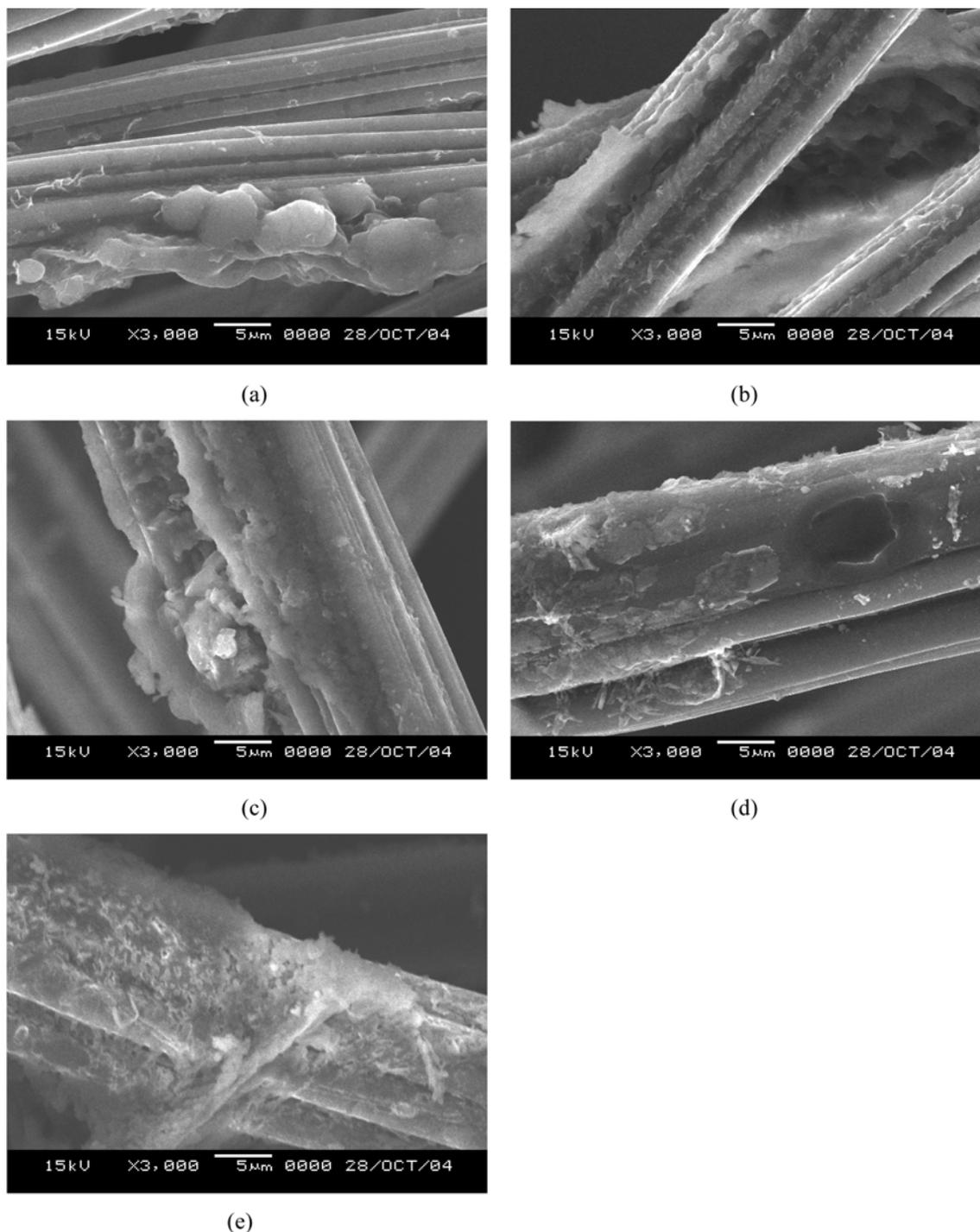


Fig. 4. SEM images obtained from B- series; (a) B-1, (b) B-30, (c) B-60, (d) B-90 and (e) B-120.

Table 3 shows the values of S_{BET} , micropore surface area, micropores volume, and average pore diameter of K-ACFs after ECR as a function of time. The values of micropore surface area, micropores volume, and average pore diameter were obtained by the Barrett-Joyner-Halenda (BJH) method from same adsorption isotherm. As shown in Table, S_{BET} s were distributed between 798.4 (B-120) and 1105 m^2/g (A-1). Increasing ECR time leads to a decrease of the values of micropore

surface area, micropore volume and average pore diameter. It can be considered that K-ACFs with increasing operation time increase with removal effect of pollutants in wastewater. For the sample B-120, the value of S_{BET} decreased nearly 50% as a result of electro-chemical removal of pollutants in the wastewater. Differences in the shape of these isotherms are not very significant, evidencing general similarities in the surface transformations of the K-ACF samples after

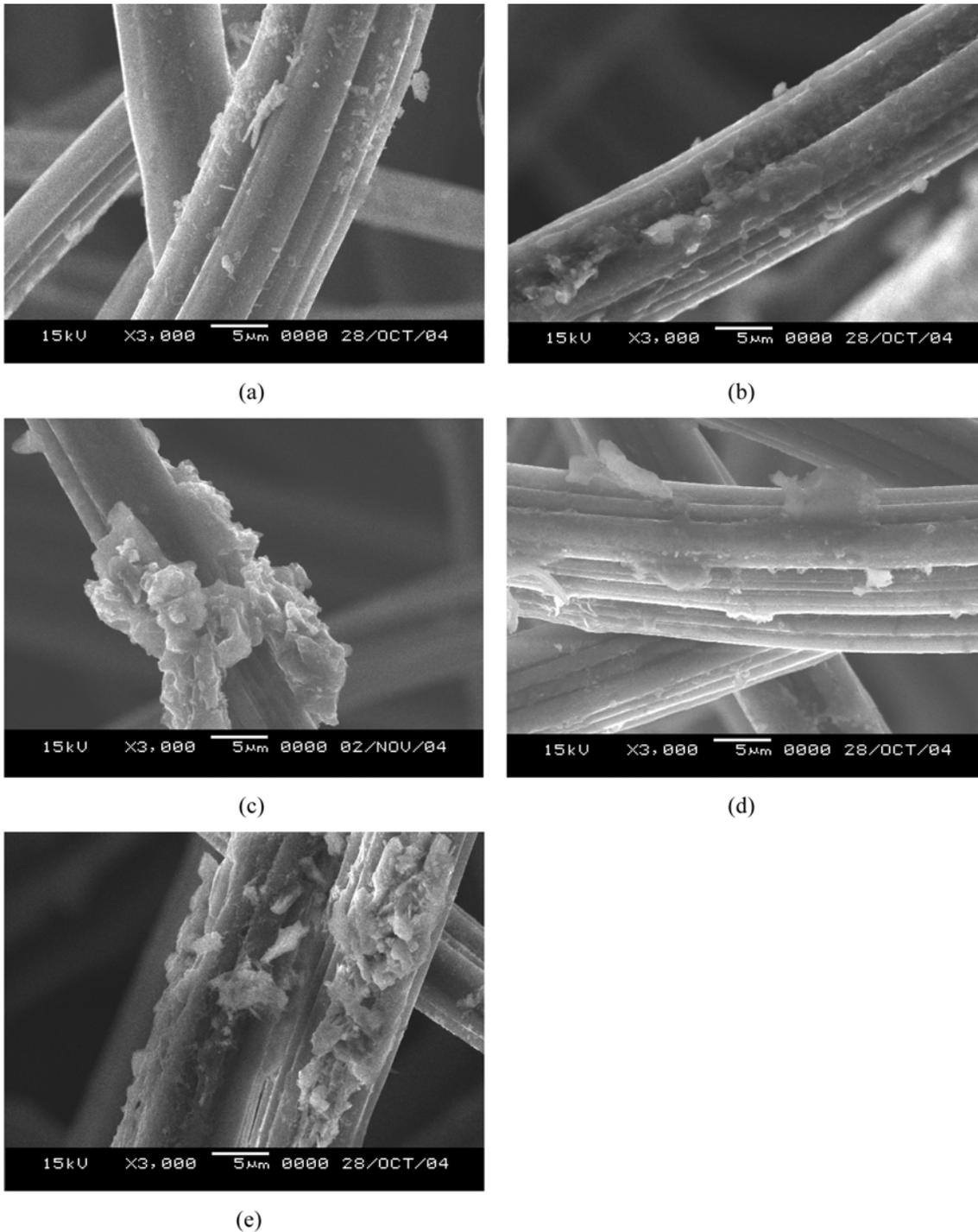


Fig. 5. SEM images obtained from C- series; (a) C-1, (b) C-30, (c) C-60, (d) C-90 and (e) C-120.

ECR with variation of reaction times. It can be believed that the surface area decreases as moderate pore blocking by the distribution of organic and inorganic pollutants on the metal-ACFs after ECR.

We examined the surface structure of the electrodes after the pollutants removal process and investigated the relation between metal deposition and change of structure. Figure 3, 4, 5 and 6 show SEM micrographs of the K-ACF series electrodes after the pollutants

removal process as function of time. These figures present results from characterization of porous texture, potassium salt localizations and contaminants distribution on the surfaces for all the materials used. It is shown that, when potassium is dispersed into ACFs, the porosity is modified in some cases, this effect being developed in microporosity in materials with a narrow starting porosity. SEM pictures of K-ACFs provide information about the distribution of metals. In addition

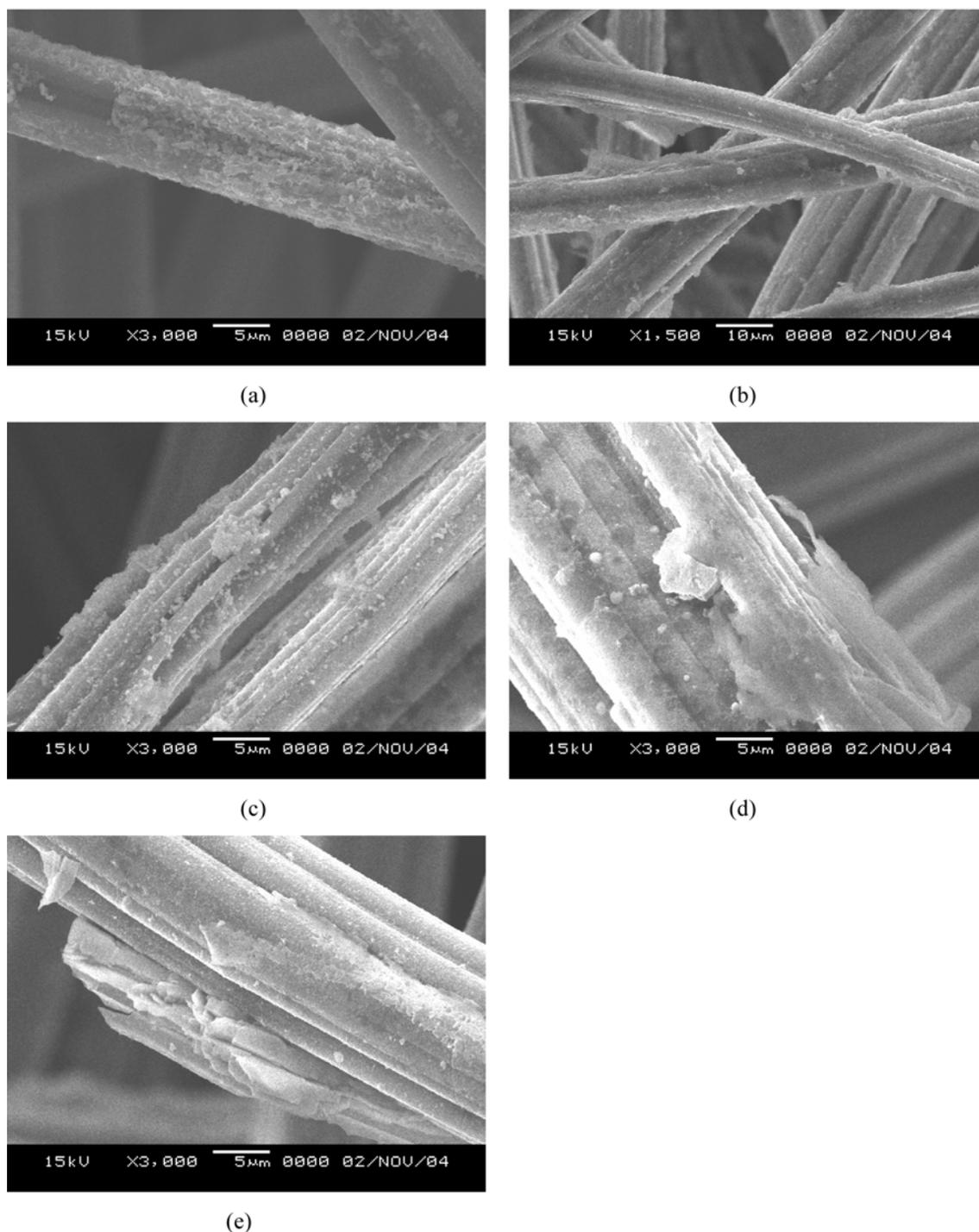
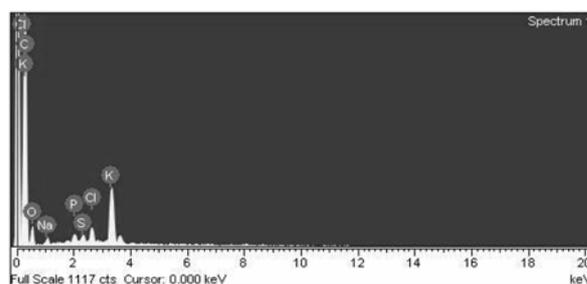


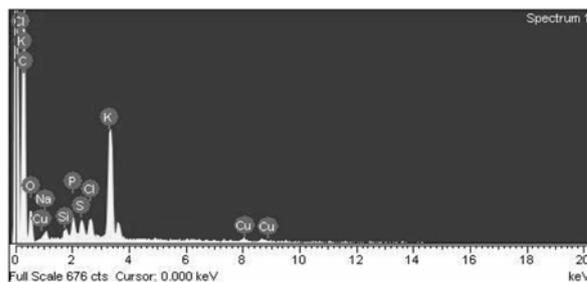
Fig. 6. SEM images obtained from D- series; (a) D-1, (b) D-30, (c) D-60, (d) D-90 and (e) D-120.

to, homogeneous distribution of potassium on the large surface area can be promoted to catalytic efficiencies for the contaminants removal. This aspect will have to be taken into account for further analysis of the removal of pollutants because porosity strongly influences both the adsorption capacity of pollutants and the catalytic activity for pollutants. Besides, if the pore size becomes too narrow with decreasing surface area after potassium ions treatment, catalytic activity for the removals will definitely appear during the liquid/K-ACF activity reaction. With potassium compounds, pollutants covered the partial surface of the K-ACF electrodes. Each of these analyses showed that contaminants on the fiber are uniformly distributed in the round and edges and that the average aggregate size was more than 5 μm . The many micropores in the fibers are blocked by contaminants. As these figures show, new cleavage cracks and large edge developed on the surface during electro-chemical reaction. Very few of the contaminants appeared to coalesce into large agglomerates. For D- series treated with KMnO_4 of Fig. 6, the mechanism of pollutants generation differed from that of any other series. Firstly, many small particles were generated, and then these particles grew and covered the surface of the ACFs. For the elemental microanalysis of K-ACFs after ECR as a function of time, these samples were analyzed by EDX. These EDX spectra of K-ACFs are shown in Fig. 7, 8, 9 and 10. These spectra are shown the presence of C, and O including major K treated. Most of samples are richer in carbon and major metals treated than any other elements. The results of EDX elemental micro-analysis of K-ACFs were listed in Table 4. In case of most of samples, carbon and potassium are present as major elements in the K-ACFs after ECR. And, these results observed for each samples are shown the spectra corresponding to almost all samples rich in major and minor elements with increasing of the amount of time operated. It should note that a increasing of the amount of O contents with decreasing C contents is observed for the over all samples, which becomes more homogeneous as the carbon fiber surface is oxidized as electrochemical red-ox reaction. The results of SEM and EDX indicate that the functional groups and surface reaction motive of ACF surface by electro-chemical reaction are affects to the dispersion of the organic and inorganic pollutants in the wastewater. Oh et al. [16] reported that removal efficiency of various metal elements from wastewater appear very excellent EDX results using primitive ACF.

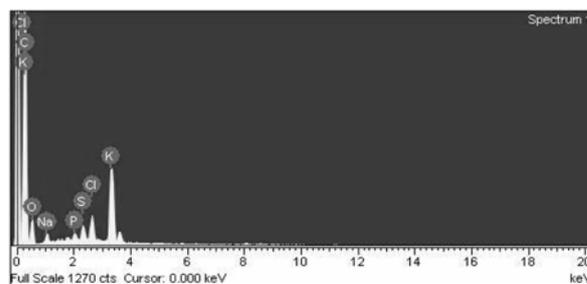
The COD, BOD, T-N and T-P removal performance of the electro-chemical reactor was investigated and these results are shown in Fig. 11. Except results for the T-P removal performance, a satisfactory organic removal performance was achieved. The average values of the initial COD, BOD, T-N and T-P of primitive waste water were about 50,000, 50,000, 426 and 512



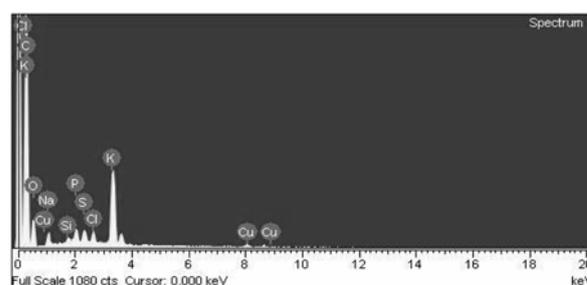
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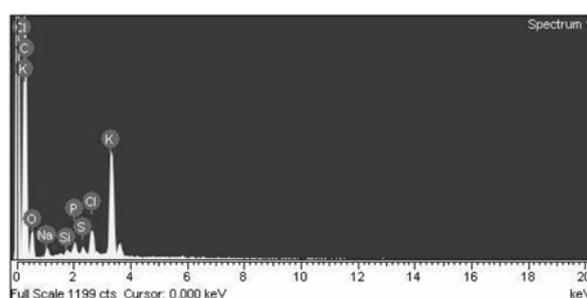
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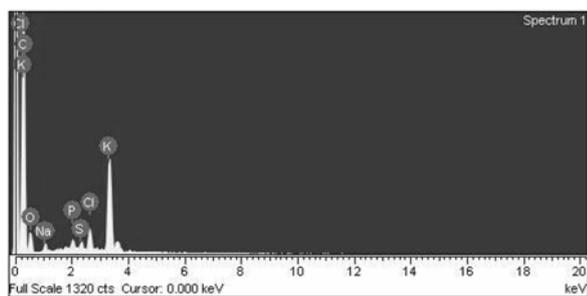


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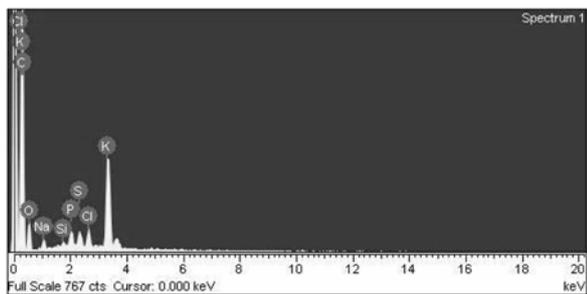


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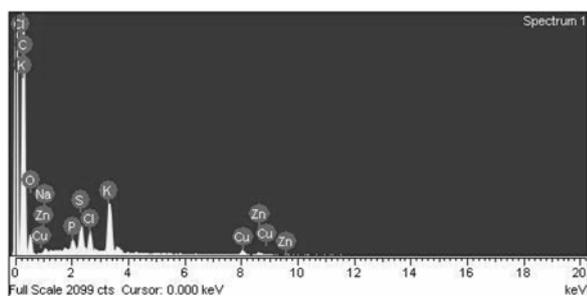
Fig. 7. Typical EDX microanalysis for A-series; (a) A-1, (b) A-30, (c) A-60, (d) A-90 and (e) A-120.



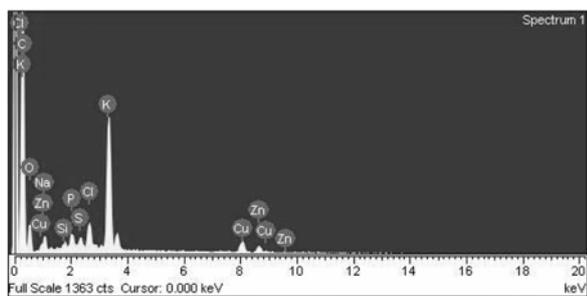
(a)



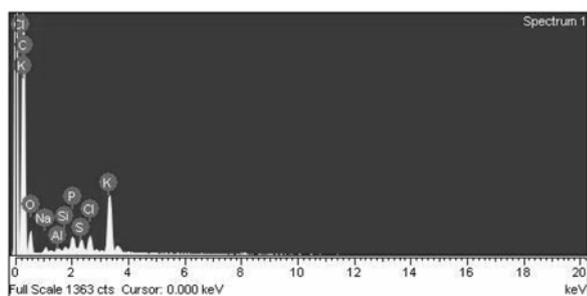
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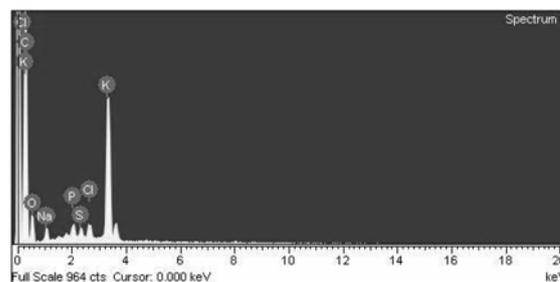


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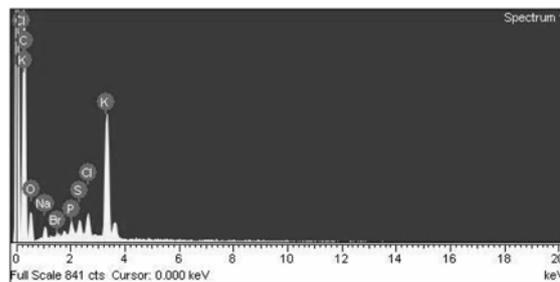


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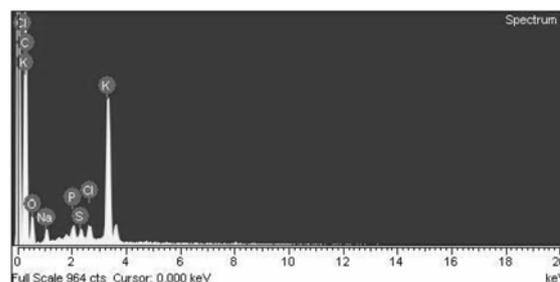
Fig. 8. Typical EDX microanalysis for B-series; (a) B-1, (b) B-30, (c) B-60, (d) B-90 and (e) B-120.



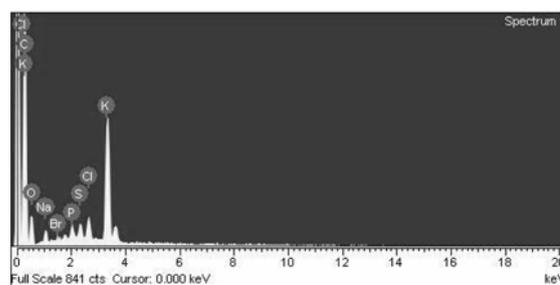
(a)



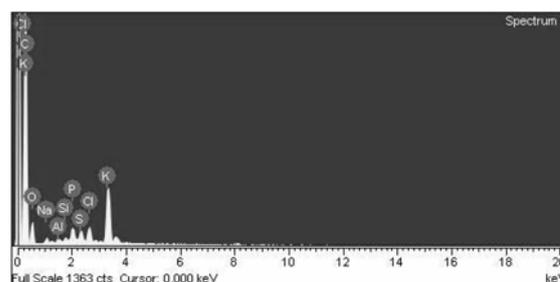
(b)



(c)



(d)



(e)

Fig. 9. Typical EDX microanalysis for C-series; (a) C-1, (b) C-30, (c) C-60, (d) C-90 and (e) C-120.

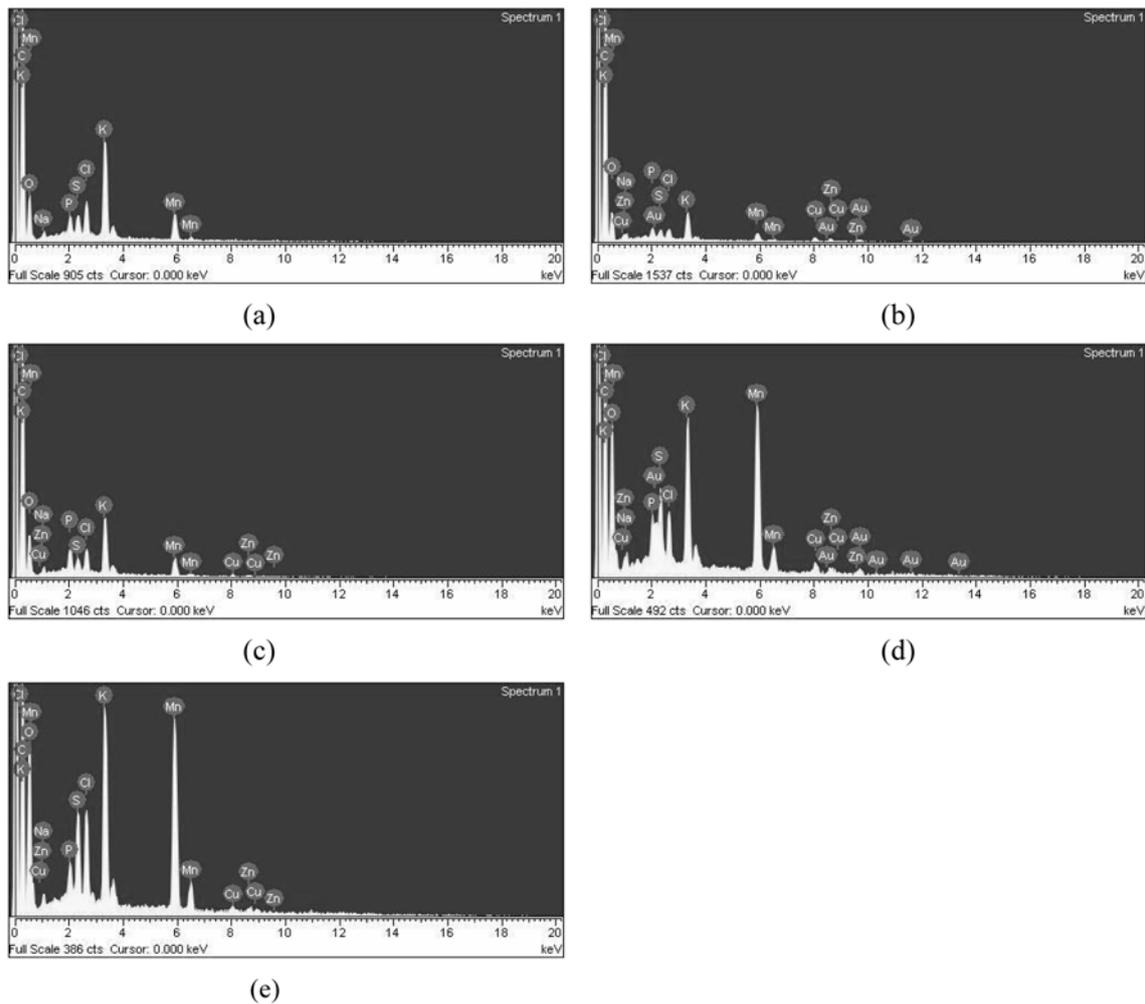


Fig. 10. Typical EDX microanalysis for D- series; (a) D-1, (b) D-30, (c) D-60, (d) D-90 and (e) D-120.

Table 4. EDX Elemental Micro-Analysis of K-ACFs after ECR

Sample	Elements (%)								
	C	O	Na	P	S	Cl	K	Cu	Others
A-1	88.2	14.3	0.53	0.27	0.18	0.34	2.07	0.14	
A-30	83.4	12.8	0.46	0.33	0.23	0.55	2.31		
A-60	80.7	14.5	0.59	0.22	0.42	0.76	2.78		
A-90	78.4	16.8	0.68	0.41	0.41	0.35	2.66	0.18	
A-120	77.7	16.8	0.52	0.46	0.47	0.54	3.43	0.30	
B-1	84.4	11.8	0.25	0.32	0.71	0.56	1.59	0.52	
B-30	80.8	14.3	0.48	0.32	0.26	0.68	3.23		
B-60	79.4	13.3	0.77	0.34	0.23	0.63	3.52	1.01	
B-90	78.9	15.9	0.48	0.33	0.20	0.75	3.37		
B-120	78.3	16.8	0.51	0.45	0.43	0.48	2.89		0.13 (Si)
C-1	81.8	14.4	0.35	0.43	0.33	0.54	1.97		0.12 (Si)
C-30	80.9	13.3	0.58	0.31	0.53	0.31	3.04	0.55	
C-60	77.2	16.5	0.86	0.38	0.42	0.65	3.93		0.10 (Br)
C-90	75.4	17.7	0.84	0.42	0.26	0.48	4.84		
C-120	74.7	18.9	0.74	0.47	0.73	0.46	3.90	0.21	
D-1	80.7	15.9	0.38	0.33	0.26	0.31	0.87	0.46	
D-30	76.4	18.5	0.61	0.66	0.37	0.65	1.58		0.85 (Mn)
D-60	75.9	18.1	0.35	0.47	0.47	0.86	2.58		1.25 (Mn)
D-90	61.8	26.8	0.44	0.66	1.09	0.82	2.29		4.77 (Mn)
D-120	58.5	29.5	0.47	0.54	1.17	1.34	2.93		5.00 (Mn)

mg/L, respectively. The analytical results for the primitive piggery waste are listed Table 1. In case of COD removal performance, the initial removal effects were shown very similar results for the all sample series. COD removal values decreased with increasing of function time. Specifically, the final values of A, C and D series were shown similarity around 4.0, 3.2 and 4.0 mg/L after 120 min as operation time. In case of BOD removal performance, the initial removal effects were shown very difference results for the all sample series. BOD removal values also decreased with increasing of function time. For A and D series, these values were shown same 21.0 mg/L after 120 min as function of time. As shown for the T-N removal results by ECR, there seems to very excellent removal effect in A series case. It was found that the more N containing compounds dissolved in water was adsorbed on the ACF surfaces and removed by electro-catalytic forces. Another application of the metal-ACFs for N- and P-compounds removal is becoming more important because of the environmental aspects. Different metals, metal oxides and zeolites have been used in the selective catalytic reduction of NH_3 and NO_x [17]. The removal of these

N-compounds by electro-catalytic method with metal-ACFs electrode might be an attractive alternative to the traditional these compounds removal methods. Metal-ACFs electrode can also be used as catalyst and catalyst support in the ECR. Ammonia is used beneficially in industry to reduce NO_x by the ECR. The NO_x in wastewater is transformed to electron acceptor. The average concentrations of N-compounds in the primary treated wastewater were over 90.6 mg/L in T-N (Table 1), while these values of final water purified by ECR was 1.4 for A series, 5.4 for B series, 2.3 for C series and 8.4 mg/L for D series, respectively. These values are acceptable for the final disposal of the treated effluent. From these results, the possibility of removal mechanism of N containing compounds was considered as formation of potassium salts or oxide compounds on the carbon fiber surface, i.e., NO_x^- -N, NH_4^+ -N and NH_2O -N react with potassium on the activated carbon fiber surface. According to the results, no T-P adsorbed by the K-ACFs seems to excellent removal effect in all cases. The average concentration of T-P in the primary treated waste was over 135 mg/L (Table 1), while the values of final water purified with K-ACFs after ECR

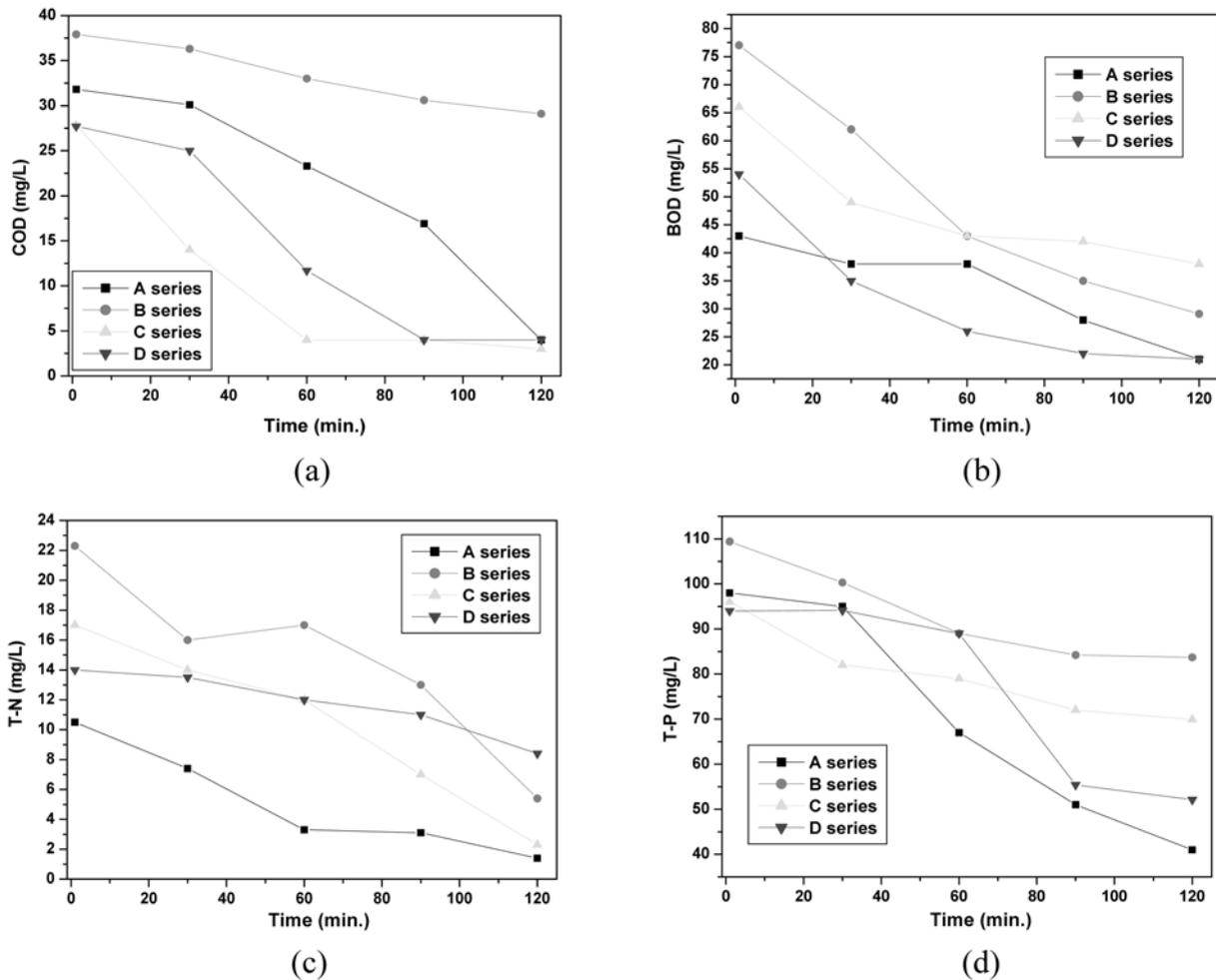


Fig. 11. Variation of oxygen, nitrogen and phosphorus compound by ECR with K-ACFs; (a) COD, (b) BOD, (c) T-N and (d) T-P.

as function of time were ranging from 41 to 83.7 mg/L. Activated carbon fiber treated with potassium also acts as a molecular sieve for some dissolved organic materials and also has a great affinity for functional groups.

Conclusion

The ECR by K-ACF electrodes from wastewater was investigated over wide range as a function of reaction time. The removal capacities of K-ACF electrodes were associated with their adsorption properties and were related to physico-chemical properties such as surface area and kind of treated potassium salts, and to reaction time. And, surface morphologies and elemental analysis for the K-ACFs after ECR as a function of time are investigated by SEM and EDX to explain the changes in removal capacities. The K-ACFs were electrochemically reacted with waste water to investigate the removal efficiencies for the COD, BOD, T-N and T-P. A satisfactory organic removal performance except results for the T-P removal performance was achieved.

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