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REMOVAL EFFICIENCY OF THE POLLUTANTS BY MULTILAYERED METAL TREATED CARBON FILTER

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Abstract : A study of the treatment of piggery wastes using a multilayered metal-activated carbon system followed by carbon bed filtration was carried out at bench scale. From the physicochemical properties obtained from samples treated with aqueous solutions containing metallic ions such as Ag^{+}, Cu^{2+}, Na^{-}, K^{+} and Mn^{2+}, main inspections are subjected to isotherm shape, pore distribution with micropore, SEM and EDX. Multilayered metal-activated carbons were contacted to waste water to investigate the simultaneous catalytic effect for the COD, BOD, T-N and T-P removal. From these removal results of the piggery waste using multilayered metal-activated carbon bed, satisfactory removal performance was achieved. The high efficiency of the multilayered metal-activated carbon bed was determined by the properties of this material for trapping, catalytic effect and adsorption of organic solid particles.

Key Words : metal-activated carbon, isotherm, SEM, EDX, COD, BOD, T-N, T-P

INTRODUCTION

Adsorption by activated carbon offers an efficient technology for removing organic materials from air and water pollution sources owing to their large specific surface areas, high pore volumes and rapid adsorption capacities. The prime objective of environmental control in the industrial setting is to prevent or reduce the generation of contaminants at their source. In general, granular activated carbon processes have been attracted interest for municipal waste water treatments with most of the academic researches into these fields concentrating on the removal of low concentrations of low molecular weight contaminants, such as phenol, from solution.[1] Especially, the use of activated carbon treated with a metal as catalytic materials has been emerged as a very interesting alternative[2,3] for the treatment of those contaminants. The drastic increase in the number of papers published on carbon as a catalyst and as a catalyst supporter also reflects the increasing interest in the catalyst field.[3,4] Although carbon is considered to be an chemical inert material in comparison with other catalyst supporters, its surface is not as inert as expected due to the formation of active sites by the presence of heteroatoms. In terms of catalyst preparation, the presence of oxygen bearing group on the carbon surface is of great interest. Treatment of chemicals such as acid, alkali and metallic salts onto internal surfaces and into the pores of activated carbon, bring about chemical adsorption and reaction and removal of polluted factors from industrial effluent can greatly be increased. Although amount of physical adsorption onto

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surfaces of carbon can be decreased by the chemical catalytic treatment, chemically and biologically polluted factors can be decomposed or neutralized by chemical reaction. The removal of the odor or the harmful substances greatly increases.

In this work, which is the first part of a study on the metal-activated carbon system, the aim is to investigate the morphology changes of metal-activated carbon and chemical treatment sequence on the properties and catalytic activities for the removal of chemically and biologically polluted factors from piggery urine effluent. Full characterization of metal-activated carbon system by nitrogen adsorption, SEM-EDX, UV/VIS and removal efficiencies of pollutants by chemical and biological factors were presented.

EXPERIMENTAL

Preparation Procedures

Homemade activated carbon used as a starting material was prepared from coconut shell based granular type. The carbonized coconut shell was heated first at 500°C for burn off, then physically activated with water vapor at the temperature range of 750~780°C. For the treatment, $NaOH$, $CuSO_4$, $KMnO_4$ and $AgNO_3$ were obtained from Duksan Chemical Co. (99+ %, ACS reagent) and used as received. In order to be free from impurities, doubly distilled water was used. For metal treatment, 500 g of activated carbons were dipped into 1 liter of 0.01M metal salt-dissolved aqueous solutions and stirred for 12 h at room temperature. Then, after removing liquid, samples treated with metals were completely dried in a oven at 105°C. 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 for the characterization were listed in Table 1. The levels can be dropped under 1000~1500 mg/L by physico-chemical primary treatment (coagulation). The samples of under 1500 mg/L leveled were used for characterization for the catalytic activities of metal-activated carbon. The procedures for characterization from piggery waste were listed in Figure 1.

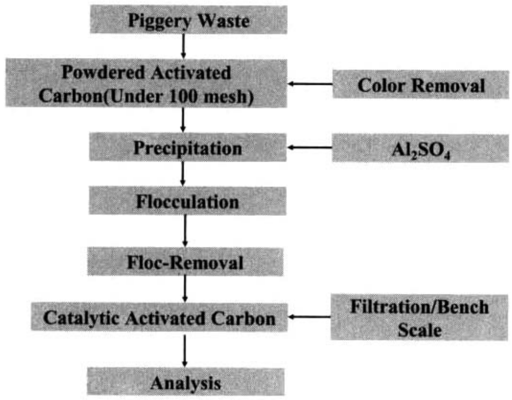

Figure 1. The procedure for characterization from piggery waste.

Measurement

Nitrogen adsorption isotherms were measured using an ASAP 2010 (Micrometrics) at 77K. Before the experiment, the samples were heated at 473K and then outgassed at this temperature under a vacuum of 1.33×10^{-3} Pa 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 metal treated acti-

Table 1. The Analytical Results for the Primitive Piggery Waste

Step	COD(mg/L)	BOD(mg/L)	T-N(mg/L)	T-P(mg/L)
Primary	50,000	50,000	500	150
Secondary	1,000	1,500	200	50
Ultimate*	Under 50	Under 350	Under 20	Under 5

* Permitation values of Ministry of Environment of Korea

vated carbon. For the elemental analysis of metal contents in activated carbon, EDX was also used. As one of the analysis of environmental inhibitor, UV/VIS spectrophotometer (Genspec III(Hitachi), Japan) was used to characterize of catalytic efficiency of metal/activated carbon. For the color removal efficiency, characterizations were carried out at the region of 200-600 nm.

Bench Scale Experimental Methods

The authors[5] describe the equipment used during these fixed bed column studies previously. It consisted of a PE (Polyethylene) make-up tank in which the process effluent added at a concentration of secondary leveled effluent (Table 1). The solution was then gravity fed to a feed tank, having a volume of 200 liters and from which the effluent was pumped using a peristaltic pump at constant flow rate of 10 m $L \cdot min^{-1}$. The effluent solution was fed through a bed of metal-activated carbons in up-flow mode. The carbon beds were contained in PVC columns with diameter 50 mm to which a both end plate with inlet and outlet nozzle was attached. The metal-activated carbon bed was packed by several different metal-activated carbon layers. The trial examples of metal-activated carbon layered and nomenclature are listed in Table 2. The columns gave a standard bed height of 500 mm which resulted in beds with metal-activated carbon mass of approximately 300 g of 2 mm particle size.

Table 2. The Trial Examples of Metal/Activated Carbon layered and Nomenclature

Sample	Nomenclature
Non treated Activated Carbon	A1
Saw Dust	B1
Mixtures of Saw Dust and Cu-AC(2:1)	B2
Na-AC	C1
KMn-AC	C2
Cu-AC	C3
Ag-AC	C4
Saw Dust/Ag-AC	D1
Saw Dust/Na-AC	D2
Saw Dust/KMn-AC	D3
Saw Dust/Cu-AC/Ag-AC	E1
Saw Dust/Na-AC/Ag-AC	E2
Saw Dust/KMn-AC/Ag-AC	E3
Saw Dust/Cu-AC/Na-AC/Ag-AC	F1
Saw Dust/Cu-AC/KMn-AC/Ag-AC	F2
Saw Dust/Cu-AC/Na-AC/KMn-AC/Ag-AC	G1

COD, BOD, T-N and T-P 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 300mL BOD bottle occupied with effluent after incubation in dark incubator at 20°C during 5 days.[6] In considering the total nitrogen (T-N) balance in the treatment process, nitrogen removal was measured as UV absorbance spectrometric method.[6] The effluents purified by multilayered metal-carbon filter could be prepared to samples for the T-N measurement by chemical treatments. T-N removal values were measured by UV spectrophotometer at 220 nm wavelengths. 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.[6] These analyses were carried out according to standard methods for the examination of water and wastewater.[7]

RESULTS AND DISCUSSION

In contrast to the results previously reported for coconut shell based activated carbon treated with aqueous solutions containing metallic ions,[8] the use of sodium hydroxide and potassium permanganate during the initial treatment stage leads to the development of wide and controllable range of surface properties. Some examples of these isotherms are illustrated in Figure 2. From the nitrogen adsorption isotherms obtained for samples treated with aqueous solutions containing metallic ions such as Ag^{+}, Cu^{2+}, Na^{+}, K^{+} and Mn^{2+}, main inspections are subjected to isotherm shape and adsorbed volume. All the isotherms for the samples are presented to Type I isotherms and characteristics of microporous solids, but these isotherms show a plateau isotherm reflecting a minimum presence of mesopores like cavities and cracks with narrow knee band regions. Even greater variation shape could be affected by kind of treated metallic ion. From this figure, it can be seen that nitrogen adsorption capacities of KMn-AC and Cu-AC are observed higher values than that of Ag-AC and Na-AC. In case of Ag-AC and Na-AC, it is believed that the formed macropore, mesopore and wider micropore on the carbon surface before treatment[9] are transformed to micropore and narrow micropore with pore filling and blocking by treated metallic ions. However in contrast to these samples, KMn-AC and Cu-AC led to the generation of mesopore and wider micropore with weak pore filling and blocking effect.

Table 3 shows the specific surface area (S_{BET}) and average pore diameter from BET method and the application of the DR equation of the obtained activated carbons treated with aqueous solutions containing metallic ions. The areas of these samples are in the range of 624.0~1172 m^2/g. The surface areas are presented to higher values for the Cu-AC and KMn-AC than those of Ag-AC and Na-AC. Average pore diameters are distributed to the range of 16.72~29.12 Å. The average pore diameter is almost constant for samples treated with metal. The biggest difference not exists among samples.

Pore size distributions evaluated from adsorption isotherms are shown in Figure 3. The peak of distribution for the activated carbon treated with aqueous solutions containing metallic ions is observed at pore sizes of ≈10 Å with standard deviation of ≈1 Å, while for non treated activated carbon the distribution's peak is shifted to value ≈5 Å higher.[9] This result demonstrates that the carbon sample prepared by treatment with aqueous solutions containing metallic ions has a more heterogeneous micropore structure and is characterized narrow micropores. Micropore size distributions due to the small diameter of the molecule can provide information only about narrow intervals of pore sizes covering the region of small micropores, but do not provide information about larger micropores. Based on comparison of micropore volumes and micropore surface area from N_2 adsorption isotherm, we have concluded that in these samples there are some contributions of wider micropores.

The surface morphology and dispersion state of metal complex on the activated carbon

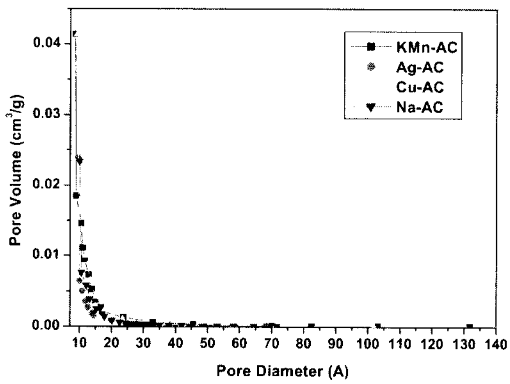

Figure 3. Pore size distributions evaluated from adsorption isotherms.

Table 3. Results of Pore and Surface Analysis for Metal/Activated Carbon

	SBET (m^2/g)	Micropore Volume (cm^3/g)	Average Pore Diameter (Å)	Micropore Area (m^2/g)
Ag-AC	624.0	0.248	16.84	616.2
Cu-AC	1127	0.443	16.86	1108
KMn-AC	1087	0.428	16.72	1073
Na-AC	672.3	0.265	29.12	663.7

surface are investigated by scanning electron microscopy. Figure 4 shows SEM pictures of some typical activated carbon after treatment with aqueous solutions containing metallic ions. SEM pictures of metal/activated carbon particles provide information about the distribution of metal or metal complex (white and gray part). In addition, homogeneous distribution of metal on the large surface area can be promoted to catalytic activities for the removal of environmental inhibitors. These figures present results from characterization of porous texture and surface metal complex localizations for all the materials used. It is shown that, when metal complex is introduced into activated carbons, the porosity is modified in some cases, this effect being developed in microporosity in materials with a narrow starting porosity. This aspect will have to be taken into account for further analysis of the removal of environmental inhibitors because porosity strongly influences both the adsorption capacity of inhibitors and the catalytic activity for inhibitors. In addition, if the pore size distribution becomes too narrow with decreasing specific surface area after metallic ion treatments, catalytic activity for the removals will definitely appear during the liquid-metal/carbon activity reaction.

For the elemental microanalysis of activated carbons treated with metals, samples were analyzed by Energy dispersed X-ray (EDX). EDX spectra of metal treated activated carbons are shown in Figure 5. From these figures, spectra are shown the presence of C, and Au including major metals treated. In case of Au, it is consider that the metal is introduced to process of

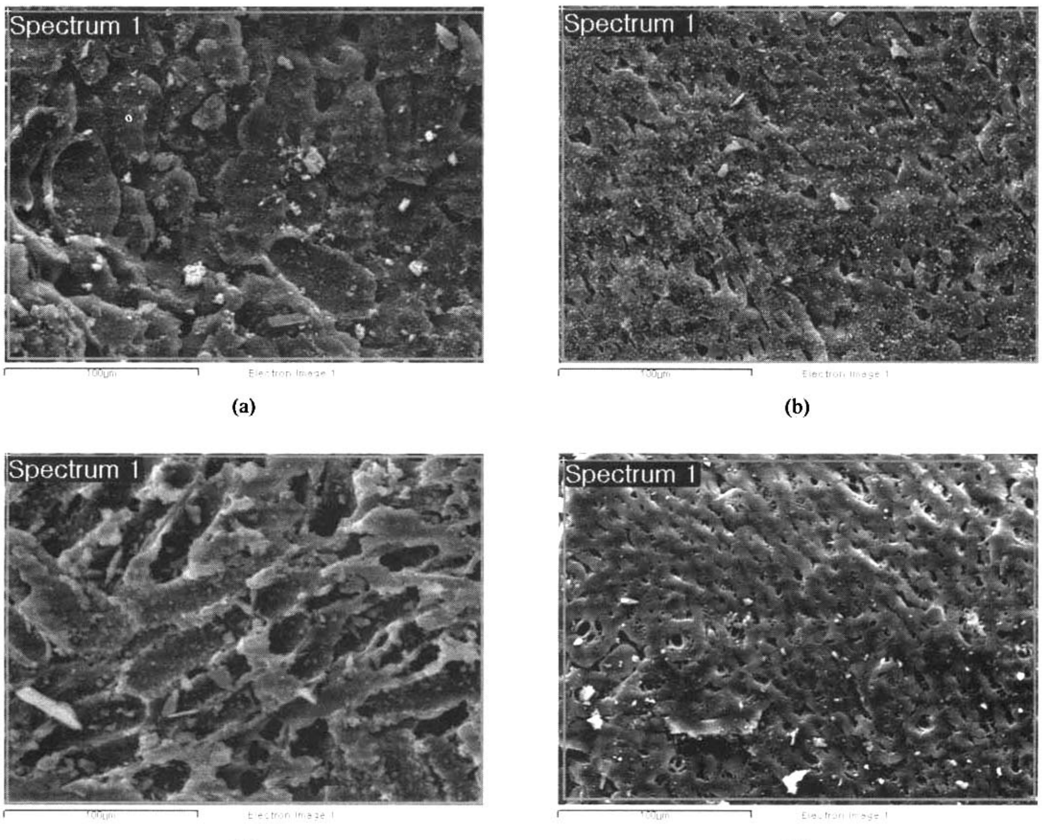

Figure 4. SEM images obtained from activated carbons treated with aqueous solutions containing metallic ions; (a) Ag-AC, (b) Cu-AC, (c) KMn-AC and (d) Na-AC.

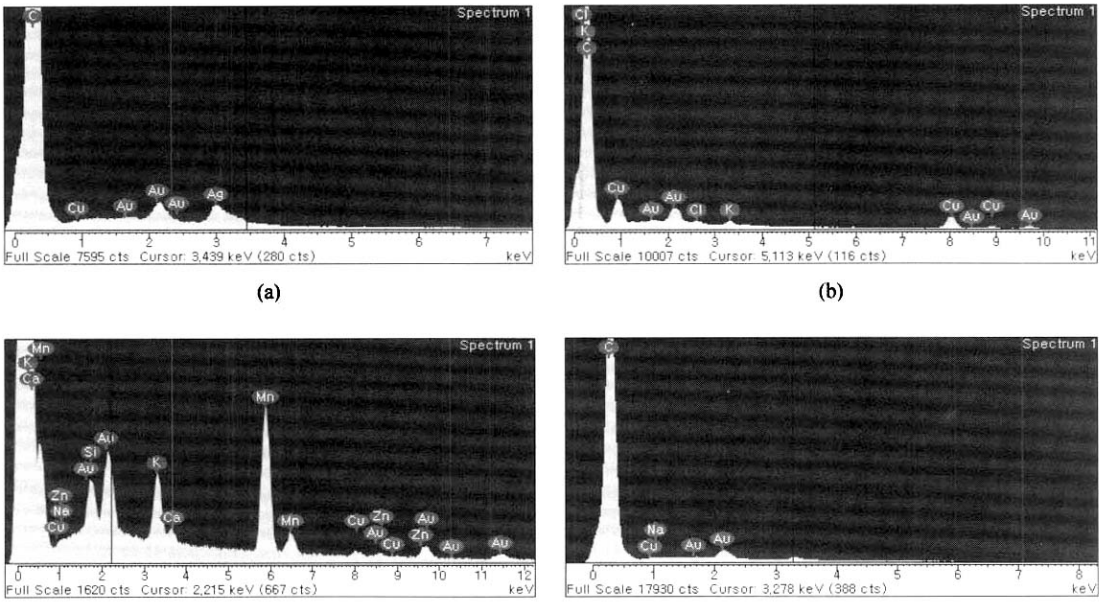

Figure 5. Typical EDX microanalysis for the activated carbons treated with aqueous solutions containing metallic ions; (a) Ag-AC, (b) Cu-AC, (c) KMn-AC and (d) Na-AC.

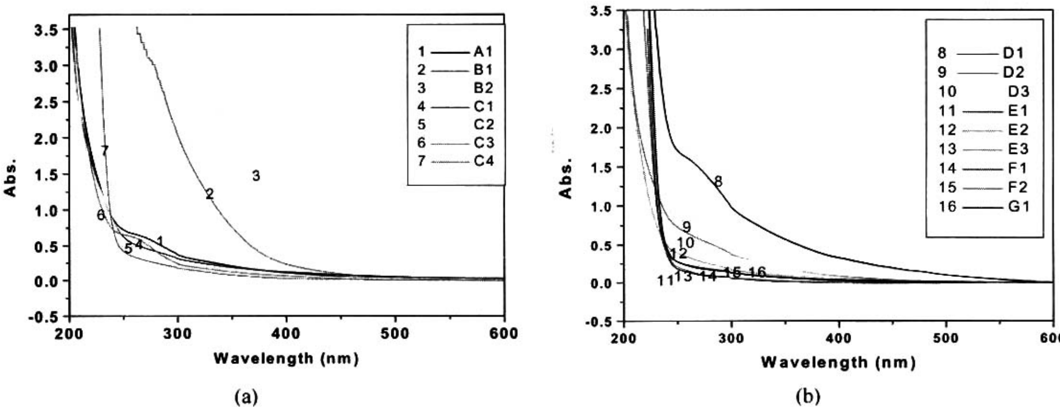

Figure 6. Variation of UV/VIS spectra for wastewater purified with the activated carbons treated with metals; (a) A1~C4 and (b) D1~G1.

pretreatment of samples for the analysis. Most of samples are richer in carbon and major metals treated than any other elements.

The color removal performance of the piggery waste using multilayered metal-activated carbon bed was investigated and the results are shown in Figure 6. A satisfactory color removal performance except B1, B2 and D1 was achieved. From these results, it is consider that sawdust with metal-activated carbons is not helpful to color removal performance. The results obtained from samples C2, E1, E2, E3, F1, F2 and G1, especially, were presented the high removal efficiency of multilayered of saw dust/metal-AC that contributed to reduce the colored organic materials. And, the color stable effluent quality was ensured by the catalytic efficient by multi-layered metal-activated carbon bed filtration system.

The average value of the initial COD of raw waste was about 50,000 mg/L. The analytical results for the primitive piggery waste are listed

Table 1. The average COD value of the waste after filtration through multilayered carbon filter was about 10mg/L. The results of catalytic effect using activated carbons treated with metals are shown Figure 7. Almost all samples are present to significant COD removal efficiency ranging from 1.5 to 27mg/L. The result obtained from sample B2, especially, show the high removal efficiency of mixtures of saw dust and Cu-AC(2:1) that contributed to reduce the COD. The results of BOD removal efficiency of our samples are shown Figure 8. Final water purified with various multilayered carbon samples was ranging from 1.3 to 197 mg/L excluding final values obtained from B2, C3, D1, E1 and E3. Results for T-N removal by various multilayered carbon filter are shown Figure 9. As shown for the types of multilayered carbon treated with metal and T-N adsorbed by the metal-activated carbon, there seems to very excellent removal effect in all cases. It was found that the more N containing compounds dissolved in water was adsorbed on the activated carbon surfaces. The average concentration of T-N in the raw waste was over 500mg/L (Table 1), while final water purified with multilayered carbon filter was 0.54 mg/L ranging from 0.01 to 2.2 mg/L. 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 metal salts on the carbon surface, i.e., NO_x—N, NH_4^+-N and NH_2O-N react with metals on the activated carbon surface. Results for T-P removal by various multilayered metal/activated carbon bed are shown Figure 10. According to the results, T-P adsorbed by the metal-activated carbon also seems to very excellent removal effect in all cases. The average concentration of T-P in the raw waste was over 150 mg/L (Table 1), while final water purified with multilayered carbon filter was 1.80 mg/L ranging from 0.05 to 2.6 mg/L. The high efficiency of the multilayered metal-activated carbon bed was determined by the properties of this material for trapping, catalytic effect and adsorption of organic solid particles. Metal-activated carbon also acts as a molecular sieve for some dissolved organic materials and also has a great affinity for functional groups.

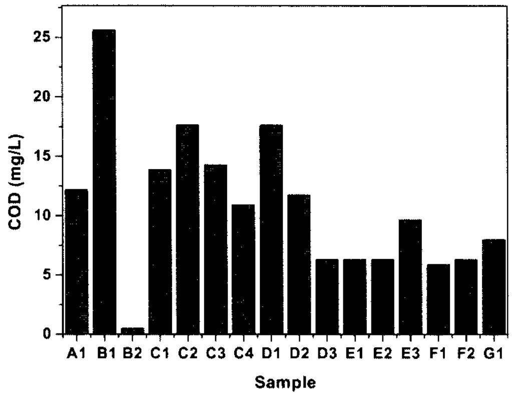

Figure 7. Results of COD removal effect by metal/activated carbon for the piggery waste.

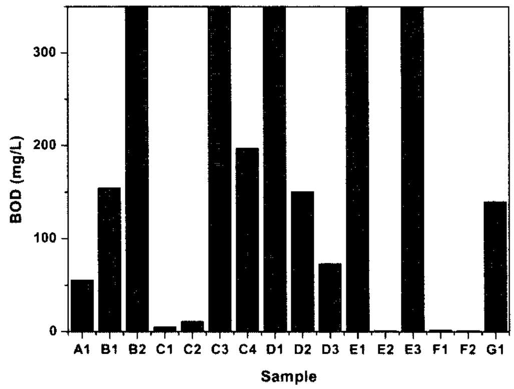

Figure 8. Results of BOD removal effect by metal/activated carbon for the piggery waste.

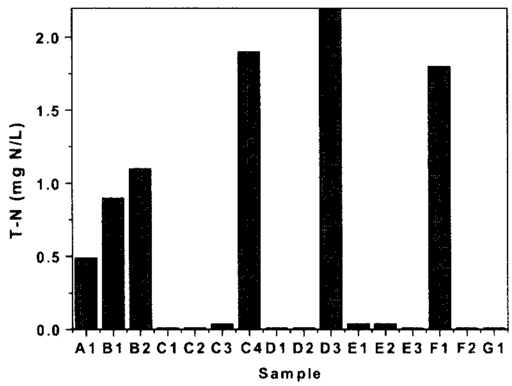

Figure 9. Results of T-N removal effect by metal/activated carbon for the piggery waste.

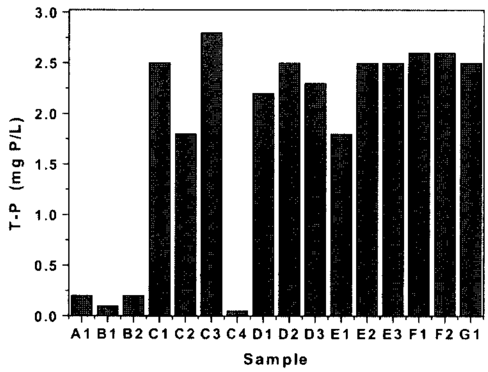

Figure 10. Results of T-P removal effect by metal /activated carbon for the piggery waste.

CONCLUSION

Various different types of multilayered metal-activated carbon bed have been used in this study to investigate the catalytic removal COD, BOD, T-N and T-P from piggery wastewater. The samples treated with aqueous solutions containing metallic ions such as Ag^{+}, Cu^{2+}, Na^{+}, K^{+} and Mn^{2+}, were investigated to isotherm shape, pore size distribution with micro and mesopore, surface state by SEM and elemental microeanalysis by EDX. At the color removal performance, the results obtained from almost all samples were presented the high removal efficiency. The result obtained from sample B2, especially, shows the high removal efficiency of mixtures of saw dust and Cu-AC(2:1) that contributed to reduce the COD. And, the result of T-N removed by the metal-activated carbons seems to excellent removal effect. Finally, T-P adsorbed by the metal-activated carbons also seems to very excellent removal effect in all cases.

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