

Physical properties of KPACFs and their pH dependence on their T-N and T-P removal

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In this study, the characterizations of powdered activated carbon fiber treated with potassium (KPACFs) systems by nitrogen adsorption, SEM-EDX, UV/VIS, Boehm titration and removal efficiencies of pollutants by variation of pH are presented. From the adsorption and surface analysis, it is shown that the ACF samples prepared by treatment with aqueous solutions containing potassium ions or salts have a more heterogeneous micropore structure. SEM images and EDX spectra show a homogeneous distribution of potassium salts on the large body fiber surface and the presence of C, O and P. Quantitative analyses of surface species including oxygen groups are determined by FT-IR and Boehm's titration methods. Finally, the color, total nitrogen (T-N) and total phosphate (T-P) removal performance of piggery waste dispersed with KPACFs is investigated and these results are acceptable for the final disposal of the treated effluent depending on pH.

Key words: KPACFs, isotherm, SEM, EDX, UV/VIS, Boehm's titration method.

Introduction

As a result of effluents including organic compounds from various industries, the level of organic pollutants in water systems has been increasing. With increasing concern for public health and environmental quality, more stringent regulations have come into effect as to the acceptable levels of these compounds. The extensive use of activated carbons and their fibers as an effective adsorbent in removing these pollutants from aqueous solutions is well known and their versatility has been studied extensively [1]. Activated carbon fiber is known to have heterogeneous physical and chemical structures on its surface. The former arises from the existence of pores of different sizes. With an increasing of variety of carbon-oxygen functional groups, the chemical properties produced during the manufacture of activated carbon fiber and their post-treatment with acids or metal salts is often a result of the presence of a high concentration of oxygen present in the precursors and treated materials [2, 3]. One of the possibilities of using activated carbon in wastewater treatment is the direct addition of powdered activated carbon fiber (PACF) to give a combined function of adsorption and biodegradation. The technical superiority of a PACF-enhanced potassium salt system over a conventional activated carbon and its fiber system has been demonstrated in many pilot and full scale test treatments [3,

4]. Our past studies have shown that the formation and nature of metal-containing activated carbon and its fiber and its subsequent effectiveness in the formation of a surface structure depends on the chemistry of the carbon precursor, the metal precursor, and their interaction [5-7].

The purpose of this paper is to present the catalytic removal properties of the activated carbon fiber supporting potassium and show how these depend on the acidity and basity of the solution. An analysis of the powdered activated carbon fiber treated with potassium (KPACFs) system by nitrogen adsorption, scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), ultraviolet/visible spectroscopy (UV/VIS), and Boehm titration will be given together with the removal efficiencies of pollutants by chemical and biological factors.

Experimental Procedure

Raw materials

Self-made ACFs used as a raw material were prepared from commercial polyacrylonitrile (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 cylindrical quartz tube in the temperature range of 1053~1073 K for 30 minutes. These activated carbon fibers were washed with deionized water and dried for 24 h at ambient temperature. The ACFs were crushed to 200 mesh size with an automatic mortar. The 0.01 M diluted sulfuric acid at boiling temperature was used in the oxidation treatment to increase the formation of

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Table 1. Nomenclatures of Powdered Activated Carbon Fiber treated with Potassium Salts

Sample	Nomenclature
0.01 M K ₂ CO ₃ + Activated Carbon Fiber	KPACF1
0.01 M KOH + Activated Carbon Fiber	KPACF2

Table 2. The Analytical Results for the Primitive Piggery Waste

Step	COD (mg/l)	BOD (mg/l)	T-N (mg/l)	T-P (mg/l)
Original Waste	Over 50,000	Over 50,000	Over 1,500	Over 500

functional groups without damaging 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 KPACF series in solutions of 0.1 M of K₂CO₃ and KOH to load with the potassium. The prepared KPACFs were also dried at 323 K for 24 h in a nitrogen atmosphere. Nomenclatures of KPACFs are listed in Table 1. For the effluent characterization, the work involved 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 are listed in Table 2. The levels can be reduced to under 365~450 mg/l by a physico-chemical primary treatment step (coagulation). Samples of under 450 mg/l level were used for characterization of powdered KACFs.

Measurement

Nitrogen adsorption isotherms were obtained by using a BET surface area apparatus (ASAP 2010, Micrometrics) at 77 K. Before the experiment the samples were heated at 473 K and then outgassed at this temperature under a vacuum of 1.33×10^{-3} Pa to a constant pressure. The isotherms were used to calculate the specific surface area and pore volume. The pore size distribution curves of micropores were obtained by the H-J method. Scanning electron microscopy (SEM, JSM-5200 JOEL, Japan) was used to observe the pore structure of the potassium treated activated carbon and the treated potassium salt state on the carbon surfaces. For the elemental analysis of metal contents in the activated carbon fiber, EDX was also used. As one of the analysis of functional groups, Fourier transform-infrared (FT-IR) spectroscopy (FTS 3000MX, Biorad Co.) was used to characterize the KACFs. The potassium loaded activated carbon fibers were examined by the KBr method using the spectroscopy. Discs for this method were prepared by first mixing 1 mg of powdered KACFs with 600 mg of KBr (for FT-IR spectroscopy) in an agitated mortar, and then pressing the resulting mixture successively under a pressure of 450 Pa for 3 minutes. The spectra of the samples were measured

between 4000 and 500 cm⁻¹. As one of the analyses of environmental color removal, a UV/VIS spectrophotometer (Genspec. III(Hitachi), Japan) was used to characterize the color adsorption efficiency of powdered KACFs.

Boehm titration

We used the Boehm titration method [8] for the identification of the oxygenated surface groups on the carbon surfaces. One gram of the carbon sample was placed in 50 ml of the following 0.05 M solutions: sodium hydroxide, sodium carbonate, sodium bicarbonate, and hydrochloric acid. The elenmeyer flasks were sealed and shaken for 24 h and then 5 ml of each filtrate was pipetted and the excess of base and acid was titrated with HCl and NaOH, respectively. The numbers of acidic sites of various types were calculated under the assumption that NaOH neutralizes carboxylic, phenolic, and lactonic groups; Na₂CO₃, carboxylic and lactonic groups; and NaHCO₃, only carboxylic groups. The number of surface basic sites was calculated from the amount of hydrochloric acid, which reacted with the carbon.

T-N and T-P contents analysis

In considering the total nitrogen (T-N) balance in the treatment process, nitrogen removal was measured by a UV absorbance spectrometric method [9]. The primary purified effluents by coagulation could be prepared in samples for the T-N measurement by chemical treatment. T-N removal values were measured by a UV spectrophotometer at 220 nm wavelength. For the analysis of NH₄-N, NO₂-N and NO₃-N, Spectrophotometer (PhotoLab S6, WTW) was also used. The measurements of total phosphorous (T-P) in these samples were carried out via vis spectrophotometer at 880 nm wavelength using an ascorbic acid reduction method [9]. These analyses were carried out according to standard methods for the examination of water and wastewater [10].

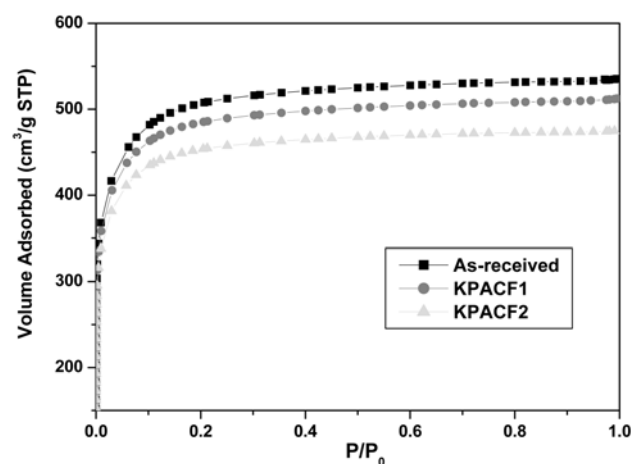
Results and Discussion

Adsorption data and surface areas

A first inspection of Table 3 shows that the external surface area does not exceed 1283 m²/g in KACF2, which is a carbon with a very high average pore diameter (16.84 Å). On the another hand, it appears that S_{BET}, the value obtained by applying the BET treatment to the overall nitrogen isotherm in the usual domain $0.05 < P/P_0 < 0.30$ -0.355, can reach realistic values in a distribution between 1347-1834 m²/g. The realistic nature of S_{BET} for the KPACF series with a small micropore volume is suggested by the BET analysis of N₂ isotherms. Figure 1 presents the nitrogen adsorption isotherms of the samples used in this study. They present a wide knee band and the slope at a relative pressure

Table 3. Comparison of Physical Parameters of K-Powdered Activated Carbon Fibers

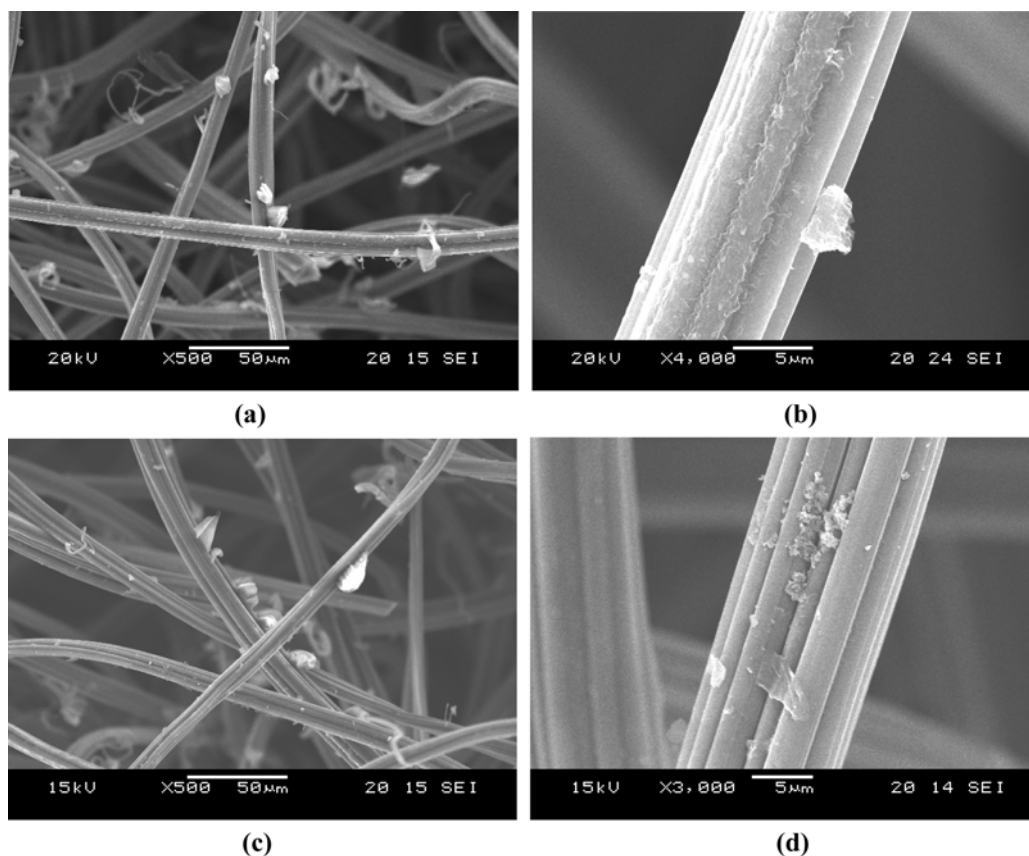
Sample	Parameter			
	S_{BET} (m^2/g)	Micropore Volume (cm^3/g)	External Surface Area (m^2/g)	Average Pore Diameter ($\text{\AA}$)
As-received	1834	0.47	1328	16.87
KPACF1	1421	0.38	1264	15.43
KPACF2	1347	0.36	1283	15.84

**Fig. 1.** Nitrogen adsorption isotherms obtained from powdered activated carbon fibers treated with potassium salts.

higher than 0.2 indicates the presence of micro- and meso-porosity. The samples prepared by the potassium treatment essentially presented a lower volume adsorbed with a decreasing knee band region. A comparison between micropore volumes calculated by nitrogen adsorption confirms the information provided by the shapes of the nitrogen adsorption isotherms. This result demonstrates that the carbon samples prepared by treatment with aqueous solutions containing potassium ions have a more heterogeneous micropore structure and are characterized by narrow micropores. The micropore size distributions due to the small diameter of the molecules 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 a comparison of micropore volumes and micropore surface areas from N_2 adsorption isotherms, we have concluded that in these samples there are some contributions from wider micropores.

Surface and elemental analysis

SEM pictures shown in Figure 2 are representative of a large body of SEM observations. SEM pictures of KPACFs provide information about the distribution of metal or metal complexes. These pictures present results from the characterization of porous texture and surface metal complex localizations for all the materials used.

**Fig. 2.** SEM images obtained from powdered activated carbon fibers treated with potassium salts; (a) KPACF1, (b) KPACF1, (c) KPACF2 and (d) KPACF2.

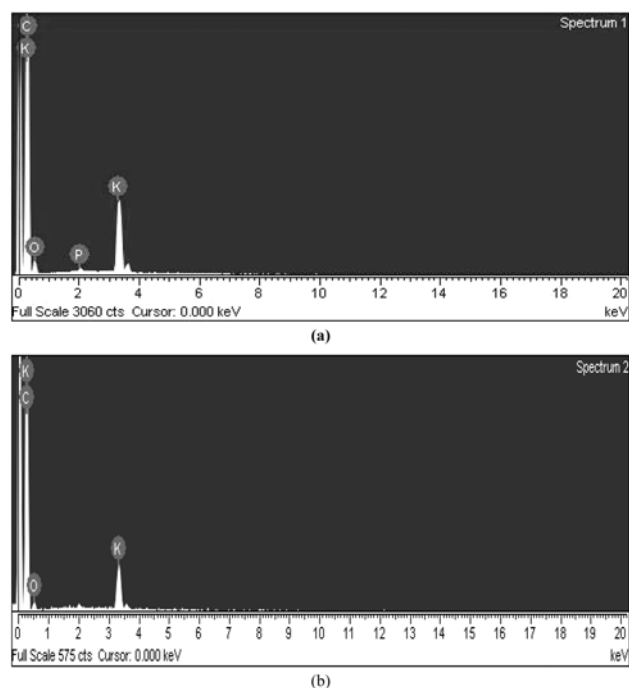


Fig. 3. Typical EDX microanalyses for the powdered activated carbon fibers treated with potassium salts; (a) KPACF1 and (b) KPACF2.

The SEM images show that the potassium salts containing particles are evenly distributed in all types of potassium containing ACFs. However, the mean particle size, estimated from SEM observations, in the ACFs prepared from potassium hydroxide was considerably smaller than that found in the fibers prepared from potassium carbonate. However, a homogeneous distribution of potassium on the large surface area can be promoted to be efficient catalytically for the removal of environmental pollutants. This aspect will have to be taken into account for further analysis of the removal of pollutants because porosity strongly influences to the adsorption capacity of pollutants. If the pore size becomes too narrow with a decreasing surface area after treatment with potassium ions, the catalytic activity for removal of pollutants will definitely diminish during the liquid/KPACFs interface activity reaction. For the elemental microanalysis of KPACFs, these samples were analyzed by EDX. These EDX spectra of KPACFs are shown in Figure 3. These spectra show the presence of C, O and P with a major contribution from K. Most of the samples were richer in carbon and K than any other elements. The results of EDX elemental microanalysis for the KPACFs were listed in Table 4.

Quantitative analysis of surface species

Figure 4 shows the IR spectra of KPACF samples for the identification of surface functional groups. Observation of the various absorption bands shows that the changes between the KPACF1 and KPACF2 samples are mainly due to the formation of functional groups by

Table 4. EDX Elemental Micro-Analysis of K-PACFs

Sample	Elements (%)				
	C	O	P	Cl	K
KPACF1	83.89	12.24	0.02	0.03	3.82
KPACF2	83.97	12.04	—	—	3.99

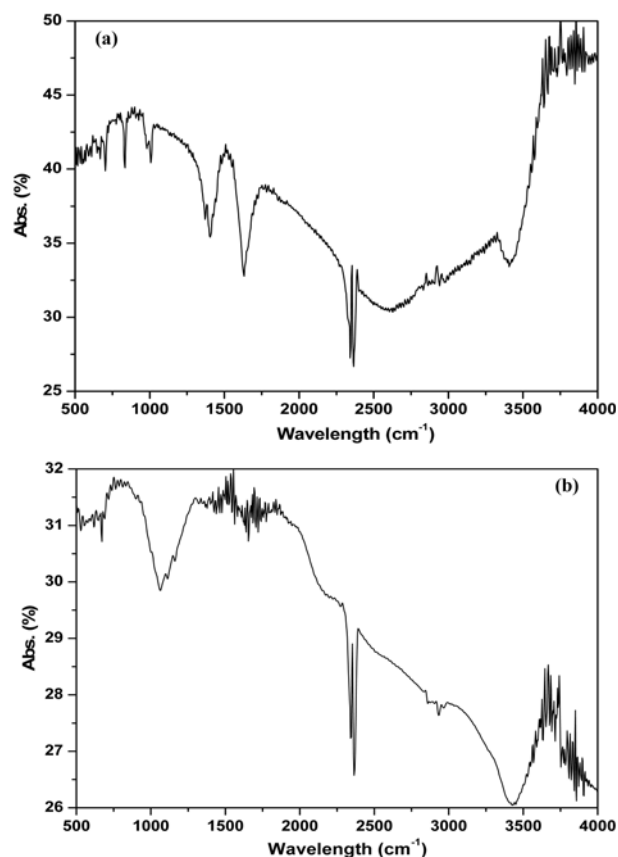


Fig. 4. FT-IR spectra recorded from the powdered activated carbon fibers loaded with potassium salts; (a) KPACF1 and (b) KPACF2.

the treatment with potassium salts. It is considered that the presence of absorption bands between 1110 and 1120 cm^{-1} maybe assigned to the ν (C-O) coordinated methoxy species. The ν (C-O) mode of the methoxy group depends on the chemical structure of the adsorption sites. The presence of at least two types of surface bound CO species is recognized by the characteristic position of the ν (C-O) bands. The frequency of the ν (C-O) of the adsorbed carbon monoxide is often treated as an indicator characterizing the local coordination. From Figure 4(a), especially, the most characteristics changes are observed at 1380 and 1570 cm^{-1} due to the presence of C-O- and N-O- containing structures. The strong bands appearing at 1380 and 1570 cm^{-1} are ascribed to the formation of oxygen functional groups like a highly conjugated C=O stretching in carboxylic and carboxylate groups [11]. These results indicate that treatment by potassium carbonate gave rise to a greater increase in C=O bonds in carboxylic and lactone groups

Table 5. Number of Surface Species (meq/g) Obtained from Boehm Titration

Sample	Functional Group (meg/g)				
	Carboxylic	Lactonic	Phenolic	Acidic	Basic
KPACF1	0.051	0.062	0.022	0.135	0.008
KPACF2	0.089	0.069	0.029	0.187	0.017

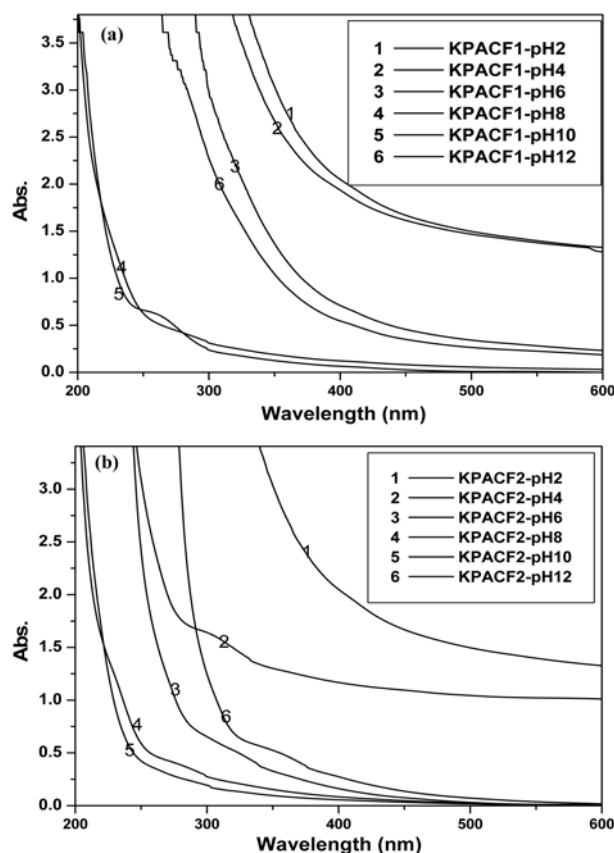
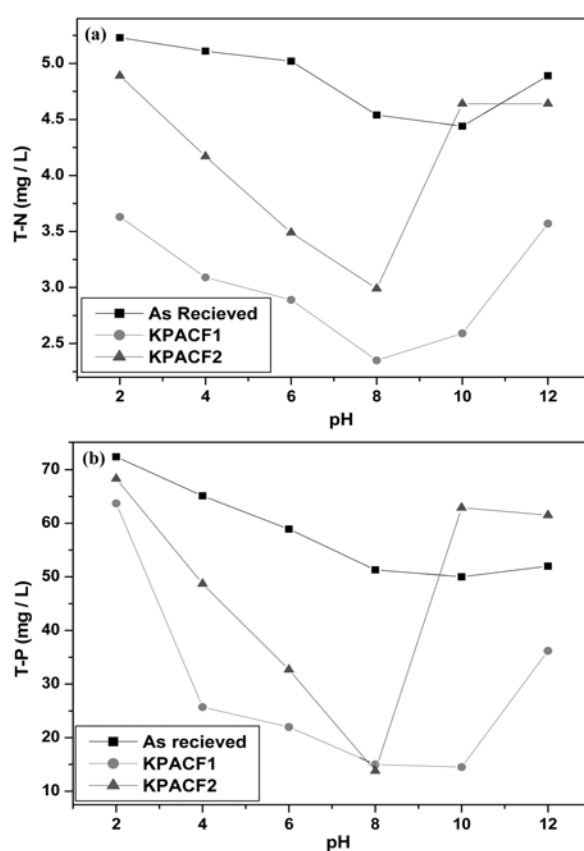
on the fiber surfaces. The two bands observed at 2350 and 2360 cm^{-1} are usually ascribed to the presence of aliphatic compounds. A broad band in the 3400–3500 cm^{-1} region is typically attributed to O-H stretching from hydroxyl, phenolic and carboxylic groups and is absent.

The changes described from the FT-IR spectra are due to an alteration of the carbon surface via introduction of oxygen groups which modified some carbon atoms from the fiber matrix. The types and quantities of oxygen groups were determined with Boehm's method [8]. The numbers of surface species obtained from the method proposed by Boehm are collected in Table 5. The total acidity and the distributions of functional groups of various strengths have very different values. The effect of surface acidity and basity was also evaluated from correlations as a function of NaOH, NaHCO_3 and Na_2CO_3 uptake. It is interesting that the

two samples which have the highest number of carboxylic, lactonic and phenolic groups also have the lowest number of basic ones. This may contribute to the lowest local pH of this carbon surface due to the treatment with potassium salts. It is considered that the affinity of activated carbon fiber for potassium or potassium salts depends on the amount of surface functional groups. When a distribution of acidic groups is properly introduced, active sites on the fiber surface should play an important role in the removal of pollutants.

Removal efficiencies of pollutants

The color, T-N and T-P removal performance of the piggery waste dispersed with KPACFs was investigated and the results are shown in Figure 5 and 6. A satisfactory color removal performance in the range of pH 8–10 was achieved. From these results, it is considered that control of pH with KPACFs is a helpful factor in color removal performance. The results obtained from samples number 5 and 6 depending on pH, especially, presented a high removal efficiency to reduce the colored organic material. Also, the color stable effluent quality was related to the catalytic efficiency by the KPACF system. The analytical results for the primitive piggery waste are listed in Table 2. As shown for the T-P and T-N adsorbed by the KPACFs, there seems to

**Fig. 5.** Variation of UV/VIS spectra depending on pH from wastewater purified with the powdered ACFs treated with potassium salts; (a) KPACF1 and (b) KPACF2.**Fig. 6.** Results of T-N and T-P removal effect depending on pH by potassium-powdered activated carbon fibers for the piggery waste; (a) T-N and (b) T-P.

very excellent removal effect in all cases. It was found that more N-containing compounds dissolved in water were adsorbed on the activated carbon fiber surfaces. The average concentration of T-N in the raw waste was over 1,500 mg/l (Table 2), while the final water purified by dispersing KPACF was 3.02 mg/l ranging from 2.35 to 3.63 mg/l for the KACF1 series and 4.13 mg/l ranging from 2.99 to 4.89 mg/l for the KACF2 series, respectively. These values are acceptable for the final disposal of the treated effluent. From these results, the possibility of the removal mechanism of N-containing compounds was considered as an oligomeric formation of potassium salts on the ACF surface, i.e., NO_x^- -N, NH_4^+ -N and NH_2O -N react with metals on the fiber surface. Results for T-P removal by the KPACF series are shown Figure 6(b). According to these results, T-P adsorbed by KPACFs also seems to give excellent removal effect depending on the pH in all cases. The average concentration of T-P in the raw waste was over 500 mg/l (Table 2), while the values of final water purified with KPACFs were 29.5 mg/l ranging from 14.5 to 63.7 mg/l for the KACF1 series and 47.9 mg/l ranging from 13.8 to 68.8 mg/L for the KACF2 series. The high efficiency of the KPACF series was determined by the properties of these materials for trapping, their catalytic effect and adsorption of organic solid particles.

Conclusions

From the adsorption and surface analysis, it has been demonstrated that the carbon samples prepared by treatment with aqueous solutions containing potassium ions have a more heterogeneous micropore structure and are characterized by narrow micropores. The SEM

images and EDX spectra show a homogeneous distribution of potassium on the large surface area and the presence of C, O and P with a major contribution from K. The types and quantities of functional groups including oxygen groups were determined by FT-IR and Boehm's method. Finally, the color, T-N and T-P removal performance of the piggery waste dispersed with KPACFs was investigated and these results are acceptable for the final disposal of the treated effluent depending on the pH.

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