

Preparation of Char-Fe₃O₄ Composites from Polyvinyl Chloride with Hydrothermal and Hydrothermal-Pyrolysis Carbonization Methods as Co(II) Adsorbents

Muslem, Agus Kuncaka*, Taffrika Nur Himah, and Roto Roto

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara BLS 21, Bulaksumur, Yogyakarta 55281, Indonesia

* **Corresponding author:**

tel: +62-8122955274

email: akuncaka@ugm.ac.id

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Abstract: Char-Fe₃O₄ Composites have been synthesized through hydrothermal carbonization method and through hydrothermal-pyrolysis carbonization method by using polyvinylchloride as a carbon source. The products were characterized by FTIR, XRD, EDX, and TEM. The products were tested for Co(II) adsorption in water. The ability of Co(II) adsorption was studied for adsorption in different pH of the solution and its adsorption isotherm. Results showed that all products had similar hydrophilic functional groups and aliphatic carbon types. Char-Fe₃O₄ Composites produced by hydrothermal carbonization method (AFe-H) has more hydrophilic functional groups (C=O and -OH) than Char-Fe₃O₄ Composites produced by hydrothermal-pyrolysis carbonization method (AFe-P). Iron content was presented and distributed in the form of Fe₃O₄. Co(II) ion uptakes increased at the basic condition for all of the char-Fe₃O₄ Composites which were used as adsorbents. High hydrophilic functional groups in hydrothermal product composites (AFe-H) was the key factor contributing to the high adsorption ability with electrostatic interaction to the metal ion. AFe-H had the best Co(II) adsorption ability following the Langmuir isotherm model with its maximum adsorption capacity to be 0.556 mg g⁻¹.

Keywords: polyvinylchloride; composite; hydrothermal; pyrolysis; adsorption

■ INTRODUCTION

Thermal decomposition of PVC such as incineration and pyrolysis are notable for their harmful compounds emission. Carbonization of PVC by incineration produces ash and smoke containing polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzo furans (PCDFs) [1]. Pyrolysis, however, is still far from ideal as it is accompanied by the release of inorganic chlorine [2], polyaromatic hydrocarbon (PAH), chlorophenol, chlorobenzene, PCDDs, PCDFs and other harmful emissions [3].

Hydrothermal carbonization (HTC) has been successfully applied to degrade PVC. HTC is known to be able to degrade PVC in supercritical [4] and subcritical water [5]. Degradation of PVC under that method will produce char and most of the chlorine in PVC will be released as an HCl solution. Therefore, HTC is considered an environmentally friendly alternative because there is

no formation of PCDDs and PCDFs in the process. Other chlorinated hydrocarbons including chlorophenol were only detected at the trace level [5].

Development of char produced from HTC has been widely conducted, one of which is the formation of char composites through the addition of metal oxides such as FeOOH [6], Co₃O₄ [7], Fe₂O₃ [8], Ag₂O [9], etc. Simultaneous carbonization and modification of char from the maize stalk with Fe₃O₄ had also been studied by hydrothermal process in the subcritical water. Utilization of the Fe₃O₄-char composite as an adsorbent showed that the adsorption capacity of phosphate ions was higher than pure Fe₃O₄, and even much higher than char without modification [10]. According to the supramolecules concept of humus, humus contains nano-sized magnetic granules coated with supramolecules resulting from the degradation of organic compounds formed through millions of years.

Co content in the soil is needed by Rhizobia to catch nitrogen. For this reason, this paper was written, to have a nano-sized magnetic particle coated with biochar from PVC as adsorbent of Co in order to evaluate whether the composite has humus-like composite behavior.

Chlorine in PVC makes pyrolysis unable to be applied directly to carbonize PVC in preparation of char-Fe₃O₄ due to the formation of toxic emissions and inorganic chlorine. Preparation of char-Fe₃O₄ can be carried out safely by indirect pyrolysis [10]. The composite formation was done through hydrothermal process and followed by pyrolysis.

In this research, char and char-Fe₃O₄ composites as humus-like adsorbents were prepared from PVC through hydrothermal and hydrothermal-pyrolysis methods. The products were characterized using infrared spectroscopy, X-ray diffraction, and microscopy images. Its ability as adsorbent was tested to adsorb Co(II) in water. The adsorption performance of the products was observed on different acidity and concentration.

■ EXPERIMENTAL SECTION

Materials

The source of carbon used was polyvinyl chloride (average Mw 62.000 Da, average Mn 35.000) and the magnetic compound used was iron(II, III)oxide (nanopowder, 50–100 nm, 97% trace metal basis) from Aldrich. Other chemicals used in this research were sodium carbonate, sulfuric acid, cobalt(II)nitrate, nitric acid and sodium hydroxide from Merck.

Instrumentation

The functional group of composites was determined in the range 4.000–400 cm⁻¹ with potassium bromide pelletizing method using Shimadzu Prestige-21 Fourier Transform Infrared Spectrophotometer. The chemical state of the iron on the adsorbent was determined by X-ray diffraction using a Shimadzu XRD-6000 with Cu K α radiation. The surface morphology of the adsorbent was studied using JEOL JSM-6510 LA Scanning Electron Microscope equipped with energy dispersive X-ray in the energy range 0–40 keV. The in-depth investigation of nanoparticles composite of the adsorbent was carried out

using a JEOL JEM-1400 transmission electron microscope. Cobalt concentration in the solution after adsorption was determined by flame atomic absorption spectrophotometry using a Perkin Elmer-3110.

Procedure

Preparation of Char-Fe₃O₄ composite AFe-H through hydrothermal carbonization

PVC (5 g), Fe₃O₄ (5 g) and sodium carbonate (5 g) were added into a beaker glass containing 500 mL of distilled water. The acidity of the mixture was adjusted to pH 6 using 2 M sulfuric acid. The mixture was introduced into the HTC reactor. HTC process was operated for 3 h at 185 ± 5 °C. This HTC procedure referred to the procedure in a publication by Poerschmann et al. [5]. Char slurry was filtered and washed with 100 mL of distilled water and 100 mL of double distilled water. Char was dried in an oven at 100 °C for 24 h. This char-Fe₃O₄ composite product was AFe-H.

Preparation of Char-Fe₃O₄ composites AFe-P through hydrothermal-pyrolysis carbonization

The sample was prepared in the same manner as the AFe-H and then pyrolyzed at 250 °C for 2 h. Char-Fe₃O₄ composites were washed with 100 mL of double distilled water and dried at 100 °C for 24 h. This product was termed as AFe-P.

Study of pH adsorption

Adsorbent (100 mg) and 20 mL of 10 mg L⁻¹ of Co(NO₃)₂ were introduced into a 50 mL vial. It was then shaken for 2 h at 25 °C. The mixture of adsorbent and Co(II) solution was filtered and analyzed using AAS. This process was carried out with 5 series of pH variation of adsorbate in the range of 5–9 to analyze the correlation between % uptakes vs pH.

Study of isotherm adsorption

Adsorbent (100 mg) and 20 mL of Co (NO₃)₂ were introduced into a 50 mL vial. The vial was shaken for 2 h at 25 °C. The solution was filtered and analyzed using AAS. This process was carried out with 4 series of concentration variations of adsorbate in the range of 1–20 mg L⁻¹. The study of isotherm was limited to the Langmuir and Freundlich isotherm models.

■ RESULTS AND DISCUSSION

Characterization Char-Fe₃O₄ Composites of AFe-H and AFe-P

FTIR spectra of PVC (Fig. 1) showed aliphatic spectra type with peaks of C–H (2908 cm⁻¹), –CH₂– (1427 cm⁻¹) and –CH₃ (1327 cm⁻¹) alkanes. The presence of a peak in wavenumber 1635–1651 from AFe-H and AFe-P products (Fig. 1) showed the presence of C=O groups. The high peaks in AFe-H products showed more carbonyl group that indicated the high polar properties in AFe-H. The decrease in intensities of peaks in the AFe-P product indicated the feature change of the product surface during the pyrolysis process. The results are in line with a previous research that reported that oxygen containing groups of pinewood decreased after pyrolysis process [11].

The chemical phase in char-Fe₃O₄ composite was analyzed using X-ray diffraction. X-ray diffractogram of both AFe-H and AFe-P composites were compared with that of pure Fe₃O₄ (Fig. 2). The diffractogram comparisons is indicative of pure Fe₃O₄ content, proven by the following 2θ (°): 30.2; 35.6; 43.2; 57.1 and 62.7. Therefore, it may be concluded that the iron oxide particles in the composites

were identified as magnetite iron (Fe₃O₄). The diffractogram of Fe₃O₄ in the composites exhibited intensity decrease as well as peak broadening, which is strongly correlated to decreasing Fe₃O₄ crystallinity.

EDX that analyzed AFe-H and AFe-P (Table 1) showed that chlorines could only be detected in AFe-H, instead of chlorine-free AFe-P. The detected amount of chlorine was 14.57% of AFe-H or 23.24% of the total mass of char in AFe-H. Compared to the preliminary chlorine content in pure PVC at 56.8% [5], 60.92% of chlorines was successfully eliminated from char during the hydrothermal process (assuming % H in char was equal with data from Poerschmann et al. [5]).

AFe-H showed higher O and Fe contents than AFe-P. Percentage decrease of O and total loss of Cl at AFe-P indicated the release of CO₂ and HCl during the pyrolysis process. AFe-P is proven to have more C content than AFe-H. The high C content indicated that decomposition during the pyrolysis process occurred on the surface of char especially on the dominant carbonyl group. The Fe content in AFe-H (36.15% w/w) was more than AFe-P (32.89% w/w). The high amount of oxygenated functional

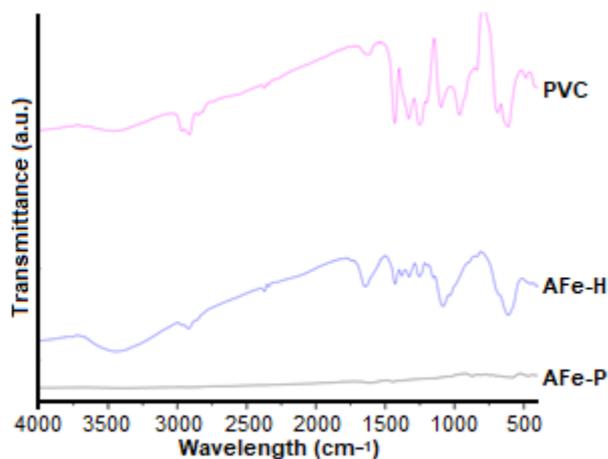


Fig 1. FTIR spectra from pure PVC, AFe-H and AFe-P

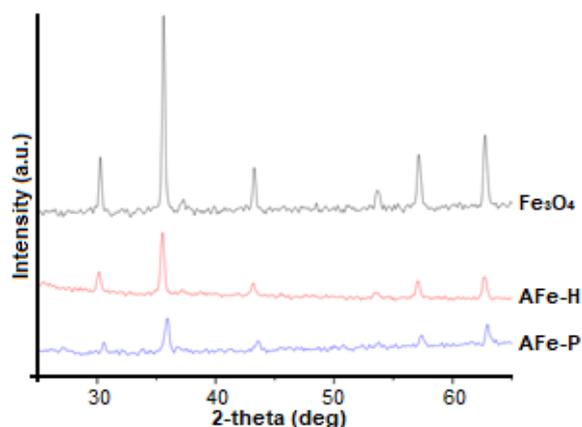


Fig 2. X-Ray diffraction pattern of pure Fe₃O₄, AFe-H and AFe-P

Table 1. Percent mass and atom of element content of AFe-H and of AFe-P from EDX analysis

No.	Element	% mass		% atom	
		AFe-H	AFe-P	AFe-H	AFe-P
1.	C	14.95	39.02	28.33	59.23
2.	Fe	36.15	32.89	14.73	10.74
3.	O	33.17	25.78	47.18	29.37
4.	Cl	14.57	0.00	9.35	0.00

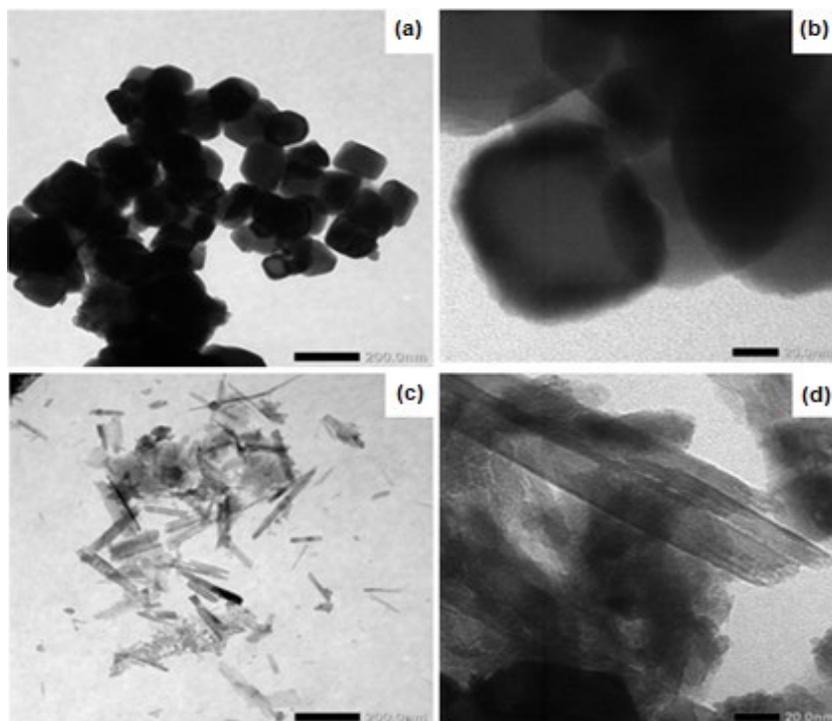


Fig 3. TEM images of AFe-H at (a) 200 nm, (b) 20 nm, (c) AFe-P at 200 nm, and (d) 20 nm

groups on the AFe-H surface is known as optimum nucleating sites for Fe_3O_4 [12]. The sites stabilized Fe_3O_4 thermodynamically.

TEM images showed that the hydrothermal product, AFe-H, displayed different shapes compared to the hydrothermal-pyrolysis product, AFe-P (Fig. 3). The AFe-H particles were uniformly round, but the AFe-P particles were cylindrical instead. Based on the particle shape, AFe-H char was granular carbon type, whereas AFe-P was carbon pellet type. The presence of Fe_3O_4 on composites was visible from the dark and bright side of the TEM images. Dark imagery represented Fe_3O_4 and bright side represented carbon.

Adsorption of Co(II)

Adsorption percentage of all adsorbents was low under acidic conditions but high under basic conditions (Fig. 4). These differences demonstrated the effect of surface characteristics towards the adsorption ability. The oxygenated functional group on the surface of adsorbents such as carboxylic acid was negatively charged under basic conditions. This negative charge increased electrostatic interaction between adsorbent surfaces and positively

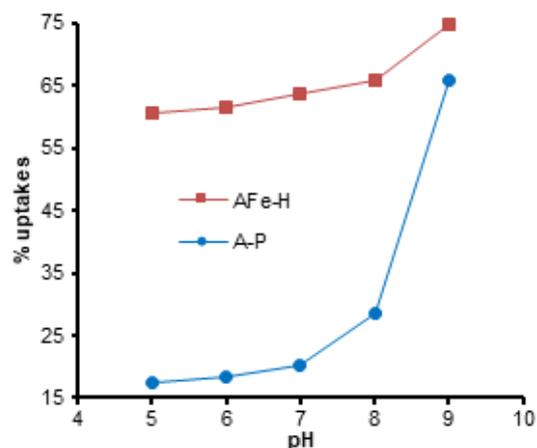


Fig 4. Influence of pH with Co(II) adsorption by the adsorbent AFe-H and AFe-P

charged metal ions [13]. The functional group would be positively charged under acidic conditions due to the presence of protons which blocked and competed with the metal ions in interacting with the adsorbent functional group.

Significant increase in the percentage of adsorption at pH 8 to pH 9 occurred due to precipitation of metal ions that formed $\text{Co}(\text{OH})_2$. The precipitation affected the calculated concentration of Co(II). Based on

Table 2. Parameter of Langmuir and Freundlich isotherm models from AFe-H and AFe-P

Adsorbent	Langmuir Parameters				Freundlich Parameters			
	Q_m (mg g ⁻¹)	K_L (L mg ⁻¹)	r^2	F_{error}	K_F (mg g ⁻¹)	n	r^2	F_{error}
AFe-H	0.556	1.192	0.988	5.25×10^{-5}	0.348	7.352	0.977	4.74×10^{-3}
AFe-P	-	-	0.868	-	0.103	2.032	0.968	-

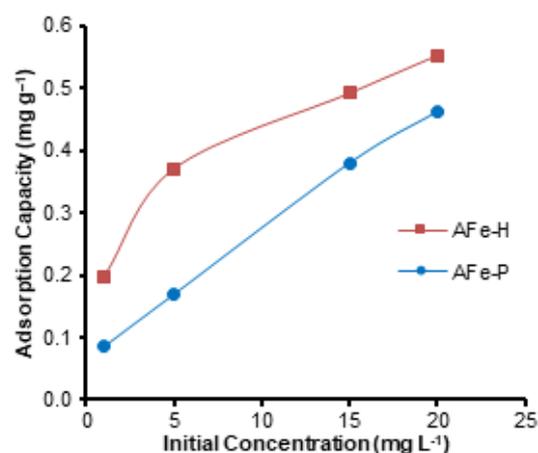
thermodynamic behavior, $\text{Co}(\text{OH})_2$ species began to form and settle at pH 8.2. At that point, 8% of $\text{Co}(\text{II})$ formed dense species and settled [14].

AFe-H composite showed a higher adsorption capacity than AFe-P (Fig. 5). These data suggest that the reduction of oxygenated functional groups in pyrolysis products was greater than the addition of the adsorption sites of Fe_3O_4 on composite surfaces. The hydrophilic parts from oxygen groups on char and magnetite significantly affect the adsorption process. It is proposed that the adsorption mechanism mostly occurred due to electrostatic interaction between metal ions and hydrophilic parts on adsorbent surfaces.

Adsorption of $\text{Co}(\text{II})$ with AFe-P followed the Freundlich isotherm model with the correlation coefficient at 0.999 (Table 2). This empirical model showcased the adsorption on heterogeneous surfaces and is often used to study thermodynamic correlation in certain cases of metal ions adsorption using carbon materials [13,15-16]. The adsorption capacity of Freundlich isotherm parameter (K_F) showed that $\text{Co}(\text{II})$ adsorption capacity of AFe-P was 0.103 mg g^{-1} .

Adsorption of $\text{Co}(\text{II})$ by AFe-H followed the Langmuir isotherm model with the correlation coefficient at 0.988 and $F_{error} 5.25 \times 10^{-5}$ for AFe-H (Table 2). The empirical model showed adsorption on a homogeneous surface. The adsorption capacity of Langmuir isotherm parameter (Q_m) showed that $\text{Co}(\text{II})$ adsorption capacity of AFe-H was 0.556 mg g^{-1} . The graph of c_e (equilibrium concentration) vs q_e (adsorption capacity) of AFe-H (Fig. 5) confirmed that $\text{Co}(\text{II})$ adsorption by AFe-H adsorbents followed the Langmuir isotherm model.

Adsorption energy calculated by the Langmuir isotherm between AFe-H with $\text{Co}(\text{II})$ was $27.83 \text{ kJ mol}^{-1}$. The adsorption energy showed the strong bonds between metal ions with active sites of the adsorbent. The adsorption energy of less than $20.92 \text{ kJ mol}^{-1}$ showed the

**Fig 5.** Adsorption isotherm of $\text{Co}(\text{II})$ by adsorbents AFe-H and AFe-P

physical adsorption energy, however, the adsorption energy of more than $20.92 \text{ kJ mol}^{-1}$ [17] is related to the chemical adsorption energy. The data confirmed that the interaction between $\text{Co}(\text{II})$ and AFe-H adsorbents was dominated by the chemical interaction (chemisorption).

CONCLUSION

Char- Fe_3O_4 composites from PVC can be prepared by both hydrothermal and hydrothermal-pyrolysis methods simultaneously. The hydrothermal product, AFe-H, had more oxygenated functional groups than the hydrothermal-pyrolysis product, AFe-P. The hydrothermal-pyrolysis product also displayed higher porosity than the hydrothermal product. In addition, AFe-H had higher Fe_3O_4 content with homogeneous surfaces, but AFe-P had less Fe_3O_4 with heterogeneous surfaces. The adsorption capacity of $\text{Co}(\text{II})$ under basic condition increased despite the adsorbent type. Adsorption of $\text{Co}(\text{II})$ by AFe-H followed the Langmuir isotherm model, whereas $\text{Co}(\text{II})$ adsorption by AFe-P followed the Freundlich isotherm model. The best $\text{Co}(\text{II})$ adsorption capacity was given by AFe-H with

0.556 mg g⁻¹. The hydrophilic parts from the adsorbent would significantly affect the adsorption process. The adsorption mechanism mostly occurred due to electrostatic interaction between metal ions and hydrophilic parts on the adsorbent surface.

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■ REFERENCES

- [1] McKay, G., 2002, Dioxin characterization, formation and minimization during municipal solid waste incineration: Review, *Chem. Eng. J.*, 86 (3), 343–368.
- [2] Sadat-Shojai, M., and Bakhshandeh, G.R., 2011, Recycling of PVC wastes, *Polym. Degrad. Stab.*, 96 (4), 404–415.
- [3] Font, R., Gálvez, A., Moltó, J., Fullana, A., and Aracil, I., 2010, Formation of polychlorinated compounds in the combustion of PVC with iron nanoparticles, *Chemosphere*, 78 (2), 152–159.
- [4] Nagai, Y., Smith, Jr., R.L., Inomata, H., and Arai, K., 2007, Direct observation of polyvinylchloride degradation in water at temperatures up to 500 °C and at pressures up to 700 Mpa, *J. Appl. Polym. Sci.*, 106 (2), 1075–1086.
- [5] Poerschmann, J., Weiner, B., Woszidlo, S., Koehler, R., and Kopinke, F.D., 2015, Hydrothermal carbonization of poly(vinyl chloride), *Chemosphere*, 119, 682–689.
- [6] Wu, P., Du, N., Zhang, H., Yu, J., and Yang, D., 2011, Carbon nanocapsules as nanoreactors for controllable synthesis of encapsulated iron and iron oxides: Magnetic properties and reversible lithium storage, *J. Phys. Chem. C.*, 115 (9), 3612–3620.
- [7] McHenry, M.E., Majetich, S.A., Artman, J.O., DeGraef, M., and Staley, A.W., 1994, Superparamagnetism in carbon-coated Co particles produced by the Kratschmer carbon arc process, *Phys. Rev. B: Condens. Matter*, 49 (16), 11358–11363.
- [8] Cui, X., Antonietti, M., and Yu, S.H., 2006, Structural effects of iron oxide nanoparticles and iron ions on the hydrothermal carbonization of starch and rice carbohydrates, *Small*, 2 (6), 756–759.
- [9] Luo, L.B., Yu, S.H., Qian, H.S., and Gong, J.Y., 2006, Large scale synthesis of uniform silver@carbon rich composite (carbon and cross-linked PVA) sub-microcables by a facile green chemistry carbonization approach, *Chem. Commun.*, 7, 793–795.
- [10] Tu, Y., Peng, Z., Xu, P., Lin, H., Wu, X., Yang, L., and Huang, J., 2017, Characterization and application of magnetic biochars from corn stalk by pyrolysis and hydrothermal treatment, *BioResources*, 12 (1), 1077–1089.
- [11] Liu, Z., Zhang, F.S., and Wu, J., 2010, Characterization and application of chars produced from pinewood pyrolysis and hydrothermal treatment, *Fuel*, 89 (2), 510–514.
- [12] Zubir, N.A., Yacau, C., Motuzas, J., Zhang, X., and Costa, J.C.D., 2014, Structural and functional investigation of graphene oxide-Fe₃O₄ nanocomposites for the heterogeneous Fenton-like reaction, *Sci. Rep.*, 4 (1), 4594.
- [13] Pyrzyńska, K., and Bystrzejewski, M., 2010, Comparative study of heavy metal ions sorption onto activated carbon, carbon nanotubes and carbon-encapsulated magnetic nanoparticles, *Colloids Surf., A*, 362 (1-3), 102–109.
- [14] Yüzer, H., Kara, M., Sabah, E., and Celik, M.S., 2008, Contribution of cobalt ion precipitation to adsorption in ion exchange dominant systems, *J. Hazard. Mater.*, 151 (1), 33–37.
- [15] Boehm, H.P., 2002, Surface oxides on carbon and their analysis: A critical assessment, *Carbon*, 40 (2), 145–149.
- [16] Stafiej, A., and Pyrzyńska, K., 2007, Adsorption of heavy metal ions with carbon nanotubes, *Sep. Purif. Technol.*, 58 (1), 49–52.
- [17] Adamson, A.W., 1990, *Physical Chemistry of Surface*, 5th Ed., John & Wiley Sons, Inc., New York.