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Utilization of fish bone as adsorbent of Fe^{3+} ion by controllable removal of its carbonaceous component

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Abstract. The performance of fish bone to adsorb Fe^{3+} ion in solution was studied. Powdered fish bone and carbonized fish bone were used as adsorbent. All absorbents were characterized by X-ray diffraction (XRD), IR spectroscopy, nitrogen adsorption, scanning electron microscopy (SEM) and TG analysis. Powdered fish bone and carbonized fish bone were effective as adsorbent for removing Fe^{3+} ion in solution. The metal adsorptions of Fe^{3+} ion were 94 and 98% for powdered fish bone and fish bone which carbonized at 400 and 500 °C.

1. Introduction

Metal elements which have a density greater than 5 g cm⁻³ and high molecular weight are classified as heavy metals. One kind of essential heavy metals is Fe element which highly soluble in water at pH less than 5 and to be toxic to human when excess. The high content of Fe metal will impact on human health such as can cause poisoning (vomiting), intestinal damage, premature aging to sudden death, Arthritis, birth defects, bleeding gums, cancer, kidney cirrhosis, constipation, diabetes, diarrhea, dizziness, tiredness, hepatitis, hypertension, insomnia.

Many methods have been used by researcher to remove heavy metal from water such as ion exchange, solvent extraction, complexation, adsorption, coagulation, phytoextraction, chemical precipitation, chemical oxidation or reduction, evaporation and reverse osmosis. The most cost-effective method which often was used by many researchers is adsorption due to easy to operate, high adsorption efficiency and low maintenance [1, 2]. Otherwise, the other methods have some shortcomings such as need a lot of reagent and energy, incomplete metal removal, low selectivity, high operational cost and unfriendly to environment [1].

Many researches have created to adsorb and remove heavy metals from solution by using absorbent. Zinc (II) was removed by using dried animal bones and powdered fish bones absorbent [1, 3]. Cu (II) ion was absorbed with absorbent from pretreated fish bones, rice husk and modified rice husk [4, 5]. Cd (II) was removed by using sweet potato (*Ipomoea batatas* L.) peel absorbent [6]. Cr (III) was absorbed by using activated carbon from alga *Ulva Lactuca* [7]. Pb (II) and Ni (II) were absorbed with natural bentonite absorbent [8].

In this research, adsorbent from Belida (*Chitalalopis*) fish bone which modified with by controllable removal of it carbonaceous component was used to adsorption and removal Fe^{3+} ion from

solution. Adsorbent from the Belida fish bone were investigated from characterization properties and adsorption efficiency for Fe^{3+} ion removing.

2. Materials and Methods
2.1. Raw Materials
The fish bone materials were collected from waste of Belida (*Chitalalopis*) fish from East Kalimantan, Indonesia.

2.2. Carbon Preparation
The fish bone from Belida fish waste was washed with boiling water to separate bone and impurities. The fish bone was dried in an oven at 110 °C for 24 hours. Furthermore, it was crushed and sieved to get a powder with size of 100 mesh and it was labeled as FB. The fish bone powder was carbonized in a furnace at variations in temperature of 300, 400, 500, 600, 700 and 900 °C for 1 hour. The results are labeled in Table 1.

Table 1. Codes and Treatments Done to The Samples

Samples	Temperature of carbonization (°C)	Time of carbonization (h)
FB	-	-
CFB-300	300	2
CFB -400	400	2
CFB -500	500	2
CFB -600	600	2
CFB -700	700	2
CFB -900	900	2

2.3. Preparation of Stock of Metal
$Fe(NO_3)_3 .9H_2O$ (Merck) was used to prepare stock solution of iron. That compound was dissolved in distilled water until concentration of Fe^{3+} ion 1000 mgL^{-1}. Another concentration of Fe^{3+} ion which used in experiment was prepared by diluting of the stock solution.

2.4. Samples Characterization
The samples were characterized by XRD, FTIR, SEM, TGA and N_2 adsorption. The crystallinity of the samples were investigated base on X-ray diffraction (XRD) pattern which recorded with a Bruker AXS Advance D8 difractometer using Cu K_{α} radiation ($\lambda = 1.5405$ Å, 40 kV and 40 mA). The functionalize groups in the samples were determine from IR spectra which recorded on a Perkin Elmer Fourier transform infrared (FTIR) spectrometer, with a spectral resolution of 2 cm^{-1}, scans 10 s, at temperature 20 °C. The surface textures in the samples were determined by using scanning electron microscopy (SEM), JEOL JSM-6701F instrument with an accelerating voltage of 15 kV. The amount of carbon in the samples was calculated from thermal gravimetric Analysis (TGA) data which collected using STA Linseis PT1600 instrument with heat rate 10 °C min^{-1} and target temperature 900 °C Surface area of the samples was calculated by N_2 adsorption at 77 K using a Quantachrome instruments version 11.0 and the pore size distribution was calculated with the Barrett-Joyner-Halenda (BJH) model.

2.5. Adsorption Test
The sorption performance of the samples was tested by contacting 0.5 g sample with 50 mL Fe^{3+} (100 mgL^{-1}) in 250 mL Erlenmeyer flasks at room temperature under stirring for 1 h. The suspension was centrifuged to separate solid and filtrate. The filtrate was analyzed for metal ion concentration by using Atomic Absorption Spectrophotometric analysis (Analysis 200 AA, Perkin Elmer, USA). The

effect of pH for sample performance to metal sorption was investigated in the range of 1.0 – 11.0. The mixing 0.1 M HCl and 0.1 M NaOH was used to arrange of the pH of metal solution. The amount of metal adsorption in the adsorbent was determined by the equation:

$$\text{Metal adsorption (\%)}=\frac{(C_i\text{-}C_f)}{C_i}\text{ x }100\%$$

where C_i and C_f are initial and final concentration of metal ion (mgL^{-1}) in the solution [8].

3. Results and Discussion
3.1. Physical Properties
The XRD pattern of (a) FB, (b) CFB-300, (c) CFB-400, (d) CFB-500, (e) CFB-600, (f) CFB-700 and (g) CFB-900 are shown in Figure 1. All of the solid samples showed the angles corresponding to the peaks at 2θ = 25.9, 31.8, 39.8, 46.8, 49.6, 53.4 and 64.4 which are represented to the crystalline phase of hydroxyapatite [9]. The intensity of the peaks of hydroxyapatite increase when the carbonization temperature is increased.
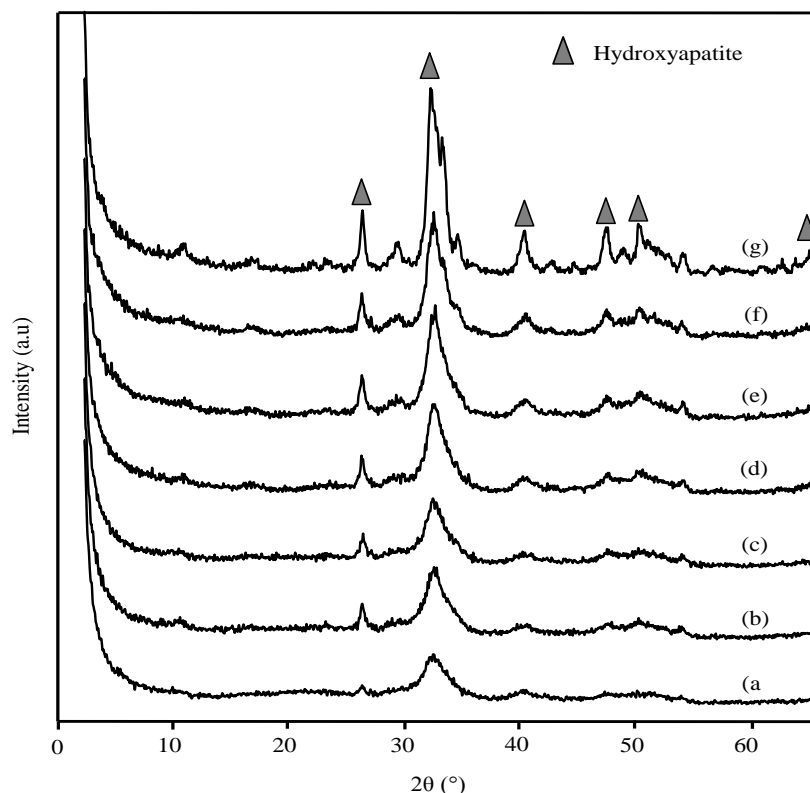

Figure 1. XRD pattern of (a) FB, (b) CFB-300, (c) CFB-400, (d) CFB-500, (e) CFB-600, (f) CFB-700 and (g) CFB-900

The FTIR spectra for the surface functional groups of (a) FB, (b) CFB-300, (c) CFB-400, (d) CFB-500, (e) CFB-600, (f) CFB-700 and (g) CFB-900 are shown in Figure 2. The IR absorption a broad peak at around 3424 cm^{-1} and 1653 cm^{-1} were attributed to hydroxyl stretching mode which indicated adsorbed water in the samples [10]. The intensity of hydroxyl groups decreased when the carbonization temperature increased. Carbonization process caused the appearance of peaks at around 2925 and 2851 cm^{-1} were assigned to the absorption of organic material as C–H and N–H group symmetric and asymmetric stretching mode. The absorption peak at around 2014, 1435 and 876 cm^{-1} were indicated of carbonate ion substitution [8]. Carbonate ion substitution clearly appear when the

carbonization temperature of samples were increased more than 600 °C. All samples showed the peak at around 1043, 600 and 564 cm^{-1} were attributed intensive phosphate group.
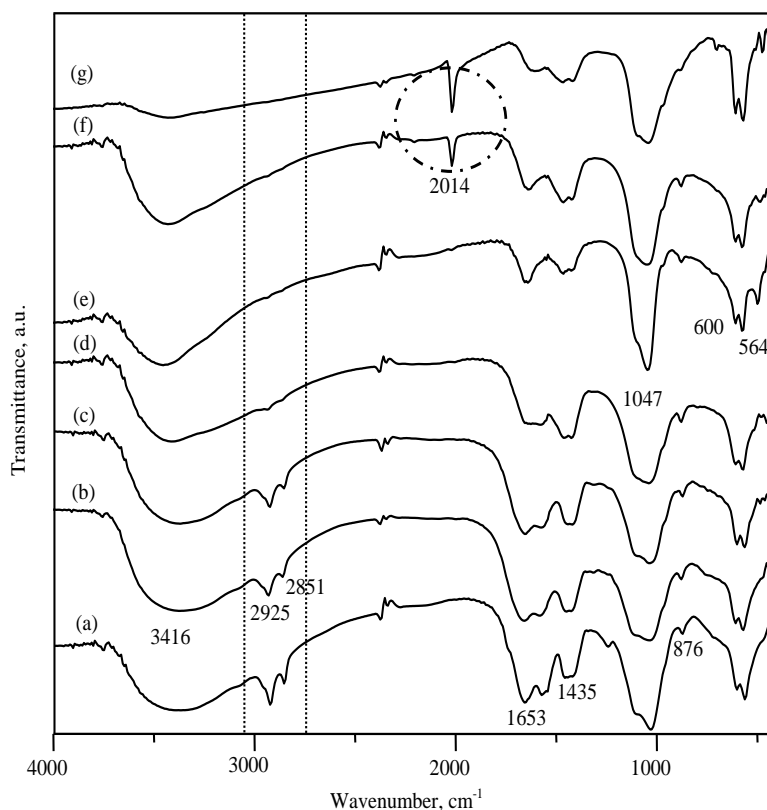

Figure 2. FTIR spectra of(a) FB, (b) CFB-300, (c) CFB-400, (d) CFB-500, (e) CFB-600, (f) CFB-700 and (g) CFB-900.

N$_2$ adsorption-desorption isotherms and pore size distributions of FB and CFB-500 are shown in Figure 3. The Isotherm of FB sample (Figure 3(a)) is III type in the IUPAC classification which indicated non porous or macro porous and no identifiable monolayer. The pore size distribution of FB sample indicated the presence of uniform pores with pore radius ~18 Å. The isotherm of CFB-500 sample (Figure 3(b)) is IV type in the IUPAC classifications of mesopores materials with clear hysteresis loops in the relative pressure range ~0.350 – 0.992 which is associated with the capillary condensation of nitrogen in the pores. According the IUPAC classification, the CFB-500 sample also possesses H1 which often associated with porous materials exhibiting a narrow distribution of relatively uniform (cylindrical-like) pores.
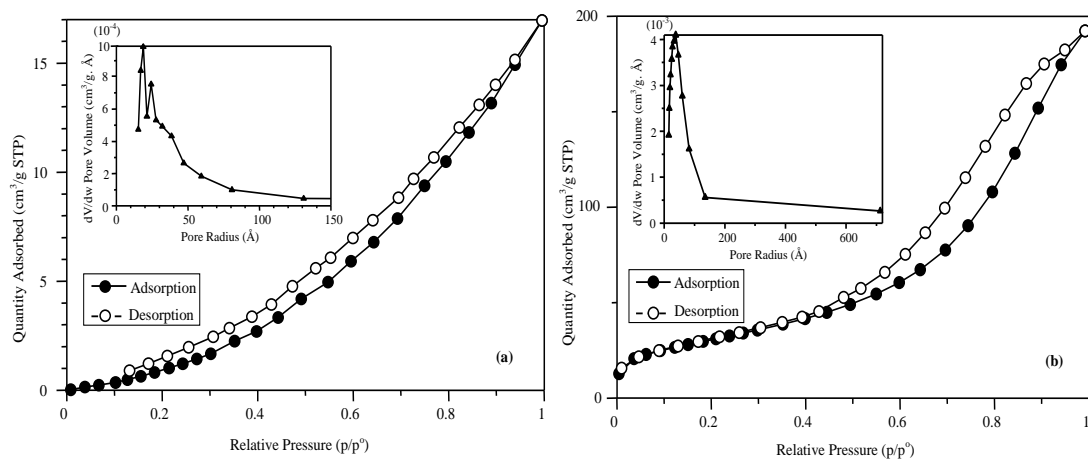
Figure 3. N_2 Adsorption-Desorption Isotherms and Pore Size Distribution of (a) FB and (b) FB-500

The pore size distribution indicates the presence of uniform mesopores with pore radius ~29 Å. The surface area of FB and CFB-500 samples were 16.0 m^2/g and 162.9 m^2/g, respectively. Base on pore radius and surface area, CFB-500 possesses pore radius and surface area larger than FB. This indicating carbonization process can cause opening and collapsing of pores. Physical properties of FB and CFB-500 samples are listed in Table 2.

Table 2. Physical Properties of FB and CFB-500

Samples	Pore Radius (Å)	Pore Volume (cc/g)	Surface Area (m^2/g)
FB	18.1	0.029	16.0
CFB -500	28.7	0.315	162.9

The morphology of FB, CFB-300, CFB-500 and CFB-900 were collected by scanning electron microscopy (SEM). A representative SEM image of samples is shown in Figure 4. From the SEM image, it can be seen that the FB before carbonization process have clean surfaces and sharp-edged porous structures. The morphology of fish bone after carbonization process in varying temperature such as CFB-300, CFB-500 and CFB-900 have roughness surfaces.
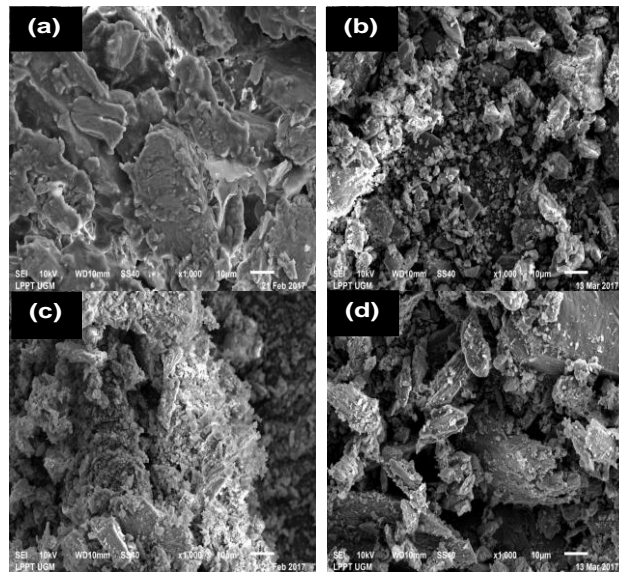
Figure 4. SEM images of(a) FB, (b) CFB-300, (c) CFB-500 and (d) CFB-900

Figure 5 shows the TG analysis plot of (a) FB (b) CFB-500 and (c) CFB-900. The weight losses of the samples were shown in two temperature ranges. In the first temperature range 32 – 196 °C, the TGA plot of all samples displayed a slight weight loss for FB (~ 9.5%), CFB-500 (9.7%) and CFB-900 (7.8%). This temperature range can be correlated with the evaporation of the water adsorbed on samples. In the second temperature range 196 – 522 °C, the TGA plot saw weight lose of FB, CFB-500 and CFB-900 are 31.8, 11.9 and 7.9%, respectively. The weight loss in the second temperature range can be associated with the decomposition of organic compounds. Decreasing of weight lose percentage in the second temperature rang also can be correlated with carbon contain in the sample which it decrease when the temperature carbonization increased.
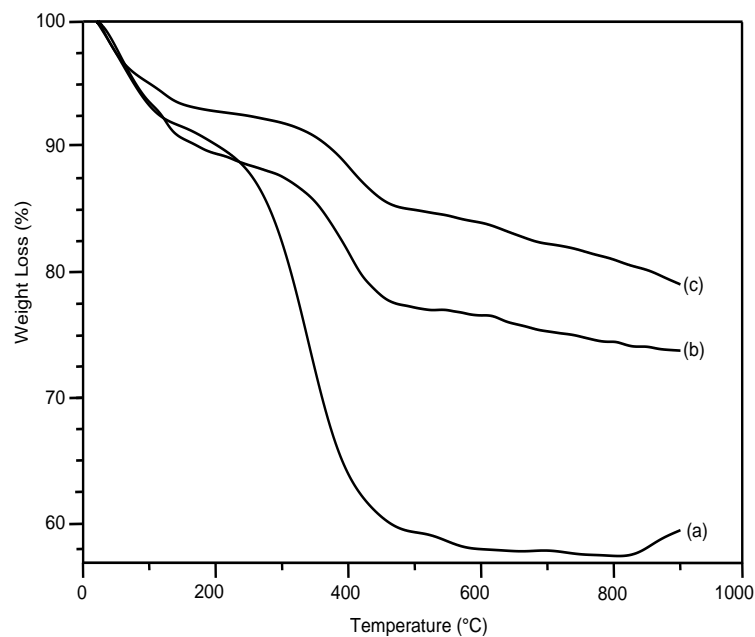

Figure 5. TG Analysis of (a) FB, (b) CFB-500 and (c) CFB-900

3.2. Effect of Carbonization Temperature on Fe^{3+} Adsorption

Figure 6 shows the histogram of the effect of carbonization temperature to Fe^{3+} ion adsorption. We could see that the metal adsorption 87% when fish bone powdered (FB) was used as adsorbent. The metal adsorption increased when the fish bone was carbonized in varying temperature. The metal adsorption 94% when used adsorbent of the fish bone that carbonized at 300 °C (CFB-300). The highest metal adsorption reached 98% when used absorbent of the fish bone was carbonized at 400 °C (CFB-400) and the same metal adsorption was obtained when the fish bone was carbonized at 500 °C (CFB-500). Carbonization of fish bone at 400 and 500 °C caused all organic compounds in fish bone changed to carbon element that it useful as adsorbent. Carbonization of the fish bone at 400 and 500 °C also cause to increasing the surface area of the adsorbent from 16.0 m^2/g (FB) to 162.9 m^2/g (CFB-500). The metal adsorption decreased when carbonization of the fish bone was created more than 500 °C. The metal adsorption 95% when carbonization of fish bone was performed at 600 °C (CFB-600) and the metal adsorption almost no change when carbonization was created at 700 and 900 °C. It was caused when the carbonization temperature increased the carbon release from samples become increase during the carbonization process and the amount of carbon inside sample becomes decreased.
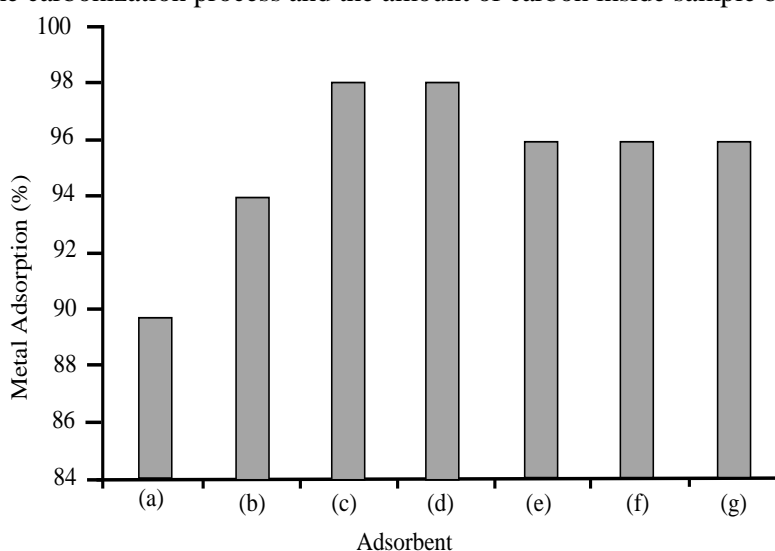

Figure 6. Metal adsorption of (a) FB, (b) CFB-300, (c) CFB-400, (d) CFB-500, (e) CFB-600, (f) CFB-700 and (g) CFB-900.

3.3. Effect of Solution pH on Fe^{3+} Adsorption

Figure 7 shows the graph of the effect solution pH on Fe^{3+} adsorption. The experiments were carried out in Fe^{3+} solution (100 mgL^{-1}; 50 mL) with 0.5 g absorbent (CFB-500) at room temperature with duration of contact time 1 h at different pH solution (pH 1 − 11). The data show that the solution pH almost did not influence to Fe^{3+} ion adsorption. Absorbent can adsorb Fe^{3+} ion with metal adsorption more than 96%. Even, metal adsorption reached 98% when the experiments were performed at pH 7 and 8.
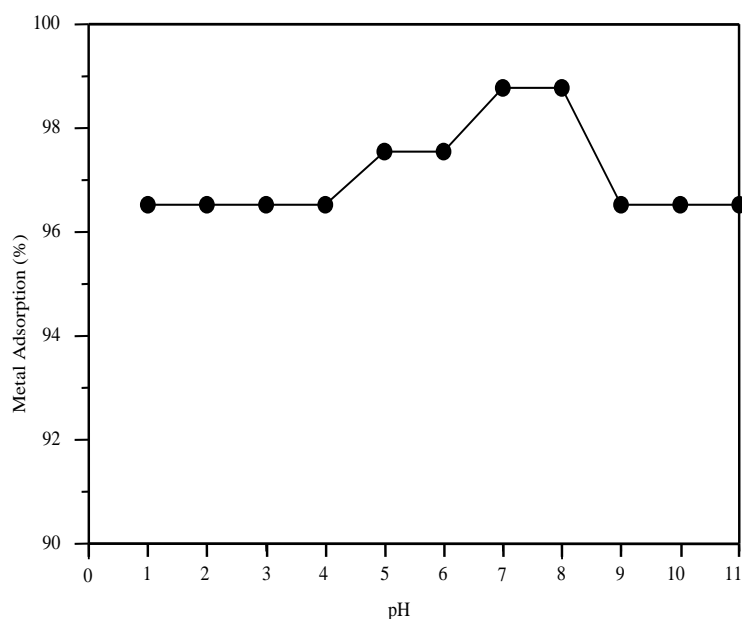
Figure 7. The Effect of pH to Metal Adsorption

4. Conclusions

The results of this research asserted that the powdered fish bone and carbonized fish bone at varying temperature can be promoted as adsorbent for adsorption and removing Fe^{3+} ion from solution. Metal adsorption reached 94% when powdered fish bone was applied as adsorbent. The best metal adsorption 98% was obtained when used adsorbent from fish bone which carbonized at 400 and 500 °C. The adsorption and removal Fe^{3+} ion from solution by carbonized fish bone as adsorbent was not influenced by pH condition.

5. References

[1]   Lima H K, Tenga T T, Ibrahima M H, Ahmad A and Chee H T 2012 *APCBEE Procedia* **1** 96 − 102
[2]   Ehab M Z, Hesham H S, Hassan M A and Ahmad M F 2013 *Ecol. Eng.* **61** 390–93
[3]   Fawzi B, Sameer A, and Fadhel M 2000 *Sep. Purif. Technol* . **21** 155–64
[4]   Bayram K, Adem T and Yusuf D 2010 *Desalination* **264** 37–47
[5]   Ayhan D 2008 *J. Hazard. Mater*. **157** 220–29
[6]   Edidiong D A and Alastair D M 2016 *J. Environ. Chem. Eng.* **4** 4207–28
[7]   Amany E, Ahmed E N, Azza K and Ola A 2007 *J. Hazard. Mater* **148** 216–28
[8]   Donat R, Akdogan A, Erdem E and Cetisli H 2005 *Colloid Interface Sci.* **286** 43–52
[9]   Chakraborty R and Chowdhury DR 2013 *Chem. Eng. J.* 215–216 and 491–99
[10]   Nurhadi M 2017 *Bull. Chem. Reac.Eng. Catal.* **12**(1) 55-61

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