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Removal of oil from simulated oilfield wastewater using modified coal fly ashes

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ABSTRACT

Three methods, HCl treatment, $FeCl_3$ treatment, and HCl–$FeCl_3$ treatment, were used to modify coal fly ash as an absorbent for oil removal from oilfield wastewater. Results from scanning electron microscopy and BET analysis indicated that the specific surface area (SSA) increased from 3.16 m^2/g for the untreated fly ash to 10.13, 28.67, and 48.89 m^2/g for fly ashes modified by $FeCl_3$ treatment, HCl–$FeCl_3$ treatment, and HCl treatment, respectively. X-ray fluorescence (XRF) analysis showed that Fe content in $FeCl_3$-treated fly ash (TFA-$FeCl_3$) and HCl–$FeCl_3$-treated fly ash (TFA-HCl–$FeCl_3$) was obviously higher than that in HCl-treated fly ash (TFA-HCl) and untreated fly ash (FA). Results from XRD and XRF analysis revealed decreased CaO content in TFA-HCl, TFA-$FeCl_3$, and TFA-HCl–$FeCl_3$. The oil removal capacity of all studied fly ashes was investigated and maximum oil removal ratio of studied fly ashes was in the following manner, TFA-HCl/$FeCl_3$ > TFA-$FeCl_3$ > TFA-HCl > FA (94.7, 86.3, 80.1, and 62.0%).The study showed that the oil removal capacity of fly ash had a close relation to SSA and Fe content, and the excellent oil removal capacity of TFA-HCl–$FeCl_3$ may stem from the synergetic effect between adsorption and flocculation. Dose, pH, contact time, and temperature affected oil removal capacity of fly ashes. In the treatment, the oil removal ratio can reach up to 96.8%, and the oil content reduced sharply from 262 to 8.4 mg/L. The method set forth in the work had potential application in deep removal of oil from oilfield wastewater.

Keywords: Coal fly ash; Modification; Simulated oilfield wastewater; Oil removal

1. Introduction

At the mid and later stages of development of the oilfield, water flood recovery is the main extraction method, and the more the water injected to the strata, the more the oilfield wastewater production. Generally, produced oilfield wastewater was reinjected to strata for reuse or discharged outside, and whether it was reinjected or discharged, it should be well disposed. Especially, when it is discharged to the outside environment, there are more strict requirements. Oil content is one of the most important appraisal parameters in the treatment of oilfield wastewater. Conventionally, oil is removed mainly through natural sedimentation [1], air floatation [2], chemical flocculation process [3], hydrocyclone separation [4], and so on. But the oil content in water is still comparatively

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high after treatment. How to remove the deeply contained oil fast and at low-cost from oilfield wastewater is still a challenge in the oilfield production.

Coal fly ash is a solid waste generated during the combustion of coal. In recent years, it caused extensive concern mainly due to two aspects: one aspect is that it can cause serious environmental and health problems, if it is directly discharged to the outside environment without any disposal [5,6]; another one is that it has some important applications. Presently, fly ash is mainly used as low-cost absorbent to remove water-soluble organic substances [7–10], toxic metal ions [11–17] and non-metal ions [18] in water, and pollutants in air [19–21]. Coal fly ash also has applications in the synthesis of zeolite [22–24] and clay bricks [25], mine backfill [26], road subbase [27], and so on. To the best of our knowledge, there has been little literature about the application of coal fly ash for the removal of non-water soluble pollutants in water, such as crude oil in oilfield wastewater.

In the experiments of the present study, coal fly ash was treated by HCl, $FeCl_3$, and HCl–$FeCl_3$, and the chemical elements, components, specific surface area (SSA), and morphology of fly ashes were characterized by X-ray fluorescence (XRF), XRD, BET, and scanning electron microscopy (SEM), respectively. All studied fly ashes were used to remove oil from simulated oilfield wastewater, and its oil removal capacities were evaluated. The relation between oil removal capacity of fly ash and SSA and Fe content was discussed. Furthermore, the effects of dose, pH, temperature, and contact time on the ratio of oil removal were further investigated.

2. Experiment

2.1. Materials

Fly ash was provided by Thermal Power Plant of Leshan, Sichuan, China. All the chemical agents used in the experiment were of analytical grade. The crude oil used for the study was obtained from LD10-1 oilfield, Liaoning, China.

2.2. Equipment

Elemental analysis was performed using energy dispersive XRF (Oxford ED2002 model). XRD patterns were recorded on an X-ray diffractometer (D/Max-IIIA) with Cu–K_α ($\lambda = 1.54$ Å) radiation. SSA was analyzed by a JW-004BET SSA analyzer. SEM studies were carried out using a Hitachi S-3000 scanning electron microanalyzer. A Shimadzu UV-1750 UV–Vis spectrophotometer was used to analyze the oil content and a VGT-1840QTD supersonic cleaner was used to accomplish the emulsification of oil and water. A motor stirrer (JB25-C-800W) was used to stir the systems of oilfield wastewater and fly ashes. An electric-heated thermostatic water bath (SKCGR2-220V-500VA) was used to control the temperature of oilfield wastewater.

2.3. Modification

2.3.1. Preparation of HCl-modified fly ash (TFA-HCl) and $FeCl_3$-modified fly ash (TFA-$FeCl_3$)

Two samples of fly ashes (FA), 80 g each, were put into two 250 mL beakers, respectively, in which 100 mL of 1 M HCl and 100 mL of 0.1 M $FeCl_3$ aqueous solutions were added, respectively. The two samples were soaked and slowly stirred in the solution for 1 h at a speed of 60 rpm, then the systems were filtered, and the samples were dried in air at room temperature, and then they were ground in a ceramic mortar to fine power.

2.3.2. Preparation of HCl–$FeCl_3$-modified fly ash (TFA-HCl–$FeCl_3$)

Eighty grams of TFA-HCl was put into a 250 mL beaker, in which 100 mL of 0.1 M $FeCl_3$ aqueous solution was added; the system was stirred for 1 h at a slow speed of 60 rpm, then the system was filtered, and the sample was dried and ground.

2.4. Simulation of oilfield wastewater

The oilfield wastewater used in the experiments was simulated by emulsifying crude oil in water, and the oil content of oilfield wastewater used in the experiments was 262 mg/L.

2.5. Treatment of simulated oilfield wastewater

Typically, 4 g raw fly ash or modified fly ash was put into 100 mL of oilfield wastewater, and the system was slowly stirred for some time at a speed of 60 rpm, then the system was filtered, and the filtrate was transferred to a separating funnel. Afterwards, 20 mL of normal octane was put into the filtrate to extract oil. To ensure that the oil was fully extracted, a few drops of 1 M HCl were added to the above filtrate. The extract was collected in a 250 mL conical flask. A certain amount of anhydrous sodium sulfate was also put into the extract to remove minute dissolved water in the filtrate, then the system was filtered, and the oil content in the filtrate was determined by UV–Vis spectrophotometer.

The effect of pH on the oil removal was investigated by adding fly ash samples of different types, 4 g each, into a series of 100 mL oilfield wastewater of different pH values to remove oil at room temperature. The pH of oilfield wastewater was adjusted by adding 0.1 M HCl and 0.1 M NaOH. The effect of temperature on the oil removal was evaluated by adding fly ash samples of different types, 4 g each, into a series of 100 mL oilfield wastewater to remove oil at different temperatures. The effect of dose of fly ash on the oil removal was assessed by adding a series of fly ash samples of different types with different quantities into a series of 100 mL oilfield wastewater to remove oil at room temperature. To remove the oil from oilfield wastewater as far as possible, in the experiments, all mixed systems of fly ashes and oilfield wastewater were stirred for 1 h at a slow speed of 60 rpm. Oil content was determined by the procedure described above.

2.6. Evaluation of oil removal

2.6.1. Determination of oil content

A series of normal octane solutions of crude oil with different oil contents were prepared. The absorbance of solutions at 252 nm was determined by UV–Vis spectrophotometer. The crude oil calibration curve was drawn (as showed in Fig. 1). According to the curve, the oil content can be figured out.

2.6.2. The ratio of oil removal

$$\text{Ratio of oil removal} = (1 - C/C_0) \times 100 \tag{1}$$

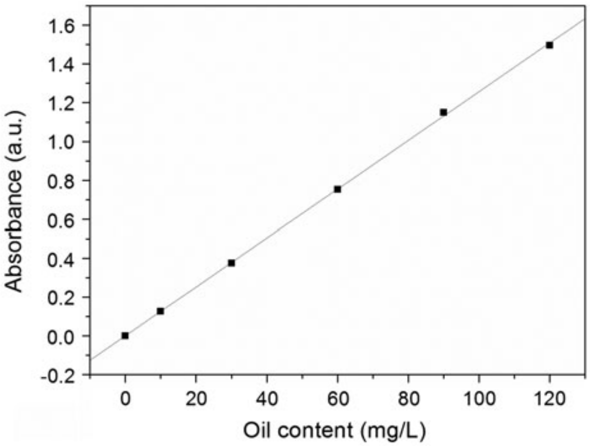

Fig. 1. Crude oil calibration curve.

where C_0: initial concentration of oilfield wastewater; C: concentration of treated oilfield wastewater.

3. Results and discussion

3.1. Physical and chemical characteristics of fly ashes

Chemical elements of fly ashes were listed in Table 1.

XRF analysis showed that the content of elements in FA and TFA-HCl was very close, but the content of all elements except Ca in TFA-HCl was higher than that in FA; it was caused by HCl modification which caused a decrease in the Ca level and other elements increase consequently. Fe content in TFA-$FeCl_3$ was close to that in TFA-HCl–$FeCl_3$, and which was obviously higher than that in FA and TFA-HCl. It indicated that the modification of $FeCl_3$ aqueous solution can increase the Fe content in fly ash.

The results of BET characterization showed that SSA of treated fly ash was greater than that of untreated FA in the following sequence: TFA-HCL > TFA-HCl/$FeCl_3$ > TFA-$FeCl_3$ > FA (48.89, 28.67, 10.13, and 3.16 m^2/g, respectively) (listed in Table 1). The greater SSA of TFA-HCl derives from surface modification by acid solution and increase of micropores caused by the dissolution of CaO [28]. The increased SSA of TFA-$FeCl_3$ was because of the hydrolysis of $FeCl_3$, which made the solution acidic, and it also had the effect of acid treatment.

XRD patterns of fly ashes are shown in Fig. 2. The TFA-HCl has a similar XRD pattern to that of FA, but the peaks of $CaCO_3$ and Fe_2O_3 became weak, which could be ascribed to the HCl treatment. After the treatment with $FeCl_3$ aqueous solution, the peaks of $CaCO_3$ and CaO in the XRD pattern of TFA-$FeCl_3$ also became weak, which was due to the acidity of $FeCl_3$ aqueous solution and it can cause the dissolution of $CaCO_3$ and CaO. Element analysis showed that the modification of $FeCl_3$ can increase the Fe content in the fly ash (listed in Table 1), but the peaks of Fe_2O_3 in the patterns of TFA-$FeCl_3$ and TFA-HCl–$FeCl_3$ did not become stronger and no other characteristic peaks of iron-containing crystal were found, which can be derived from the fact that iron-containing compounds formed by the modification of $FeCl_3$ were non-crystalline.

SEM images of the fly ash samples were presented in Fig. 3. SEM images (Fig. 3(a)) of FA showed that the sample was composed of irregular particles and no cenospheres, as the literature reported [28,29], were observed. The shapes of coal fly ash particles had a close relation to combustion time and temperature [30], and the coal fly ash used in the experiments was circulating fluidized bed boiler ash which was

Table 1
Chemical elements and SSA of samples

	Conc. (%)			
Element	FA	TFA-HCl	TFA-$FeCl_3$	TFA-HCl–$FeCl_3$
O	45.09	45.16	44.69	44.11
Si	20.93	23.10	20.88	20.66
Ca	11.39	8.61	8.95	8.82
Al	10.66	11.22	10.15	10.04
Fe	2.80	2.81	6.19	6.33
Mg	2.74	2.76	2.52	2.54
K	0.43	0.42	0.43	0.42
Cu	0.37	0.36	0.36	0.36
Na	0.22	0.21	0.23	0.22
Zn	0.18	0.17	0.17	0.18
Ti	0.16	0.17	0.17	0.16
Specific surface area (m^2/g)	3.16	48.89	10.13	28.67

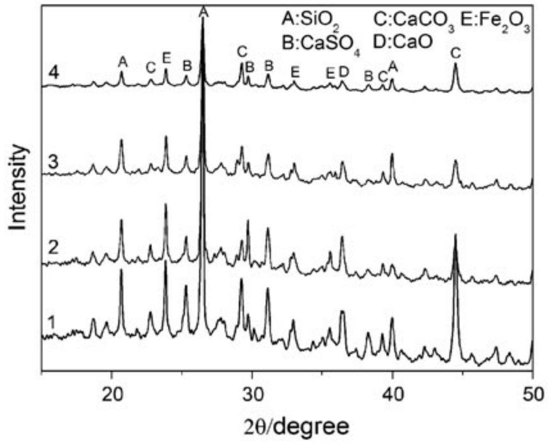

Fig. 2. XRD patterns of fly ash samples: (1) FA; (2) TFA-HCl; (3) TFA-$FeCl_3$; and (4) TFA-HCl–$FeCl_3$.

produced at a comparatively low combustion temperature. After being treated with the HCl aqueous solution, the surface of the particles became very rough (Fig. 3(b)). Fly ash particles became small and many other minute particles emerged (Fig. 3(c)), after being treated with the $FeCl_3$ aqueous solution. Compared with TFA-$FeCl_3$, the particles in TFA-HCl/$FeCl_3$ were smaller (Fig. 3(d)) and the hydrolysis product of $FeCl_3$ cohered to fly ash particles to form porous aggregations.

3.2. Oil removal

The maximum oil removal capacities of treated fly ashes were higher than that of the untreated FA in the following manner: TFA-HCl/$FeCl_3$ > TFA-$FeCl_3$ > TFA-HCl > FA (94.7, 86.3, 80.1, and 62.0%) (Fig. 4). The SSA of the fly ash can be increased by treating with HCl from 3.16 to 48.89 m^2/g (Table 1), and so the adsorption capacity of TFA-HCl also increased. While the modification of $FeCl_3$ can increase the Fe content in fly ash, Fe^{3+} ions have the effect of flocculation [31–33], in addition, $FeCl_3$ aqueous solution possess acidic property because of hydrolysis, which can also increase the SSA of fly ash; so, it was concluded that the two above factors resulted in the ratio of oil removal with TFA-$FeCl_3$ being slightly higher than that of TFA-HCl. The highest oil removal capacity of TFA-$FeCl_3$–HCl may be derived from the synergetic effect between adsorption and flocculation. It also showed that all studied fly ashes have capacities of removing oil fast, in particular during the first 30 min. After 1–4 h of treatment, only TFA-$FeCl_3$ and TFA-HCl–$FeCl_3$ showed an additional capacity of oil removal.

3.3. The effect of pH on the treatment

It was found that the ratio of oil removal of all studied fly ashes first increased and later decreased as the pH increased (as shown in Fig. 5). In general, the ratio reached the maximum in alkaline condition (pH 8–10). As to TFA-HCl–$FeCl_3$, the ratio reached maximum when pH 10. In alkaline condition, Fe^{3+} and OH^- can form charged $Fe(OH)_3$ colloids, which can make oppositely charged colloids that aggregate and settle by flocculation. There is a synergistic effect between flocculation and adsorption which makes the effect of oil removal better. But hydroxylation appears when the pH of the solution is too high [34], which would lead to the decrease of the absorption capacity.

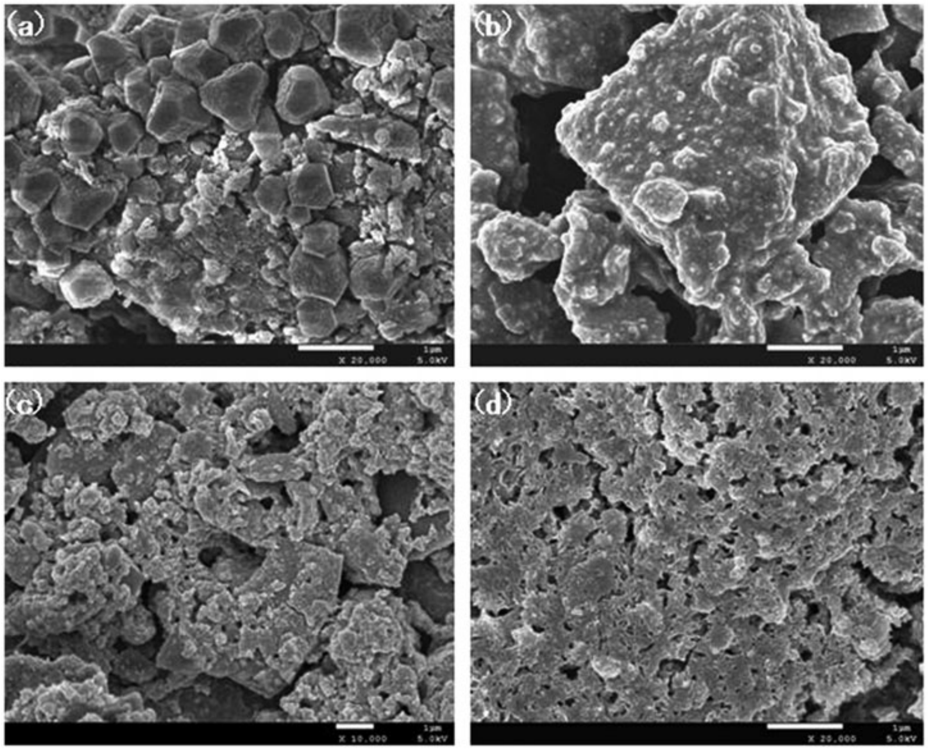

Fig. 3. SEM images of fly ash samples: (a) FA; (b) TFA-HCl; (c) TFA-$FeCl_3$; and (d) TFA-HCl–$FeCl_3$.

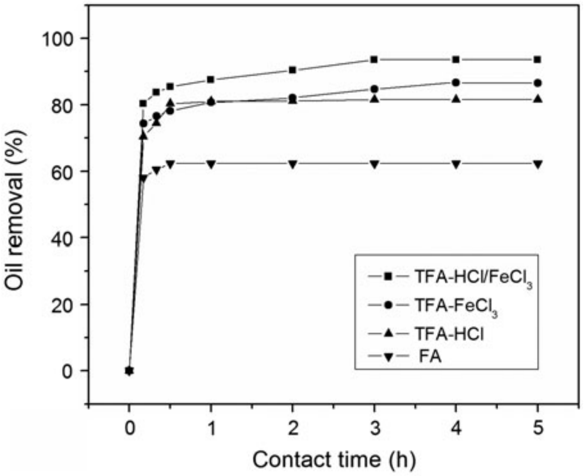

Fig. 4. Capacities of oil removal of fly ashes; experimental condition: dose 4% (W/V); temperature 20℃; and pH 7.0.

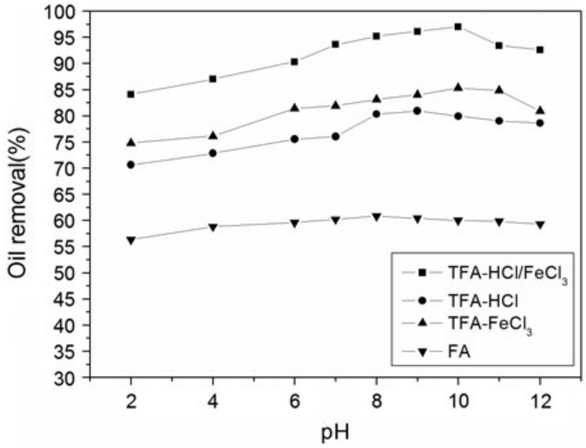

Fig. 5. Effect of pH on the ratio of oil removal; experimental condition: dose 4% (W/V); contact time 3 h; and temperature 20℃.

3.4. The effect of dose on the treatment

Generally, as showed in Fig. 6, the ratio of oil removal increased as the dose of fly ash increased, but the ratio increased with a very small amplitude when the dose was more than a certain value. Although the ratio of oil removal could be increased by increasing the dose of fly ash, but from a practical view point, large amounts of fly ash would increase sewage sludge and the cost of treatment.

3.5. The effect of temperature on the treatment

On the whole, as Fig. 7 shows, the ratio of oil removal of all studied fly ashes decreased as the

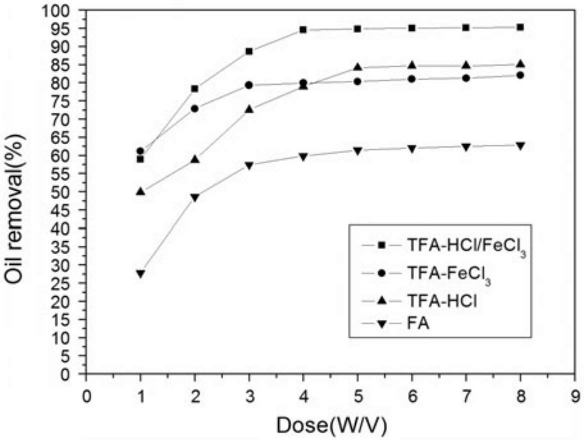

Fig. 6. Effect of dose on the ratio of oil removal; experimental condition: contact time 3 h; pH 7; and temperature 20℃.

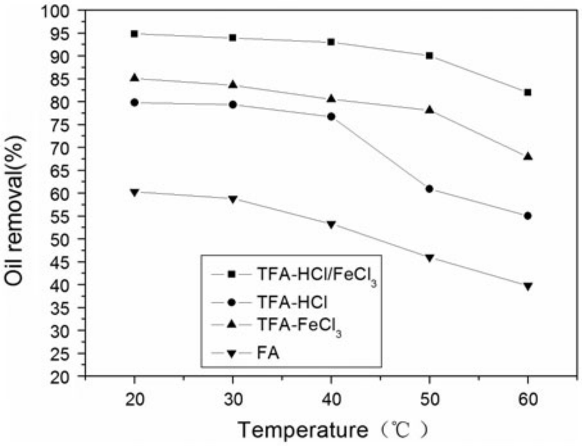

Fig. 7. The effect of temperature on the ratio of oil removal; experimental condition: dose 4% (W/V); pH 7; and contact time 3 h.

temperature increased. The capacity of oil removal of TFA-HCl–FeCl$_3$, TFA-FeCl$_3$, and TFA-HCl decreased slowly from 20 to 40℃, and the ratio declined obviously when the temperature was higher than 40℃, especially for TFA-HCl. To FA, the capacity of oil removal declined in a linear trend to some extent, when temperature was higher than 30℃.

4. Conclusion

Fly ash was treated with HCl, FeCl$_3$, and HCl–FeCl$_3$, and all studied fly ashes were used to remove oil from oilfield wastewater. Physical and chemical properties of all fly ashes were characterized. SEM and BET analysis showed that HCl treatment can increase the SSA of FA. The XRF analysis revealed that FeCl$_3$ aqueous solution treatment can increase the Fe content in the fly ash. XRD patterns indicated that HCl treatment and FeCl$_3$ treatment can both cause the decrease of CaCO$_3$ and CaO in FA. Oil removal experiments showed that the capacity of oil removal of FA can be effectively enhanced by HCl, FeCl$_3$, and HCl–FeCl$_3$ treatment. HCl–FeCl$_3$ treated fly ash has the best oil removal capacity, which may stem from the synergetic effect between adsorption and flocculation. Meanwhile, contact time, temperature, pH, and dose affect the effect of oil removal. In the oil removal experiment with TFA-HCl–FeCl$_3$, the ratio of oil removal can reach up to 96.8% and the content of oil reduced sharply from 262 to 8.4 mg/L. The method set forth in the paper has potential application in fast and deep removal of oil from oilfield wastewater.

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References

[1] D. Feng, L. Liu, P. Wang, H. Zhang, X. Xie, The experimental study of natural sedimentation in heavy oil, Adv. Mater. Res. 413 (2011) 60–64.
[2] R. Moosai, R.A. Dawe, Gas attachment of oil droplets for gas flotation for oily wastewater cleanup, Sep. Purif. Technol. 33 (2003) 303–314.
[3] A.L. Ahmad, S. Sumathi, B.H. Hameed, Coagulation of residue oil and suspended solid in palm oil mill effluent by chitosan, alum and PAC, Chem. Eng. J. 118 (2006) 99–105.
[4] F.P.M. Farias, C.J.O. Buriti, W.C.P.B. Lima, S.R. Farias Neto, A.G.B. Lima, The effect of droplet diameter on the separation of heavy-oil from water using a hydrocyclone, Defect Diffus. Forum 303–304 (2010) 131–137.
[5] P.J. Borm, Toxicity and occupational health hazards of coal fly ash (cfa). A review of data and comparison to coal mine dust, Ann. Occup. Hyg. 41 (1997) 659–676.
[6] S. Aziz, S.A. Soomro, A.H. Tunio, I. Nazir, K.M. Qureshi, R. Begum, Environmental & health hazards of fly ash & SO$_x$ from FBC power plant at Khanote, Pak. J. Anal. Environ. Chem. 11 (2010) 56–62.
[7] A. Akgerman, M. Zardkoohi, Adsorption of phenolic compounds on fly ash, J. Chem. Eng. Data 41 (1996) 185–187.
[8] B. Dutta, J.K. Basu, S. DasGupta, Removal of cresol from aqueous solution using fly ash as adsorbent: Experiments and modeling, Sep. Sci. Technol. 38 (2003) 1345–1360.

[9] D. Batabyal, A. Sahu, S.K. Chaudhuri, Kinetics and mechanism of removal of 2,4-dimethyl phenol from aqueous solutions with coal fly ash, Sep. Technol. 5 (1995) 179–186.

[10] H. Nollet, M. Roels, P. Lutgen, P. Van der Meeren, W. Verstraete, Removal of PCBs from wastewater using fly ash, Chemosphere 53 (2003) 655–665.

[11] A.K. Sen, A.K. De, Adsorption of mercury(II) by coal fly ash, Water Res. 21 (1987) 885–888.

[12] R. Apak, E. Tütem, M. Hügül, J. Hizal, Heavy metal cation retention by unconventional sorbents (red muds and fly ashes), Water Res. 32 (1998) 430–440.

[13] J. Ayala, F. Blanco, P. García, P. Rodriguez, J. Sancho, Asturian fly ash as a heavy metals removal material, Fuel 77 (1998) 1147–1154.

[14] B.P. Kelleher, M.N. O'Callaghan, M.J. Leahy, T.F. O'Dwyer, J.J. Leahy, The use of fly ash from the combustion of poultry litter for the adsorption of chromium(III) from aqueous solution, J. Chem. Technol. Biotechnol. 77 (2002) 1212–1218.

[15] A.K. Bhattacharya, T.K. Naiya, S.N. Mandal, S.K. Das, Adsorption, kinetics and equilibrium studies on removal of Cr (VI) from aqueous solutions using different low-cost adsorbents, Chem. Eng. J. 137 (2008) 529–541.

[16] N. Koukouzas, C. Vasilatos, G. Itskos, I. Mitsis, A. Moutsatsou, Removal of heavy metals from wastewater using CFB-coal fly ash zeolitic materials, J. Hazard. Mater. 173 (2010) 581–588.

[17] G. Itskos, N. Koukouzas, C. Vasilatos, I. Megremi, A. Moutsatsou, Comparative uptake study of toxic elements from aqueous media by the different particle-size-fractions of fly ash, J. Hazard. Mater. 183 (2010) 787–792.

[18] C.A. Gray, A.P. Schwab, Phosphorus-fixing ability of high pH, high calcium, coal-combustion, waste materials, Water Air Soil Pollut. 69 (1993) 309–320.

[19] A. Al-Shawabkeh, H. Maisuda, M. Hasatani, Comparative reactivity of treated FBC- and PCC-fly ash for SO_2 removal, Can. J. Chem. Eng. 73 (1995) 678–685.

[20] P. Davini, Flue gas treatment by activated carbon obtained from oil-fired fly ash, Carbon 40 (2002) 1973–1979.

[21] G.Q. Lu, D.D. Do, Adsorption properties of fly ash particles for NO_x removal from flue gases, Fuel Process. Technol. 27 (1991) 95–107.

[22] X. Querol, A. Alastuey, J.L. Fernández-Turiel, A. López-Soler, Synthesis of zeolites by alkaline activation of ferro-aluminous fly ash, Fuel 74 (1995) 1226–1231.

[23] X. Querol, A. Alastuey, A. López-Soler, F. Plana, A fast method for recycling fly ash: Microwave-assisted zeolite synthesis, Environ. Sci. Technol. 31 (1997) 2527–2533.

[24] X. Querol, J.C. Umaña, F. Plana, A. Alastuey, A. Lopez-Soler, A. Medinaceli, A. Valero, M.J. Domingo, E. Garcia-Rojo, Synthesis of zeolites from fly ash at pilot plant scale. Examples of potential applications, Fuel 80 (2001) 857–865.

[25] N. Koukouzas, C. Ketikidis, G. Itskos, X. Spiliotis, V. Karayannis, G. Papapolymerou, Synthesis of CFB-coal fly ash clay bricks and their characterisation, Waste Biomass Valorization 2 (2011) 87–94.

[26] A.K. Mathur, Ash utilisation in NTPC, in: Proceedings of the Workshop on Fly Ash Utilisation: Issues and Strategies, New Delhi, 2000, pp. 41–45.

[27] Y.K. Lin, Compressibility, strength, and frost susceptibility of compacted fly ash, PhD thesis, University of Michigan, MI, 1971.

[28] P. Pengthamkeerati, T. Satapanajaru, P. Chularuengoaksorn, Chemical modification of coal fly ash for the removal of phosphate from aqueous solution, Fuel 87 (2008) 2469–2476.

[29] S. Katara, S. Kabra, A. Sharma, R. Hada, A. Rani, Surface modification of fly ash by thermal activation: A DR/FTIR study, Int. Res. J. Pure Appl. Chem. 3 (2013) 299–307.

[30] S.C. Openshaw, Utilization of Coal Fly Ash, M.Sc thesis, University of Florida, FL, 1992.

[31] T. Tripathy, B.R. De, Flocculation: A new way to treat the waste water, J. Phys. Sci. 10 (2006) 93–127.

[32] O.P. Sahu, P.K. Chaudhari, Review on chemical treatment of industrial waste water, J. Appl. Sci. Environ. Man. 17 (2013) 241–257.

[33] J. Gregory, J. Duan, Hydrolyzing metal salts as coagulants, Pure Appl. Chem. 73 (2001) 2017–2026.

[34] T. Lopez, I. Garcia-Cruz, R. Gomez, Synthesis of magnesium oxide by the sol–gel method: Effect of the pH on the surface hydroxylation, J. Catal. 127 (1991) 75–85.