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Effect of catalytic ozonation on the TOC removal and anions separation treating coal chemical brine by nanofiltration membranes

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ABSTRACT

This study explored the performance of catalytic ozonation hybrid two-stage nanofiltration (NF) membrane processes treating the coal chemical brine which has high levels of salinity and organic pollutants. A novel catalyst composed of waste coal fly ash and biogas residues was used in catalytic ozonation, which led organic compounds concentrated in a smaller molecular weight distribution. It was observed that flux of catalytic ozonation hybrid two-stage NF membranes was 1.9 times higher than two-stage NF membrane after 15 h operation. Meanwhile, the total organic carbon (TOC), SO_4^{2-}, and Cl^{-1} removal efficiencies of catalytic ozonation hybrid two-stage NF membranes increased by 24%, 12%, and –11%, contrast to the only two-stage NF membranes and it significantly improved the NF performance of the TOC removal and anions separation. And the results offered new insights for sustainable use of waste sources.

Keywords: Coal chemical brine; Catalytic ozonation; Nanofiltration; Anions separation; TOC removal

1. Introduction

In recent years, zero liquid discharge should be strictly achieved for individual coal chemical industries to reduce water consumption and protect environment. And series of reverse osmosis (RO) membrane was applied to reuse the biologically pretreated coal chemical industrial wastewater to provide the high-quality water. And RO brine (defined as coal chemical brine) was further treated by evaporating and crystallizing as the key processes to produce the industrial salt [1,2].

The coal chemical brine contained high concentrations of SO_4^{2-}, Cl^{-1}, NO_3^{-1} and other cations of Na^+, K^+, Ca^{2+}, and Mg^{2+}. As a result, the industrial salt from the crystallizer was mixed by high concentrations of metabolic and intermediate product biodegraded from phenolic compounds, polynuclear aromatic hydrocarbons, nitrogenous heterocyclic compounds, and so on [3]. And nowadays, reuse of the industrial salt has drawn the wide attention to resolve the issues of high salt production and its expensive cost. However, the high concentration of organic compounds in the brine not only seriously limited the stable operation of evaporator and crystallizer, but also reduced the quality of the salt [4]. Moreover, separation of the mixed salt to produce high-quality single salt was another resource recycling issue which should be broke through [5].

Ozone is a powerful oxidant, which can result in degradation and mineralization of refractory pollutants by the ozone and hydroxyl radicals (•OH) in a series of chain reactions [6,7]. Additionally, ozonation using the transition metals as catalyst has drawn wide attention in organic

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compounds degradation [8,9]. Coal fly ash (CFA) loading on activated biochar from biogas residue as catalyst was a promising material owing to low cost, high efficiency, and additional economic benefits of waste sources [10], but it was rarely studied. Therefore, the catalytic ozonation was speculated to be a promising process to oxide organic compounds in the coal chemical brine [7]. Nanofiltration (NF) is a pressure-driven membrane separation process and the pores are typically near 1 nm in diameter and have fixed charges [11]. NF process represented the typical ability to retain multivalent complexions and permeate small uncharged solutes and low charged ions, due to the combination of size and electrical effects [12–14]. Therefore, NF process provided a feasible method to separate the sulfate and chloride to achieve the goal of separation of the industrial salt. However, the high levels of organic compounds in the coal chemical brine would cause serious organic membrane fouling in the NF membrane which should be properly resolved.

In this study, catalytic ozonation hybrid two-stage NF membranes were developed as a novel system to treat the coal chemical brine. The main objects were to investigate the effect of novel catalyst on performance of the ozonation, the influences of ozonation on the organic compounds removal, anions separation, and fouling mitigation of the two-stage NF.

2. Materials and methods

2.1. Coal chemical brine characteristics

The RO concentrate was taken from the brine of the two-stage RO membranes in a coal gasification wastewater treatment plant, the main characteristics were as follows: 200–240 mg/L of total organic carbon (TOC), 500–530 mmol/L of chloride, 200–210 mmol/L of sulfate, 30–36 mg/L of nitrite, and 45–57 mmol/L of nitrate. The pH ranged between 9.0 and 10.0.

2.2. Experimental procedure

Laboratory-scale experiments were carried out. The ozone dosage was 50 mg/L, the catalyst dosage was 3 g/L and the hydraulic reaction time (HRT) was 60 min. Valve and peristaltic pump were used to control the ozone dosage and HRT. Catalyst was added only one time after saturation. In addition, a buffer reactor (HRT of 30 min) was set between catalytic ozonation and NF membranes. The NF operation pressure was 20 bar and the original flux was 150 L/m^2 h (maximum flux of the NF membrane), and the samples of the effluent were measured after 15 h operation. The experiments were divided into three periods: (1) experiments with only NF for 10 d; (2) experiments with ozonation hybrid NF for 10 d; and (3) experiments with catalytic ozonation hybrid NF for 10 d, all the data shown in the study were the average values (three times). The CFA was loaded on the biochar (made from biogas residue) by one-step method combining the carbonization and metal-loaded as the novel catalyst in the experiments.

2.3. Analytical methods

The TOC was determined by a TOC analyzer (TOC-CPN, Shimadzu, Japan). The analyses of Cl^-, SO_4^{2-}, and NO_3^- were carried out using ion chromatography equipment (ICS-1100, Thermo Fisher Scientific, USA). Scanning electron microscopy (SEM, FEI Helios NanoLab 600i) was used to visualize the surface structures of the samples, and X-ray diffraction (XRD, RigakuD/max-2000) was used for analysis of elemental composition with monochromatic Cu Ka radiation (45 kV, 50 mA). In order to reveal the characteristics of the organic compositions of the effluent, specimens were analyzed by gas chromatography–mass spectrometry (GC-MS) (Agilent 6890N-5973N) and molecular weight. In addition, the main characteristics of the catalyst were analyzed by N_2 adsorption–desorption experiments (Micromeritics ASAP 2020).

3. Results and discussion

3.1. Effect of NF

The ions separation performance using NF treating coal chemical brine was examined via the one-stage NF membrane (defined as NF I) and two-stage NF membranes (defined as NF II). As shown in Fig. 1, NF represented different influence on the TOC and ions removal. Remarkable SO_4^{2-} removal was observed with NF I, giving the removal efficiency of 71%, while the TOC removal was lower than SO_4^{2-}. But in contrast, the concentrations of Cl^{-1} and NO_3^- have been slightly increased, it was mainly related with the NF membrane characteristics of passage of an appreciable amount of monovalent ions and substantially higher rejection of divalent ions than monovalents [15], and the Donnan effect was another important role on the observation. In order to further improve the performance of anions separation, two-stage NF membranes were studied and the results were also illustrated in Fig. 1. As revealed that the NF II represented higher TOC and SO_4^{2-} removal efficiencies than NF I, while more Cl^{-1} and NO_3^- were accumulated in the production water. According to the results, the TOC removal efficiencies of NF I and NF II reached 25% and 42%, respectively, however, remarkably higher TOC removal efficiency was observed in NF I than NF II in the previous literature [16], and it was mainly owing to the different organic compounds molecular weight in the brine.

GC-MS was applied to realize the main organic compositions in the coal chemical brine and the effluent of NF I and NF II, and the results are shown in Fig. 2. It was indicated that the hydrocarbon, naphthalene, benzene, ester, phenol, and

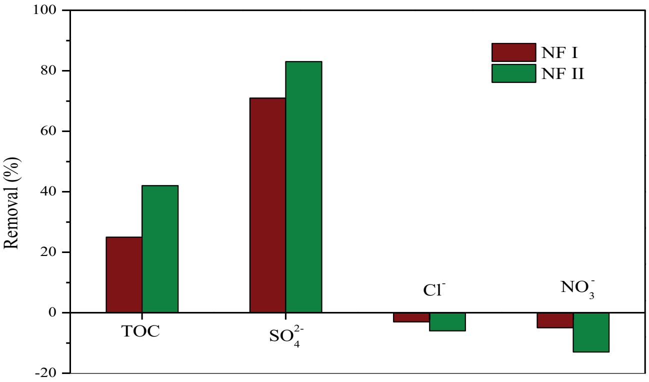

Fig. 1. TOC and anions removal by the NF membrane (NF I, one-stage NF membrane; NF II, two-stage NF membranes).

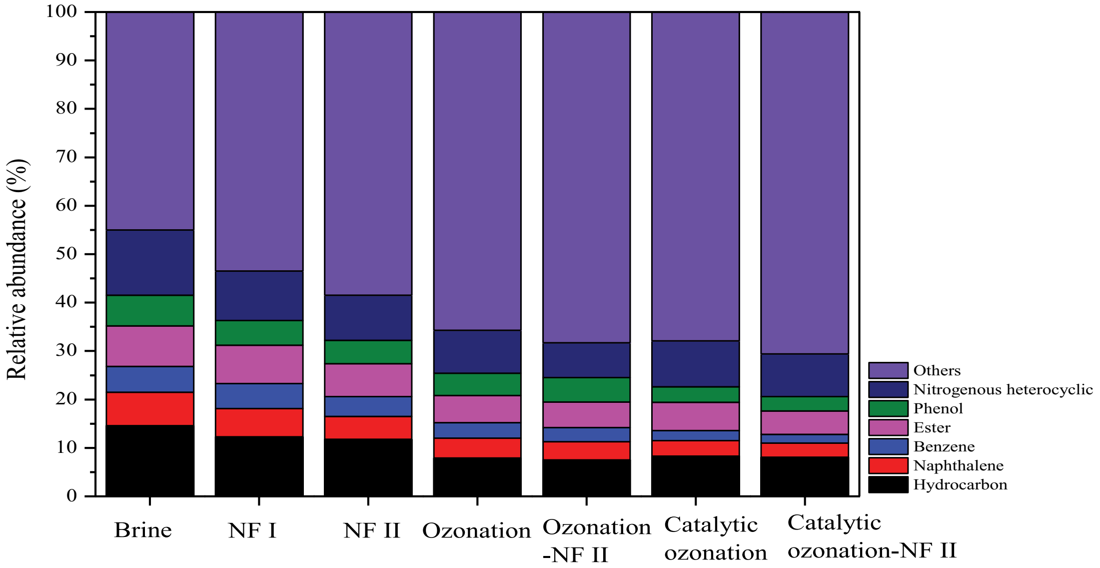

Fig. 2. Main organic compositions of the effluent in different processes (NF I, one-stage NF membrane; NF II, two-stage NF membranes; ozonation-NF II, ozonation hybrid two-stage NF membranes; catalytic ozonation-NF II, catalytic ozonation hybrid two-stage NF membranes).

nitrogenous heterocyclic composed the main compositions and slight variations were observed between influent and effluent of NF I and NF II, and it was possibly related with the molecular weight distribution in a small range. As shown in Table 1, the high molecular weight in the brine accounted a small portion because the brine was concentrated from the effluent of the coal chemical industrial wastewater treated by biodegradable processes. Therefore, most of the high molecular weight compounds have been oxidized to smaller one which was also demonstrated by the previous literature [17], while the TOC removal effect of the NF was significantly limited. Relying on the previous report, the rejections of higher molecular weight compounds by NF were increased as the molecular weight increased [18].

3.2. *Effect of catalytic ozonation on performance of NF*

3.2.1. TOC removal

Ozone is a powerful oxidant ($E = 2.07$ eV), which can react as an electrophilic and nucleophilic agent, and in alkaline medium, the oxidation capacity of ozone can be enhanced by the formation of highly reactive $^{\bullet}$OH ($E = 2.8$ eV) in a series of chain reactions [7]. As shown in Fig. 3, ozonation played an important role on the TOC removal, which was 10% higher than NF II process. Contrast to the influent of coal chemical brine, 83 types of organics were reduced after oxidation. Furthermore, the distribution of molecular weight higher than 700 was decreased, while slight increment of the range of 700–400 was observed, it was speculated that ozonation in this study was inclined to create middle molecular weight organics rather than smaller organics (Table 1). And the TOC removal efficiency was increased by 8% when the NF II was used to treat the effluent of ozonation. In order to further improve the ozonation performance on the TOC removal, specific catalyst was investigated to stimulate the oxidation capacity, and the TOC removal was increased by 13% using the catalyst of CFA/BRAC (biogas residues activated carbon). Zhuang et al. [17] have reported that the enhanced ozonation ability by catalyst was attributed to generating more hydroxyl radicals and most of the toxic and refractory compounds were removed in ozonation with catalysts and this was possibly related with the constructer and compositions of the catalyst.

As shown in Fig. 4(a), a slightly rough porous surface was observed for the biochars before loading the CFA catalyst.

Table 1
Variations of organics type number and molecular weight distribution

Process	Type no.	Molecular weight distribution (%)						
		>700	600–700	500–600	400–500	300–400	200–300	<200
Brine	145	6.1	4.8	6.2	5.5	27.6	24.1	25.7
Ozonation	62	4.8	7.5	9.1	6.5	17.7	24.2	30.2
Ozonation-NF II	62	2.1	4.2	7.5	6.3	17.9	26.3	35.7
Catalytic ozonation	55	3.5	5.7	7.3	8.5	23.6	18.5	32.9
Catalytic ozonation-NF II	55	3.4	4.5	6.5	8.3	22.6	19.9	34.8

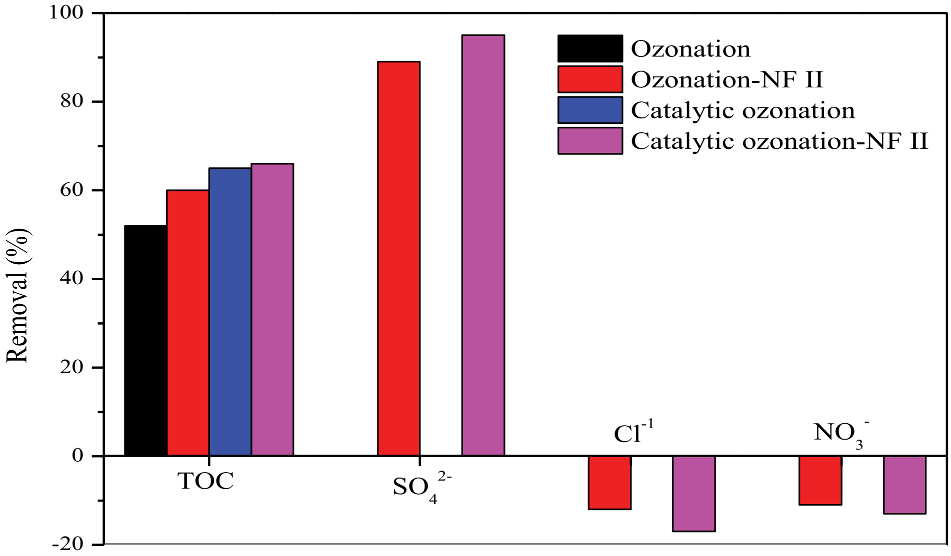

Fig. 3. TOC and anions removal by different processes (ozonation-NF II, ozonation hybrid two-stage NF; catalytic ozonation-NF II, catalytic ozonation hybrid two-stage NF).

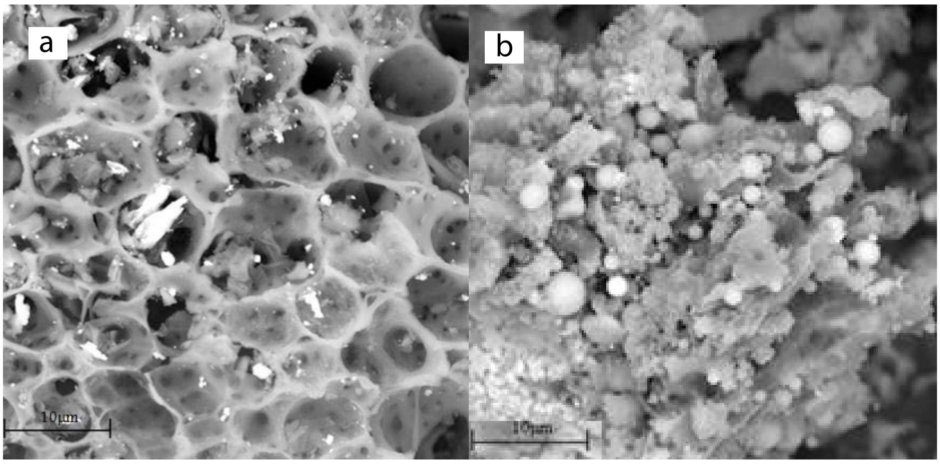

Fig. 4. SEM images of (a) BRAC and (b) CFA/BRAC composite (BRAC, biogas residues activated carbon; CFA/BRAC, coal fly ash loading on biogas residues activated carbon).

It was clear that the CFA particles successfully coated the surface of the BRAC or embedded in porous structure (Fig. 4(b)), and it was shown that the CFA was spherical in shape with the diameter in the range of 2–5 μm. As shown in Table S1, C, Si, Al, and Fe were detected as the domain elements in the catalyst with the ratio of 38.49%, 10.73%, 9.57%, and 7.22%, respectively. Fig. S1 displayed the XRD patterns of the CFA, BRAC, and CFA/BRAC. The diffraction peaks of CFA exhibited the similar crystal structure characteristic peaks of the Fe_3O_4 particles and this indicated that the Fe oxide was probably of Fe_3O_4 in this composite. In addition, it was shown that almost all of the diffraction peaks for CFA appeared in the XRD pattern of the CFA/BRAC catalyst, which indicated that the Fe_3O_4 particles were successfully loaded onto the surface of the BRAC. It was speculated that Fe_3O_4 contained both Fe^{2+} and Fe^{3+}, electron transfer between high and low valence of metal ion could promote the chain reactions, furtherly, the ozonation was enhanced, this observation was consistent with the previous literatures [17].

3.2.2. Anions separation and possible mechanisms

It was observed that both ozonation and catalytic ozonation represented slight effect on anions separation. However, contrast to only NF II, catalytic ozonation hybrid NF II represented enhanced anions separation performance, specially, the SO_4^{2-} removal efficiency increased by 6% while the Cl^{-1} removal efficiency decreased by 6% (Fig. 3). Therefore, increasing ratio of Cl^{-1}/SO_4^{2-} can further meet the standards of chlor-alkali industry, which requires the sodium chloride content higher than 95%.

As shown in Table 1, the catalytic ozonation remarkably changed the molecular weight distribution by oxidizing high-molecular weight organics (700–500) to smaller

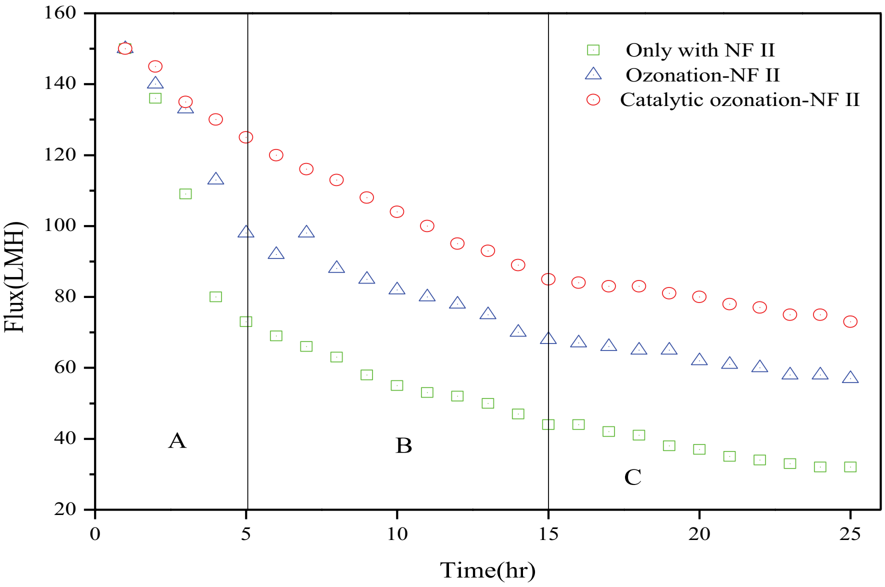

Fig. 5. Flux decline of brine only with NF II, with ozonation-NF II, and with catalytic ozonation-NF II.

molecular weight organics (<200), which revealed the catalyst might increase the contact opportunity between $^\bullet$OH and smaller molecular weight organics and to some extent enhanced the reaction strength.

Additionally, it was observed that the NF II process could not affect the organic types of the effluent after ozonation or catalytic ozonation (Table 1), but could concentrate the molecular distributions in a smaller range. It was speculated that the NF II showed excellent capacity to reject the higher molecular weight organics, therefore, the catalytic ozonation created much lower molecular weight organics which could not be efficiently rejected by NF II.

The influences of ozonation and catalytic ozonation on the permeate flux of the NF II process are shown in Fig. 5. All the variations of permeate flux could be divided into three periods, sudden decline period (A), slow decline period (B), and steady period (C) which was associated with the serious fouling, the observation of period C revealed that the NF membrane cleaning was needed. It was clearly observed that the catalytic ozonation represented more excellent performance than only ozonation on maintaining NF permeate flux, and this was mainly related with the decreasing molecular weight (shown in Table 1), which can prevent making a membrane with a denser skin layer as well as a lower flux [14,19]. More importantly, it has been reported that many desalination plants experienced production lost due to incidents of organic and fouling while the ozonation could be effective in reducing the NF membrane fouling and significantly improve the NF performance [20,21], and this might be the possible causes for the improved rejection of SO$_4^{2-}$ and permeation of Cl^{-1}. The only NF II was faced with macromolecules organic compounds causing more serious fouling potential [19], and this inevitably changed the surface properties of pore size and electrical effects of the NF membrane and furthermore, negatively influenced the separation of multivalent and monatomic ions. While the ozonation process created smaller organic compounds which significantly mitigated the fouling and maintained the original characteristics of the NF membrane, and it resulted in 12% increment on SO$_4^{2-}$ removal and 11% increment on Cl^{-1} permeation contrast to only NF II, while catalytic ozonation represented 6% and –5% higher removal than ozonation alone. Therefore, the catalytic ozonation represented more promotion to improve the NF II performance in organic removal and anions separation, and it could be beneficial to the sequencing evaporation and crystallization, and finally achieve the zero liquid discharge.

4. Conclusions

Contrast to two-stage NF membranes, ozonation improved the TOC removal and anions separation and this performance was further enhanced by catalytic ozonation. This observation was mainly associated with specific characteristic of the CFA loading on the BRAC which stimulated the ozonation performance resulting in smaller molecular organic compounds, and it significantly mitigated the fouling, promoted the NF flux, and maintained the original characteristics of the NF membrane. Meanwhile, the organics compositions of the NF were affected by the pretreatment of ozonation or catalytic ozonation. Thus, catalytic ozonation hybrid two-stage NF process represented positive effect on improving salt quality from the coal chemical brine which facilitated resource reuse of the salt.

Acknowledgments

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Supplementary information

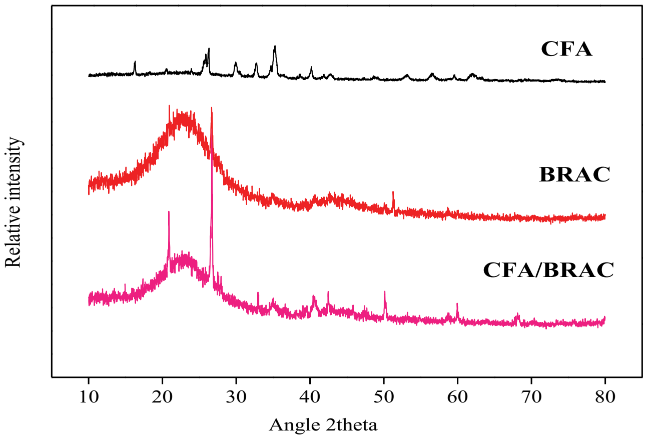

Fig. S1. XRD patterns of CFA, BRAC, and CFA/BRAC (CFA, coal fly ash; BRAC, biogas residues activated carbon; CFA/BRAC, coal fly ash and the biogas residues composite as the catalyst).

Table S1
Main characteristics of the biochars, CFA and CFA/BRAC

Parameters	BRAC	CFA	CFA/BRAC
S_{BET} (m^2/g)	475.3	3.2	424.7
$V_{meso(macro)}$ (cm^3/g)	0.352	–	0.317
V_{micro} (cm^3/g)	0.217	–	0.191
Pore size (nm)	6.513	–	5.642
Si (wt %)	5.22	21.71	10.73
Al (wt %)	2.08	23.52	9.57
Fe (wt %)	1.48	17.89	7.22
Ca	1.69		1.01
C (wt %)	35.87	–	38.49
H (wt %)	4.17	–	2.15
N (wt %)	1.55	–	1.23
P	6.52		4.32
K	1.62		1.17

CFA, coal fly ash; BRAC, biogas residues activated carbon; CFA/BRAC, coal fly ash and the biogas residues composite.