



Research article

Valorization of coal fired-fly ash for potential heavy metal removal from the single and multi-contaminated system



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ABSTRACT

In this study, adsorption of three different heavy metals i.e. cadmium (Cd (II)), copper (Cu (II)) and nickel (Ni (II)) was carried out in single and multi-contaminated system using coal-fired fly ash (CFFA). Initially, for the single contaminated system, various physical process parameters were selected for optimization by deploying Box–Behnken design of experiments. Further, the evaluation of CFFA for removal of heavy metals in a multi-component system from aqueous solution was performed by employing Plackett–Burman design of experiments with all the three heavy metals at two different levels by varying their initial concentration (10–50 mg L⁻¹). In both the aforementioned cases, CFFA showed its great potential for heavy metal removal, i.e. single and multi-component system and followed the order: Cu (II) > Ni (II) > Cd (II). Further, FTIR study confirmed the involvement of amide, aldehyde, alkoxy, alkanes, and alkene groups for heavy metal adsorption by CFFA.

1. Introduction

With a rapid increase in the industrialization, globally, wastewater generated from the metallurgical industries, chemical, paint, leather industries, pesticides processing factories and acid mine drainage etc. has led to increase in the discharge of heavy metals (HMs) into the aquatic stream (Kumar et al., 2018; Goswami et al., 2018a; Kushwaha et al., 2018, Wang et al., 2018). The discharge of heavy metals such as cadmium, lead, nickel, cobalt, copper, zinc, chromium and iron etc. has nowadays enhanced prominently, thus, diminishing the water eminence to the alarming levels (Wang et al., 2019a,b; Goswami et al., 2017a,b; Manikandan et al., 2016; Visa, 2016). Heavy metals are toxic and non-biodegradable pollutants which impose high toxicity even at a very low concentration and get accumulated in the food chain and adsorbed by the organisms resulting in severe health issues (Nebeska et al., 2018; Sathe et al., 2018; Kushwaha et al., 2019, 2017; Min et al., 2008).

Utilization of various physicochemical techniques including adsorption, chemical precipitation, electrochemical treatment, ion-exchange, advanced oxidation and membrane separation are well-known for heavy metal contaminated wastewater (Goswami et al., 2019a,b; Kumar et al., 2016). Amongst these techniques, adsorption phenomenon is well-accepted as it is economical, efficient, passive, eco-friendly, readily

available and minimum by-product after the treatment (Kushwaha et al., 2015). Numerous literature have reported the utilization of waste materials as the suitable adsorbents viz., food industry and agricultural wastes for HM removal (Kumar et al., 2014). Furthermore, the heavy metals contaminants mostly occur along with other organic and/or inorganic pollutants in the wastewater stream which imposes mostly antagonistic effect on HM removal efficiency in a multi-contaminated system. Therefore, a proper selection of adsorbent should be kept in mind so that it is well-capable in removing the heavy metals from the single as well as multi-contaminated system.

Coal-fired fly ash (CFFA), a waste material polluting air, water and soil, contains a trace amount of heavy metals, viz., mercury, arsenic, chromium, selenium, barium, and manganese etc. that is generated after the coal combustion (Zhao et al., 2018). It is among the major anthropogenic emission that is generated by the coal-fired power plants for power production. In 2015, the production of CFFA from the USA, China and India was approximately 130, 580 and 190 million tonnes per year, respectively (Yao et al., 2015). In accordance with its characteristic properties viz., chemical, physical and mineralogical, CFFA is utilized for various applications such as in construction industry, ceramic industry, catalysis, zeolite synthesis, valuable metal recovery, geo-polymers and adsorbents (Gupt et al., 2018; Zanoletti et al., 2017; He et al., 2016).

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Hence, there is a huge potential scope of utilizing CFFA, which in another way, is a kind of solid waste management and utilization that can also further leads to the circular economy.

In consideration with the aforementioned aspects, along with lacunae in the literature, addressing the different interactions of heavy metals in multi-pollutant system, the design of experiments for the present work was framed accordingly. Henceforth, in this study, potential evaluation of CFFA as an adsorbent for cadmium, copper and nickel in a single and multi-heavy metal contaminated systems. Initially, the adsorbent was characterized by various physical, chemical, magnetic, and morphological properties. Further, the effect of various process parameters was evaluated in the batch for single and multi-contaminated system, separately. Statistical tools such as response surface methodology (RSM) and Plackett-Burman design of experiment were further used to optimize the process parameters in the individual simulated system and to determine the antagonistic effect of HMs on each other's removal in the multi-contaminated system, respectively.

2. Experimental

2.1. Source and characterization of CFFA

The adsorbent, coal-fired fly ash (CFFA) was collected from a local thermal power plant. Initially the sample was washed with 0.5 M HNO₃, followed by pulverizing using the ball mill and was further sieved to collect the powder of size ≤ 45 nm. The ash content was determined by following the ASTM D1762-84 standard (Bind et al., 2018) while zeta potential (ZP) and average particle size were measured using a laser particle size analyzer (DelsaTM Nano, Beckman Coulter, England). Brunauer-Emmett-Teller (BET) analysis of the sample was carried out to determine its surface area by N₂ multilayer adsorption using Autosorb-IQ MP instrument (Quantachrome, USA) (Table 1). The crystallization behavior of CFFA was determined using X-ray diffractometer (XRD) (D8Advance, Bruker AXS, Germany) utilizing Cu K α as the radiation source recorded at 45 kV and in the range of 7 - 70°. Elemental composition of CFFA was determined using elemental analyzer (Eurovector EA3000, Germany) whereas the magnetic property was determined using a vibrating sample magnetometer (Lake Shore Cryotronics, USA) (Nguyen et al., 2011). Fourier transform infrared (FTIR) spectrophotometer was utilized for determining the presence of different functional groups onto the adsorbent (Borah et al., 2019; Bhasney et al., 2017). The surface morphology was examined under field emission scanning electron microscope equipped with energy dispersive spectroscopy (FESEM-EDX). Micrographs of the samples were recorded at an operating condition of 3.0 kV (Goswami et al., 2017c).

2.2. Chemicals

Analytical grade chemicals procured from Merck (Mumbai, India) was utilized for making the individual HM stock solutions of Cu (II), Cd (II) and Ni (II) of concentration 100 mg L⁻¹ each were prepared utilizing CuCl₂·2H₂O, Cd (NO₃)₂ and NiCl₂·6H₂O, respectively. The subsequent volume of HM solutions was prepared deionized water (18.1 Ω) with proper dilution for both the individual and multi-component studies.

2.3. Batch experiment set-up

Batch experiments were performed in the Erlenmeyer flasks (250 mL)

Table 1
Surface and magnetic properties of the adsorbent.

Surface area and pore diameter	Magnetic Properties		
BET surface area (m ² g ⁻¹)	17.4	Retentivity (emu g ⁻¹)	2.1 $\times 10^{-3}$
Average Pore diameter (nm)	1.09	Magnetization (emu g ⁻¹)	91.4 $\times 10^{-3}$
		Coercivity (Oe)	10.87

having 100 mL of the respective concentration of an aqueous heavy metal solution with a continuous agitation speed of 120 rpm, for both the individual and multi-component studies.

2.3.1. Individual component study

For examining the effect of different process parameters onto the adsorption phenomena, five different parameters viz., pH (A: 3–7), initial metal concentration (B: 10–50 mg L⁻¹), adsorbent dose (C: 0.05–0.5 g L⁻¹), temperature (D: 20–50 °C) and contact time (E: 5–90 min) were analyzed. Further, the samples were collected, filtered and analyzed for residual HM concentrations by atomic absorption spectroscopy (Perkin Elmer, Analyst 400, England) (APHA, 2005).

Also, Box-Behnken design of experiment was utilized for optimizing the process parameters utilizing statistical software Minitab (Version 16, PA, USA). Three different levels, i.e. -1, 0 and +1 signifying low, medium and high values for each factor was varied. Table S1 shows all of the experimental runs (46) to optimize the levels of the selected process parameter variables which was selected based on the preliminary experiments and literature and were performed in triplicates.

2.3.2. HM removal from the multi-contaminated system

For examining HM removal in a multi-contaminated system, a Plackett-Burman experimental design having 12 experimental runs with various combination levels of Cd (II), Cu (II) and Ni (II) was selected (Table 2) (Goswami et al., 2018b). The lower and upper limits of the concentration for each of Cd, Cu and Ni were selected as 10 and 50 mg L⁻¹, respectively. All of the initial levels of HM were based on the aforementioned single contaminated system.

2.4. Characterization of metal-loaded CFFA

Characterization of the HM-loaded samples obtained after the two experiments (single and multi-component) was performed by FESEM-EDX and FTIR spectroscopy (Goswami et al., 2019c). The samples were investigated for the morphological and elemental composition utilizing FESEM-EDX (Zeiss, Sigma, Germany). For FTIR analysis, CFFA and HM-loaded CFFA samples were examined using the FTIR spectroscopy (Perkin Elmer, Singapore).

2.5. Regeneration of the exhausted biosorbents and cost estimation

For evaluating the cost-efficiency, desorption experiments were performed using 0.1 N of HCl, H₂SO₄, and HNO₃ as the stripping agents. The metal-loaded adsorbed was further transferred to the flasks and kept in an orbital shaker at 150 rpm for 24 h. Following this, filtrates were further analyzed to evaluate the percentage fraction of desorbed heavy metal ions. Successive biosorption-desorption cycles were repeated

Table 2

Plackett-Burman experimental design matrix showing the various combination levels of the heavy metals in the multi-component study along with the removal efficiencies by coal-fired fly ash.

Exp. Run	Cd	Cu	Ni	Heavy metal removal (%)		
				Cd (%)	Cu (%)	Ni (%)
1	-	+	-	88.07	95.51	91.37
2	+	-	+	89.23	96.11	92.84
3	-	+	+	79.16	93.59	87.79
4	+	+	+	74.03	91.18	86.51
5	-	-	-	91.17	96.96	94.48
6	+	-	+	89.28	96.14	92.81
7	-	-	-	91.16	96.95	94.48
8	+	+	-	86.57	95.13	90.86
9	+	+	-	86.54	95.19	90.87
10	-	-	+	90.67	96.21	93.36
11	-	+	+	79.14	93.67	87.76
12	+	-	-	90.92	96.87	94.4

thrice for similar adsorbent.

3. Results and discussion

3.1. CFFA characterization

Table 1 and Fig. 1 represent the surface properties, magnetic and surface morphology of the adsorbent. FESEM micrographs of CFFA clear reveal a smooth, clear and porous morphology of the material (Fig. 2). CHNS analyzer shows the percentage content of carbon, hydrogen nitrogen and sulfur 71.2%, 8.7%, 1.7% and 2.9% respectively. The zeta potential value of -11.3 mV indicates that CFFA surface negatively charged whereas the average particle size was <45 nm with a total surface area of $17.4 \text{ m}^2 \text{ g}^{-1}$ and 59.3% ash content. Fig. 1 (a) shows the XRD profile of CFFA where the peak intensity ranging from 7-70° is attributed to the presence of quartz, calcite, sillimanite, hematite and magnetite in the sample along with a crystallinity index (I_{C_r}) of 63.4%.

FTIR spectra depict the different vibrational frequencies of CFFA because of various functional groups at the surface (Fig. 1 (b)). The wide band spectrum at 3441 cm^{-1} , represents the amide stretch (N-H) (Bind et al., 2018). At 2921 cm^{-1} , a band of $-\text{CH}_3$ was observed followed by a band spectrum at 2921 cm^{-1} representing the aldehyde group; a peak at 1636 cm^{-1} was assigned to $-\text{C}=\text{C}-$ band spectra. The absorption band around 1382 cm^{-1} signifies again the $-\text{CH}_3$ band spectra. A band with an intense peak at 1078 cm^{-1} signifies the alkoxy stretching. Also, the band spectra at 795 cm^{-1} show the presence of $-\text{C}=\text{C}-$ (sp^2) carbon atom. Henceforth, FTIR spectra reveal the presence of different band stretch corresponding to the functional groups viz., amide, aldehyde, alkoxy, alkanes, and alkene, respectively.

Fig. 1 (c) shows the hysteresis loop of the CFFA by following the VSM technique where magnetization (M) versus magnetic field (Oe) at room temperature is plotted and represented in Table 1. A low H_c value depicts that the material can be simply separated with the help of a magnet or an externally applied magnetic field and, therefore, the material is easy to separate, recover and reuse in any process (Nguyen et al., 2011). Furthermore, following the separation process, the material can again be easily re-dispersed into the solution and reutilized owing to its low M_r value (Ahmed and Ahmaruzzaman, 2015).

3.2. Effect of different parameters on heavy metal removal individually

In the present study, Box-Behnken design of experiment was utilized for the potential evaluation of CFFA for removal of three different model heavy metals viz. Cd (II), Cu (II) and Ni (II) from the single contaminated system. A maximum removal of 95.6%, 99.2% and 97.9% was obtained with the central values of all the selected physical parameters viz., pH 5.0, biomass dosage 0.275 g L^{-1} , initial heavy metal concentration 55 mg L^{-1} , temperature of 35°C and contact time of 47.5 min for all the heavy metals (Table S1).

Analysis of variance (ANOVA) showed F-value of 14.9, 12.61, and 10.63 and R^2 of 0.88, 0.86 and 0.84 which affirmed that the model is highly significant and the experiments were accurate, prominent and reliable. Among all the terms, the linear effects of pH (A), biomass dosage (B), initial metal concentration (C) and temperature (D) were found to be significant for all the three HMs. Among the various interaction factors, the linear effect was more effective for all the five parameters except the contact time (E), for all the three heavy metals. These results were further validated by the elliptical nature of the 3-D plots (Fig. 3). Furthermore, in the interaction effect only, pH and heavy metal concentration were found to be effective for Ni (II) and Cu (II) removal in the single contaminated system, whereas for Cd (II), no interaction effect was validated by *P*-value. Henceforth, the results from Box-Behnken design of experiment depicted that that factors pH, adsorbent dosage, initial metal concentration and temperature were very critical in comparison to their center points and a slight deviation led to a decrease in all the three heavy metals in an individual (single) contaminated system.

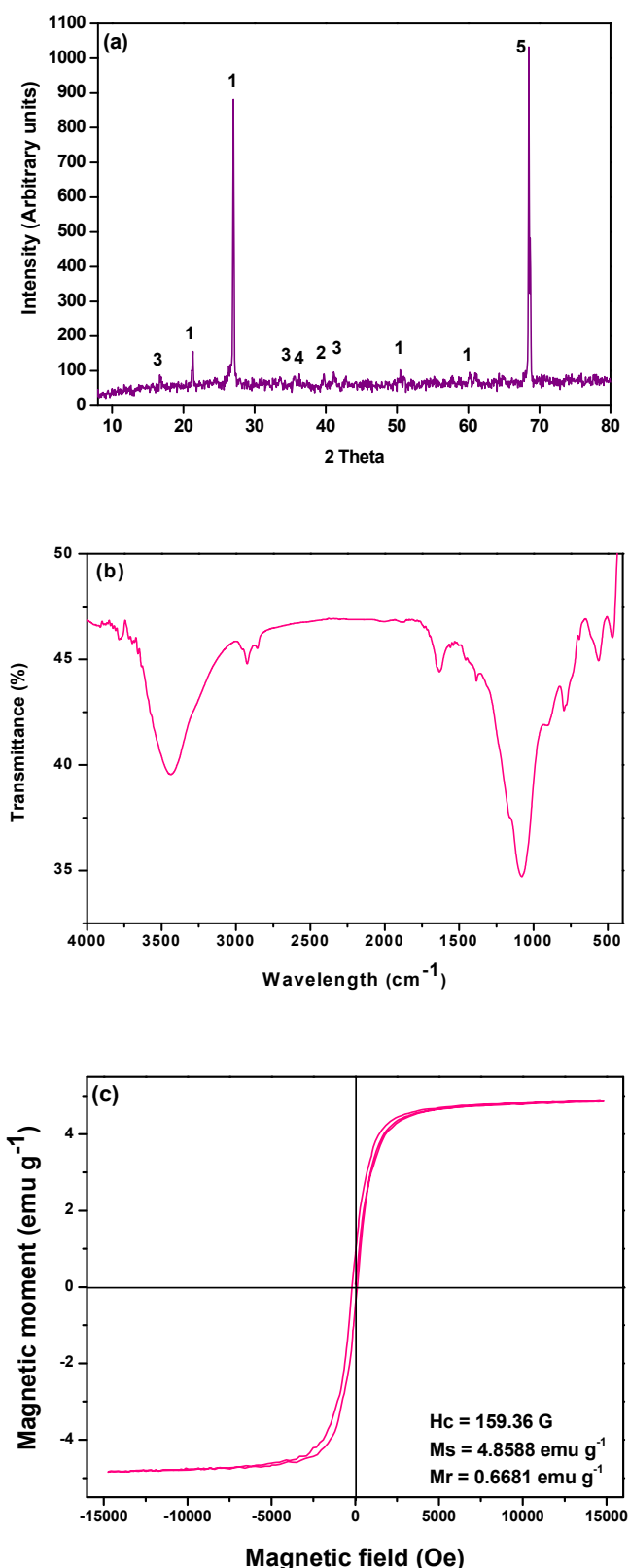


Fig. 1. (a) XRD results of CFFA sample (1- Quartz, 2-Calcite, 3-Sillimanite, 4- Magnetite, 5-Mullite), (b) Fourier transform infrared spectroscopy and (c) Vibrating sample magnetometer analyses.

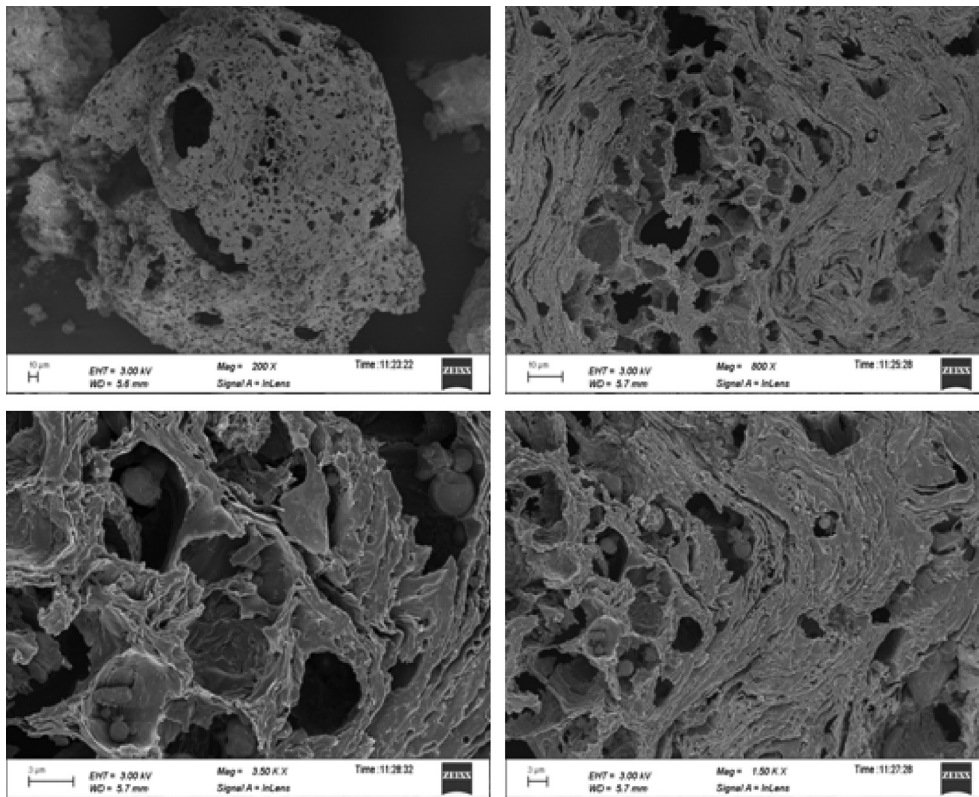


Fig. 2. FESEM micrographs of coal-fired fly ash.

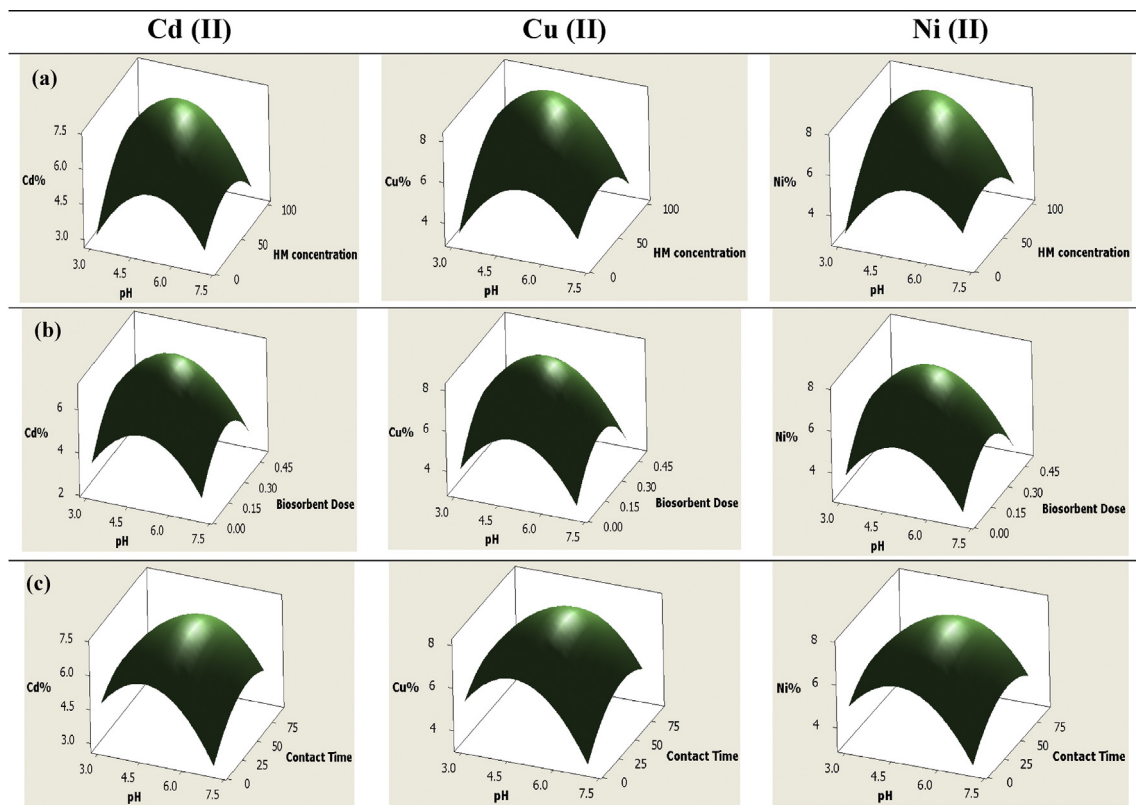


Fig. 3. Response surface plots representing the effect of pH and its interaction with heavy metal concentration, adsorbent dose and contact time on heavy metal removal.

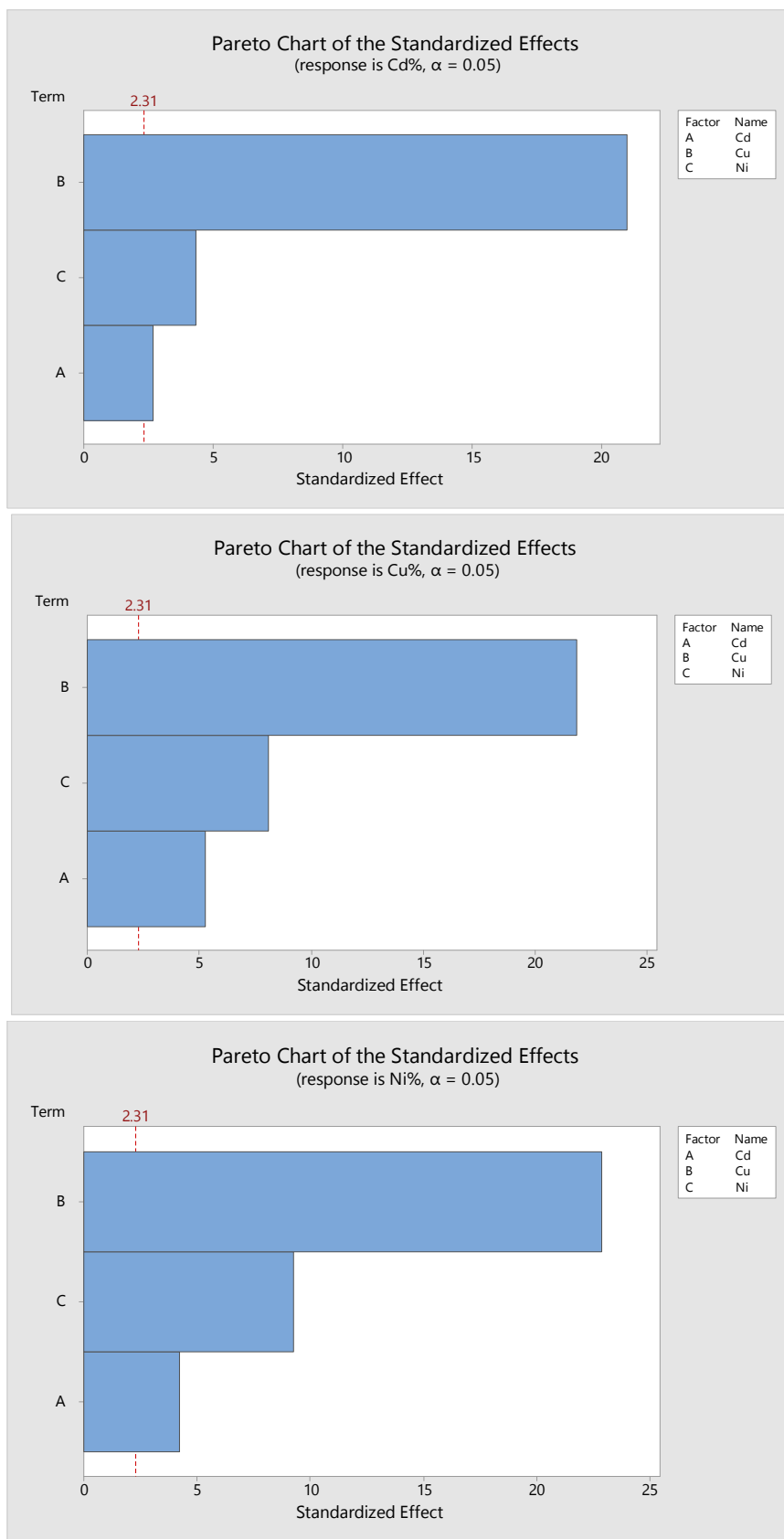


Fig. 4. Pareto chart showing the effect of different heavy metals on each other's removal by adsorbent: (a) Cu (II) removal, (b) Cd (II) removal and (c) Ni (III) removal (vertical line shows significance cutoff at P value less than 0.05).

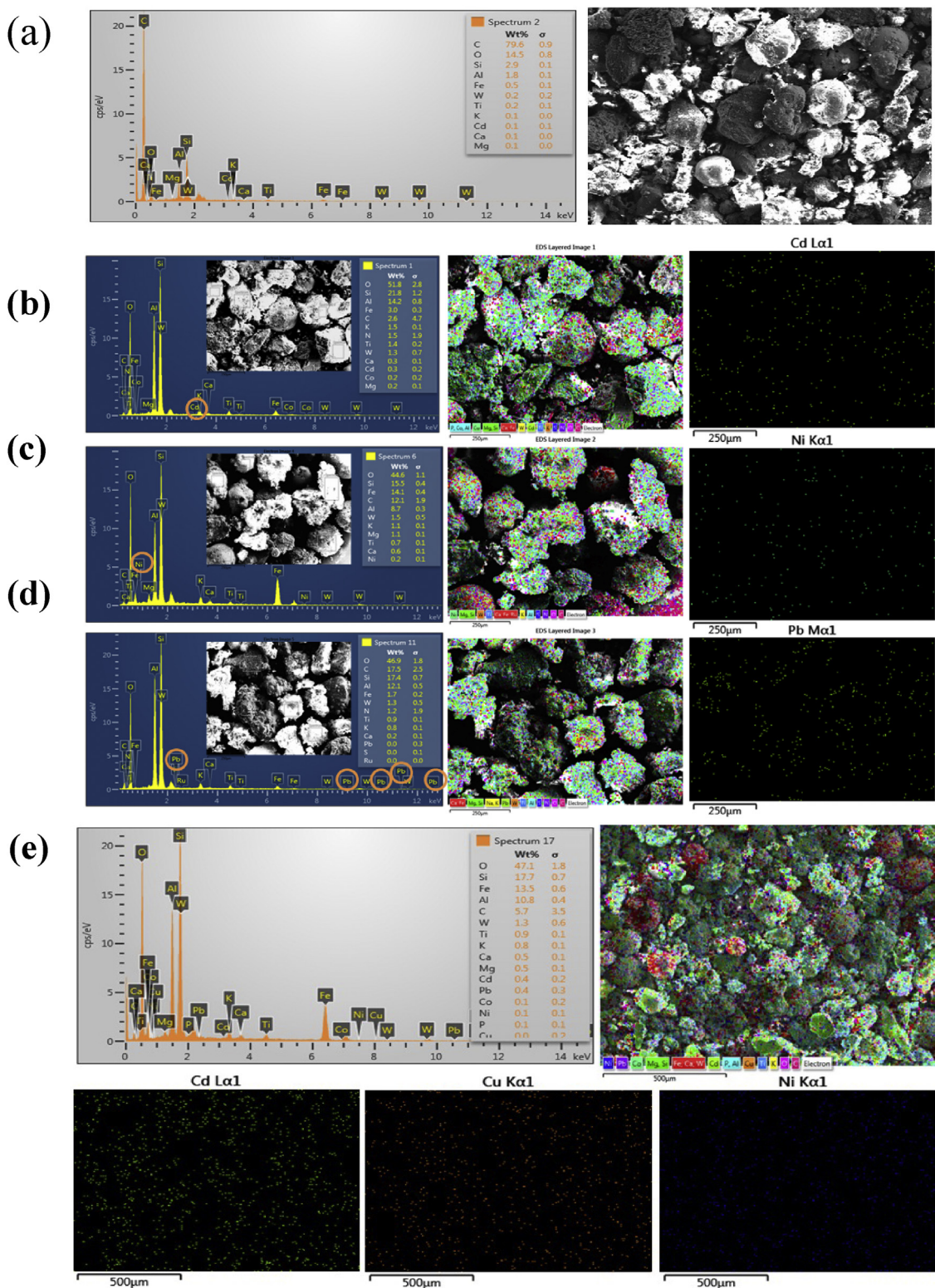


Fig. 5. FESEM-EDX spectrum of (a) control (CFFA) and (b) CFFA loaded with Cd (II); (c) Ni (III); (d) Cu (II); (e) Mixture of Cd, Ni and Cu. Insert shows the FESEM micrographs of CFFA loaded with heavy metals.

A similar trend was reported by Das and Das (2015) where the three parameters viz. adsorbent dosage, initial metal concentration, and contact time showed the individual effect for Pr (III) biosorption onto bio-waste materials viz., crab shell (57.8 mg g^{-1}) and orange peel (49.9 mg g^{-1}) was achieved. Sen et al. (2018) also examined the biosorption of Pb (II) and Cd (II) onto the seeds of *Adenanthera pavonina* from single and

binary HM solutions. Also, Das et al. (2012) studied Zn (II) removal using dead biomass of *Candida laurentii* and *Candida rugosa* as the novel bio-sorbents from aqueous environment and reported a removal efficiency of 54.8 and 65.4% at pH 6 in the presence of 90 mg L^{-1} at 30°C in the batch system. Recently, Loredana Brinza et al. (2019) carried out a multifaceted approach of Zn adsorption onto dry *Fucus vesiculosus*. Here, Zn adsorption

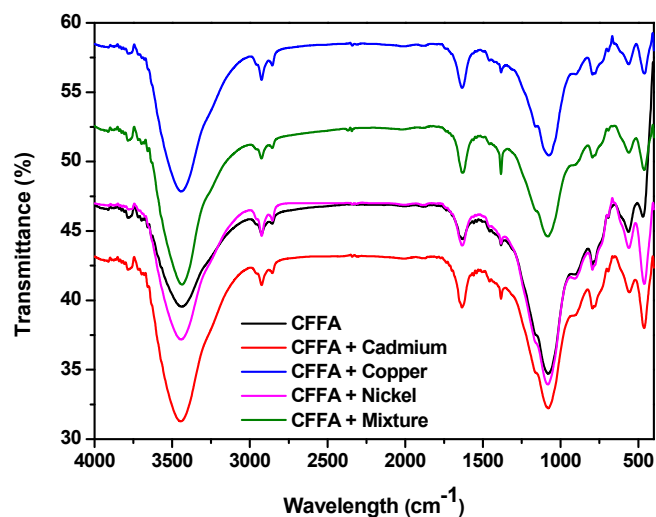


Fig. 6. FTIR spectra of the control and metal loaded coal-fired fly ash.

onto *F. vesiculosus* was a function of: pH, algae concentration and HM source. Varghese and Das (2015) reported a high removal of >90% of Hg (II) ions utilizing a nano-biocomposite hydrogel modified by triethylene tetra amine and β -cyclodextrin.

3.3. Heavy metal removal from the multi-component system

In this study, the removal efficiencies of the aforementioned heavy metals by CFFA in the multi-contaminated system were examined (Table 2). Initial range of individual heavy metals was chosen in accordance with the aforementioned experimental runs for the individual contaminated systems (10–50 mg L⁻¹). Heavy metal removal was assorted following the combination level of these heavy metals in the respective mixture system. The maximum removal efficiency for Cu (II) was obtained by CFFA within 150 min of the experimental run, with an initial concentration of 10 mg L⁻¹ for all the heavy metals. Followed by Cu (II) removal, a declining trend in the removal (%) for Ni (II) and Cd (II) was obtained. Also, the minimum removal (%) for all the experimental runs was attained at 50 mg L⁻¹ (maximum) for all the heavy metal concentration level.

Furthermore, in the multi-contaminated study, heavy metal removal was achieved from the aqueous solution were analyzed statistically by employing analysis of variance (ANOVA) and Student's t-test for the relative significance of Cd (II), Cu (II) and Ni (II) on individual and each other in the multi-component system. According to the ANOVA, the individual effect had a greater impact on the adsorption in comparison to than the 2-way and 3-way interaction effects. Also, with the increase in heavy metal concentration from 10 mg L⁻¹ to 50 mg L⁻¹ showed an inhibitory effect ($P < 0.05$) because of the competitive effect.

Fig. 4 (a, b and c), the Pareto chart, shows the significance of interaction among the three different heavy metals on their adsorption. The influence due to Cd (II) along with its concentration on the adsorption phenomena was the highest (negative effect) followed by Ni (II) and then Cu (II). Two-way interactions were statistically insignificant ($P > 0.05$) and it was higher compared to the effect of an individual component.

The mechanistic insights of all the three heavy metal removal in a multi-component system are very different from the single metal-contaminated system (Sen et al., 2018). The competitiveness between different heavy metals and their inhibitory effect on to each other played an important role in the biosorption phenomena in multi-component system which better/aply resembles with the real wastewater contaminated system (Gikas, 2008) while the initial concentration also plays an important role in heavy metal removal in the single as well as in multi-contaminated system (Babu et al., 2014). Here, the biosorption of

all the three heavy metals involves the inhibitory effect onto each other and it also increases with the increase in the heavy metal concentration. Roy et al. (2015) also reported similar phenomena for the heavy metal removal in the multi-component system by *Nostoc muscorum* which involved very fast sorption initially onto the microbial surface along with by slow uptake of heavy metals inside cyanobacteria. Here, Pb (II) illustrated a better removal in the multi-contaminated system containing three different heavy metals.

3.4. Characterization of heavy metal loaded

Further, the metal-loaded CFFA, FESEM-EDX and FTIR analyses were performed to examine the micro-morphology and elemental composition of the metal loaded CFFA. Fig. 5 (a, b and c) shows FESEM-EDX spectra of metal-loaded CFFA for both the single and multi-component system. The presence of selected heavy metals was confirmed by the EDX spectra obtained from the surface of the adsorbent. In general, the result from FESEM-EDX depicted that heavy metals were primarily removed by CFFA associated onto the sorbent surface. The elemental mapping of the respective heavy metals clearly shows the binding place onto the adsorbent.

FTIR analysis of the control and metal loaded biomass in both the cases (individual and multi-component) were performed to examine the functional group/s involved in the interactions between the heavy metal/s and CFFA surface (Fig. 6). The stretching was observed in between the range 795–3441 cm⁻¹ for the control and metal loaded CFFA. The band spectra at 795 cm⁻¹ show the presence of $-C=C-$ (sp^2) carbon atom. Another band at 1078 cm⁻¹ represents the alkoxy stretching. The absorption band around 1382 cm⁻¹ signifies the involvement of $-CH_3$ band spectra whereas a peak at 2921 cm⁻¹, corresponds to $-CH_3$ for the phenomena. Band spectra, at 2921 cm⁻¹ represents aldehyde group; and at 1636 cm⁻¹ was assigned to $-C=C-$ band spectrum, were also involved in the adsorption. Lastly, a wide band spectrum at around 3441 cm⁻¹, presents amide stretch (N-H) (Bind et al., 2018). Henceforth, the FTIR spectra revealed the involvement of different band stretch corresponding to the amide, aldehyde, alkoxy, alkanes, and alkene functional groups.

3.5. Regeneration/reusability studies of the exhausted CFFA

To evaluate the potential of CFFA, the regeneration/reusability study was performed. Desorption of all the three different heavy metals by CFFA was considered indispensable for its long-term, sustainable and repetitive extraction-elution cycles. Desorption experiments were performed in three cycles and in each cycle, the loss in weight of adsorbent was observed. For the first two cycles, significant weight loss was observed because of the washing of soluble material. In the final cycle, no significant weight loss was evaluated as the leftover adsorbent might have resistant material. This steady decline in sorption with an increase in the number of cycles was also might be due to corrosive nature of acid and washing away of the functional group present at the surface of the adsorbent (Bunluesin et al., 2007; Kaur et al., 2013; Zhao et al., 1999). Desorption of adsorbed heavy metals (Cu, Ni and Cd) on CFFA were studied using 0.1 N H₂SO₄, 0.1 N HCl, 0.1 N HNO₃ and was obtained maximum with 0.1 N H₂SO₄ that follows the trend: 79.8% for Cu, 72.1% for Ni, and 67.3% (Bind et al., 2018). Besides, the declining trend for desorption followed 0.1 N H₂SO₄ > 0.1 N HNO₃ > 0.1 N HCl trend.

3.6. Cost estimation

Activated carbons are utilized from many decades for the removal of heavy metal contaminated wastewater that costs approximately \$2000 USD per ton in India (Manikandan et al., 2016). Furthermore, for the processing and transportation of any adsorbent, approximately 100–200 USD per ton of the adsorbent is predicted. In relation to this, CFFA is among the most easily accessible, efficient and economic adsorbent in comparison to treat a similar volume of heavy metal contaminated

wastewater than the activated carbon. Therefore, it can well be accomplished that CFFA can be utilized as an efficient and cost-effective adsorbent for treating heavy metal-laden wastewater.

4. Conclusions

The valorization of coal-fired fly ash as a potential adsorbent for heavy metal-containing solutions (individually and in the multi-contaminated system) was found to be potent. The removal efficiencies of the three different heavy metal followed the following trend: Cu (II) > Ni (II) > Cd (II). Although the removal efficiency in the multi-component system, was slightly lower than the individual system, the maximum removal was obtained at 10 mg L⁻¹ for the initial heavy metal concentration. Also, the individual effect of each heavy metal, significantly govern the removal efficiencies in all the cases. Hence, for both the contaminated system (single and multi-component systems) the adsorbent had shown its great potential for heavy metal removal.

Declarations

Author contribution statement

M. Kumar: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

L. Goswami: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

A. K. Singh, M. Sikandar: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

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