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Moringa oleifera seed composite a novel material for hazardous heavy metals (Cd, Cr and Pb) removal from aqueous systems

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Abstract

In this study *Moringa oleifera*-bentonite clay nanocomposite was successfully prepared by the solution intercalation process. The intercalation of the cationic biopolymer *Moringa oleifera* seed into layered silicate bentonite clay through cation exchange process results in nano-composite with interesting structural and functional properties. By the method of adsorption filtration study through clay-polymer composite media of *Moringa oleifera* seed and bentonite clay, the heavy metals removal for a particular flow rate of 50 ml per minute at optimum pH was attained and it showed that the average removal efficiency of cadmium, chromium and lead at 20cm from the base of the column were 99.98% (pH range 7-8), 99.99% (pH range 2-3) and 99.99% (pH range 6-7) respectively in the cases of 2 to 20mg/l of heavy metals. So, clay-polymer composite media adsorption using *Moringa oleifera* seed composite is suitable for drinking water treatment with necessary pH adjustments. During this processes the metal interacts physico-chemically with the composite to form clay-polymer-metal exfoliated complexes. The major advantages of the process are the more shelf life of clay-polymer media, high regeneration efficiency and easier sludge disposal.

1. Introduction

Water safety and quality are fundamental to human development and well-being [WHO, 2018]. In recent years, heavy metal pollution has become one of the most serious environmental problems. Heavy metals are found naturally in the earth's crust, but due to indiscriminate human activities, their geochemical and biochemical balance have drastically been changed and they enter in to our drinking water supply [1]. Heavy metals are non-biodegradable, carcinogenic and they bioaccumulate to cause a wide range of diseases and disorders [2]. Major heavy metal pollutants are cadmium, chromium and lead and they are hazardous to health. Ionic cadmium is released in to the environment through waste water from electroplating, pigments, plastic, battery and zinc refining industries [3]. The main sources of hexavalent chromium contamination are leather tanning industries, pigment manufacturing industries and metal finishing industries [4]. Lead was used for manufacturing of building materials, pigments to glaze ceramics, water pipes, ammunition, ceramics glazers, glass and crystals, paints, protective coatings, acid storage batteries, gasoline additives and cosmetics [5].

Many conventional materials such as activated carbon have been used in the removal of these heavy metals, mainly by the process of adsorption. But the use of these materials is usually expensive and involves a number of technicalities which led to the studies to find out alternative low cost adsorbents for treating heavy metals in water [6]. Synthetic coagulants such as alum produce aluminium as secondary pollutant. Aluminium in excess of the limit causes Alzhimer's disease and it is neuro toxic [7]. Natural materials are widely used for preparing coagulants and adsorbents as they are non toxic and do not produce secondary pollution [6]. Further a single coagulant or adsorbent cannot remove all the pollutants at a time. More complex structural and functional coagulant/adsorbent properties are obtained by preparing composite coagulants. Nowadays natural polymers as coagulant and clays as adsorbent are used for preparing novel nano-composites. Solution processing method is most suitable for preparing clay polymer nano-composites because many natural polymers are water soluble in nature and clay layers are separated by water molecules that make intercalated or exfoliated layered-silicate (or clay) polymer composites [8]. Clay-polymer composites have more significant advantages than the established adsorbents for water treatment [9]. Biodegradable polymers which have been used for making composites are cellulose [10], chitosan [11-12], polylactide (PLA) [13], gelatin [14] and poly 3-hydroxy butyrate (PHB) [15]. Cellulose contains hydroxyl (-OH) groups on the glucose ring and they act as coordination sites to heavy metal ions making it an attractive natural adsorbent [16-18]. Studies of polypyrrole-montmorillonite composite for hexavalent chromium removal have results indicating that water quality parameters and flow dynamics have profound effect on performance. Indications are that natural clay-polymer composites are competitive materials for water quality improvement [19]. Studies and the analyses of adsorption processes of nickel ions from aqueous solutions showed that the clay-based polymer nano-composites have high degree of affinity with heavy metal ions. The bentonite-containing acrylic nano-composites were used as absorbents for the removal of polyvalent ions from aqueous solution [20]. The clay-polymer composite of poly (4-vinylpyridine-co-styrene)-montmorillonite filter succeeded in reducing atrazine concentrations below the current EPA (U.S Environmental Protection Agency) standard [21]. Clay-polymer complexes were more toxic to bacteria than the polymers alone [22]. Bentonite has advantages such as high surface area for adsorption, high porosity, and high cation exchange capacity and low cost. Modification of the structure of clay helped in increasing the surface area and sorption site and thereby enhances the adsorption capacity. The bentonite can be modified by addition of polymer in the interlayer of the clay spaces with the help of any simple process like physical adsorption or chemical grafting. The modification of bentonite with polymer improves the chemical and physical properties. Most of the modified bentonite has good potential for adsorption of heavy metals [23]. The cation exchange capacity of clay with respect to heavy metal removal is shown by a two-step clay-coagulation combined process. An excess clay addition in powder form to contaminated water was followed by coagulation with aluminum sulphate. This removes the heavy metals by synergy with the clay adsorption and settlement of the clay adsorbent through flocculation. High percentage removal of heavy metals ranging from 96 to 99% has been observed [24]. The adsorption capacity of bentonite clay for heavy metal removal from contaminated water can be significantly enhanced by a high loading of chitosan on the surface. An optimal chitosan loading will enhance the adsorption capacity of the clay, without clogging its adsorption channels [25].

Moringa oleifera seed (MOS) coagulant was used traditionally for water purification. The Moringa oleifera press cake can be recommended to be a good coagulant for turbidity and heavy metal removal [26]. Previous studies of the author [27 - 32] show the potential of *Moringa oleifera* (MO) as a coagulant, clarifier and adsorbent. Ravikumar and Sheeja, (2013) [29] conducted the analysis of the heavy metals cadmium, copper, chromium and lead, before and after treatment of water with MO seed biopolymer. The results showed that the percentage removal by MOS were 95% for copper, 93% for lead, 76% for cadmium and 70 % for chromium. The final concentration of copper was below the desirable limit for drinking water (<1mg/l). But the removal of cadmium, chromium and lead after coagulation with MO cake coagulant was not as per the limits of drinking water standards. So, additional treatments are needed to achieve BIS/WHO standards. To improve further on the previous studies, a new composite media was prepared by using MOS biopolymer and bentonite clay (BC) and was tested for its ability to remove Cd(II), Cr(VI) and Pb(II) from aqueous solutions. The advantages of these materials are their natural abundance, non-toxicity, environment friendliness and cost effectiveness.

2. Materials and Methods

2.1 Preparation of bentonite clay

Bentonite was sieved using Vibrator Sieve Shaker Number 230 to collect the 63μm size fraction, because that size was fixed to be the appropriate for maximum adsorption.

2. 2 Preparation of *Moringa oleifera* seed cake coagulant

Dry *Moringa oleifera* pods were collected, pod shells removed manually; kernels were grounded in a domestic blender and sieved through 600 micro meter stainless steel sieve (Figure 1)

Fig. 1 *Moringa oleifera* seed cake Preparation

Oil was removed by mixing the seed powder in ethanol. This was stirred with a magnetic stirrer for 30-45 min and subsequently separation of the residue from the supernatant was done by centrifuging for 45 min at 3000 revolutions per minute (rpm). The supernatant was decanted and the residual solid was dried at room temperature. This residual solid was the *Moringa oleifera* seed cake. The supernatant containing oil and ethanol when mixed with potassium hydroxide catalyst produced biodiesel and glycerol.

Aqueous extract was prepared by using 200 ml of distilled water and 10 g of *Moringa oleifera* seed cake powder, mixed by a magnetic stirrer for 60 minutes and settled for 20 minutes. *Moringa oleifera* aqueous extract was finally filtered through 20µm paper filter.

2.3 Preparation of clay-polymer composites

Solution processing method (33) is used for the preparation of bio-polymer composite using MOS with BC. MOS coagulant contains water-soluble cationic polymers. In this method, the layered silicates were dispersed in a suitable solvent in which the polymer was soluble. Composite coagulo-adsorbent was prepared by using bentonite and MOS aqueous extract in the ratio 1:1 by weight and it mixed by a magnetic stirrer for 60 minutes. On evaporation of the water, the silicate sheets sandwiched the polymer to form an ordered, multilayered structure. Figure 2 shows the steps in the preparation of *Moringa oleifera* seed composite (MOSC).

This technique is especially employed with water-soluble polymers. MO polymer is water soluble. Due to the polarity of these polymers, they contribute an enthalpy gain to help intercalation. Remarkably, this method produces a high degree of intercalation of clay polymer systems.

2.4 Experiment

Three PVC pipes with an inner diameter of 110 mm and a length 100 cm were selected. The clay-polymer composite media was compacted tightly inside the pipe. The bottom of the pipe was sealed off with a plastic cap to prevent the loss of adsorbent during the process. Three different outlets were provided to the column, one at 20 cm from the bottom, the second at 20 cm from the first and the third at 40cm from the second.

Fig. 2 *Moringa oleifera* seed composite preparation method

A water reservoir (bucket) containing synthetically prepared heavy metal solution in water was kept at the top of the column and was allowed to flow under the action of gravity into the column for adsorption-filtration processes. A clinical drip was attached from the synthetic water reservoir to the column to maintain a constant flow rate of water, through which the sample water flowed down. Head loss was constantly maintained for the proper functioning of the apparatus. Finally, the water passing through the composite medium was collected from one of the outlets into a collecting device (beaker). The flow rate was kept in the range of 50 ml/min to 150 ml/min. At one point of time, treated water was collected through a single outlet only, while the others were closed using clips. Experiment was performed in synthetic heavy metals contaminated water with different initial concentrations of 2, 4, 6, 8, 10, 12, 14, 16, 18 and 20 mg/l. The treated water was analyzed for determining the concentration of heavy metals in them.

3. Results and discussion

Due to different ionic forms of heavy metals and ionization state of the surface functional groups, pH plays the most significant role in adsorption studies. The mechanism of removal of the selected heavy metals like Cd, Cr and Pb was dependent on pH and it was mainly by the structural and functional characteristics of the clay-polymer composite.

3.1 Influence of pH on MOSC composite adsorbent

Figure 3, 4 and 5 shows the influence of pH in the heavy metals removal efficiency by MOSC composite media at 20cm above the bottom of the column and 50ml/min flow rate.

The clay-polymer composite adsorption studies with MOSC confirmed that optimum condition for metal ions removal were pH 7 to 8 for cadmium, pH 2 to 3 for chromium and pH 6 to 7 for lead. At very low pH values, metal uptake has been found to be very less in the case of cadmium and lead. But chromium has more removal efficiency at very low pH values.

3.1.1 Cadmium removal

The comprehensive influences of all functional groups determine pHpzc of an adsorbent, the pH at which the new charge on the adsorbent surface is zero. The cadmium removal efficiencies of MOSC with respect to pH of the synthetic water are shown in Figure 3.

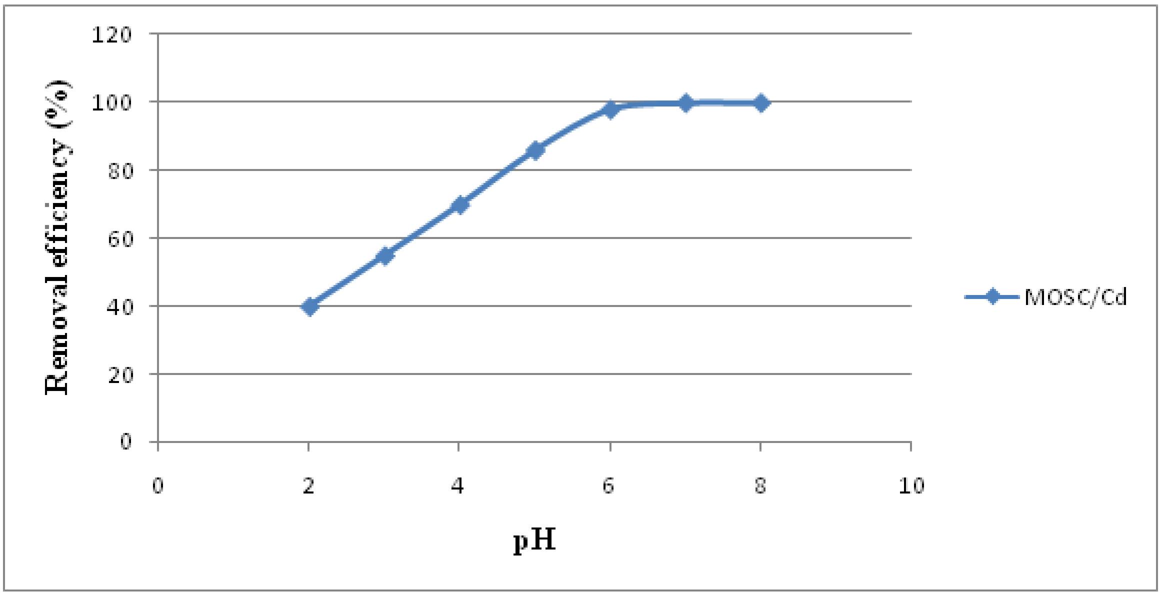

Fig. 3 Influence of pH in the heavy metals removal efficiency by MOSC at 20cm above the bottom of the column and 50ml/min flow rate, initial concentration 6mg/l.

In the case of MOSC the adsorption % of Cd ions increases with an increase in pH of the solution. The amount of Cd ions adsorbed was smallest at pH values less than 5, but increased at higher pH values and remained more or less constant at pH values greater than 6 (99.99%). The zero point charge or isoelectric point (pHzpc) of the MOS was about 6.2 and shifted to 5.7 in the case MOSC. The difference in pHzpc between them confirmed that MOS polymer was successfully intercalated on bentonite composite. The isoelectric pH of MOSC was around 5.7, the Cd ions removal increased with increase in pH of the solution. At lower pH, hydrogen ions were adsorbed onto the clay-polymer surface, and thus, suppressed the Cd ions adsorption. Further increase in the hydrogen ions concentration (decreasing pH) would only lower the adsorptive capacity of Cd ions (34). As the pH increased, hydrogen ions concentration decreased and provided more space for Cd ions to get adsorbed on to the clay-polymer surface. Overall cadmium ions removal by MOSC was found to be extremely good (up to 100 - 99.97% of adsorption) in all cases of initial concentrations ranging from 2 to 20 mg/l at flow rate of 50ml/min and heights up to 20 cm from the base of the column (Table 1).

3.1.2 Chromium removal

The chromium removal efficiencies of MOSC with respect to pH of the synthetic water are shown in Figure 4. The zeta potential of MOSC surface at pH below 5.7 was positive because the amine groups of MOS were protonated at pH below 5.7 and Cr(VI) ions existed as $Cr_2O_7^{2-}$, CrO_4^{2-} and $HCrO^{4-}$ polyanions at pH < 5.7. Cr ions adsorption on to MOSC at low pH was found to be extremely good and adsorption percentage of Cr ions decreased with an increase in pH of the solution. The amount of Cr ions adsorbed was highest at pH values less than 3, but decreased at higher pH values and the highest percentage (100%) of adsorption at pH values between 2 and 3 was obtained. MOSC had high percentage adsorption of Cr ions even at low pH values (35). The high removal of chromium was only obtained at low pH in the case MOSC and at natural pH chromium removal dramatically decreased due to deprotonation of the functional groups present in MOSC which compromised the formation of hydrogen bonds between chromium and the clay-polymer.

Overall chromium ions removal by MOSC was found to be extremely good (up to 100 - 99.98% of adsorption) in all cases of initial concentrations ranging from 2 to 20 mg/l, at flow rate of 50ml/min and heights up to 20 cm from the base of the column (Table 1).

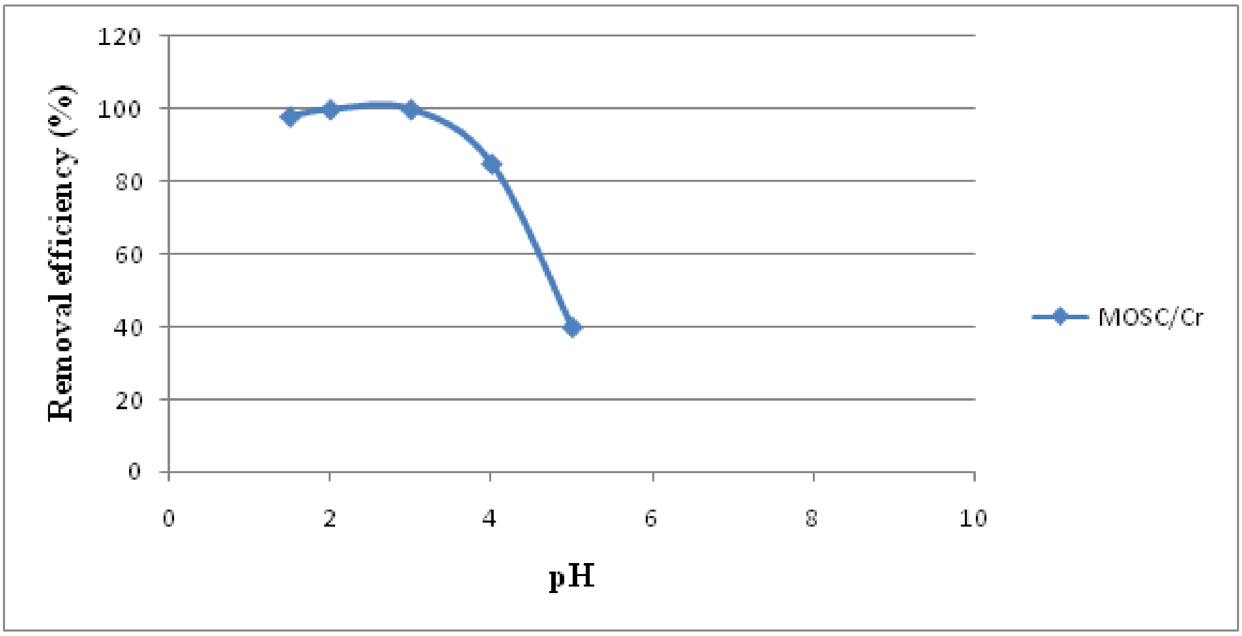

Fig. 4 Influence of pH in the heavy metals removal efficiency by MOSC at 20cm above the bottom of the column and 50ml/min flow rate and nitial concentration of 6mg/l.

3.1.3 Lead removal

The lead removal efficiencies of MOSC with respect to pH of the synthetic water are shown in Figure 5. The clay-polymer MOSC used in this study has an experimental pHzpc of 5.7. Therefore, at a pH value above their point of zero charge, the net charge on MOSC became negative while at a pH value below their point of zero charge the net surface charge became positive. Based on this, the negative charges increased with the increase in the solution pH. Hence, the adsorbent gained a high charge resulting from the spread of isomorphous substitution in tetrahedral and octahedral sheets for bentonite clay. It can also be mentioned that both MOSC particles have a higher adsorption affinity to adsorb lead ions at high pH values. As the pH increased and the balance between H_3O^+ and OH^- became equal and then more of the positively charged metal ions in the solution were adsorbed on the negative clay-polymer surface and thus, the removal percentage of the metal ions increased.

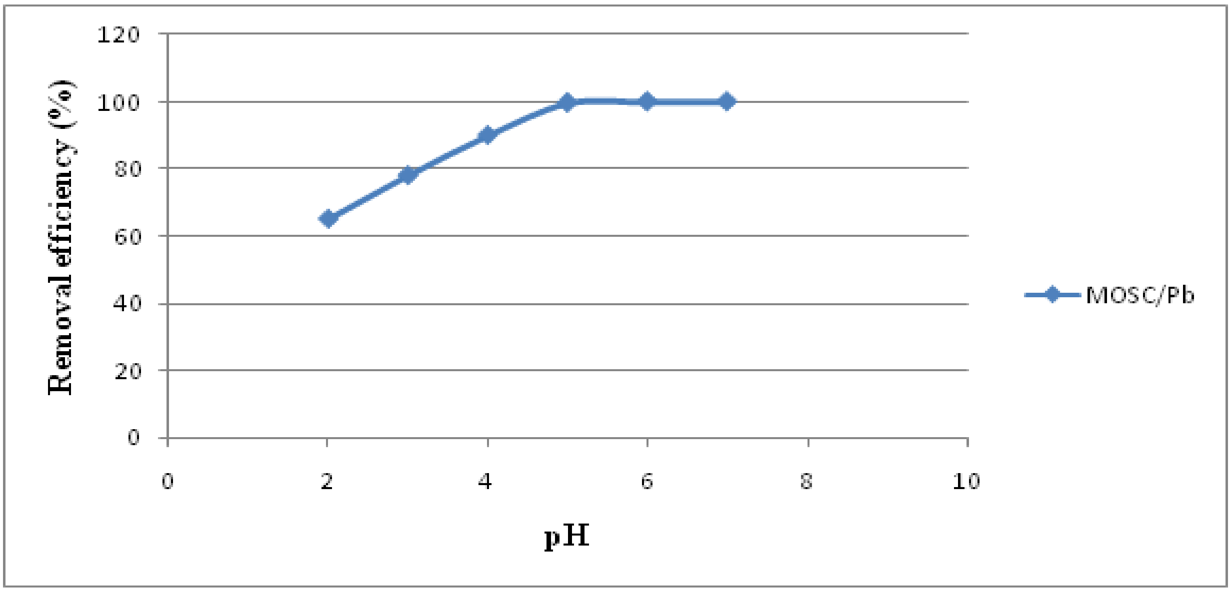

Fig. 5 Influence of pH in the heavy metals removal efficiency by MOSC at 20cm above the bottom of the column and 50ml/min flow rate and at initial concentration of 6mg/l.

Lead ions tried to form a precipitate at pH higher than 7.0 and therefore the adsorption of Pb^{2+} ions by MOSC clay-polymer composites were difficult to quantify at pH values higher than 7.0. The true adsorption at this pH was masked by precipitation (36). Removal of Pb ions by MOSC was attributed to adsorption and precipitation on to the clay-polymer surface and within the pores. Adsorptive capacity of Pb ions increased with increasing pH of the solution up to pH=6-7, beyond which it started declining. Maximum removal was noticed at pH values of 6 and 7.

Overall lead ions removal by MOSC was found to be extremely good (up to 100 - 99.99% of adsorption) in all cases of initial concentrations ranging from 2 to 20 mg/l, at flow rate of 50ml/min and heights up to 20 cm from the base of the column (Table 1). The experimental study involving the flow of synthetic heavy metals solution through the adsorbent column containing MOSC was performed to reveal the heavy metal removal efficiency of these materials at different flow rates. Table 1 shows the experiment at a flow rate of 50 ml per minute at optimum pH for MOSC column adsorbent.

MOSC media adsorption study for a particular flow rate of 50 ml per minute showed the average removal efficiency of cadmium at 20cm, 40cm and 80cm from the base of the column as 99.98%, 97.02% and 87.91% respectively. Similarly in the case of chromium it was 99.99%, 95.22% and 84.36% and in the case of lead, it was 99.99%, 99.34% and 96.56% respectively (Table 1).

Similar experiment carried out at a flow rate of 100 ml per minute had given a different result (Table 2).

Table 1 Experiment at flow rate of 50 ml/min and at various heights from the base of the column - adsorption of cadmium, chromium and lead at optimum pH for MOSC

Initial metal concentration (mg/L)	**Cadmium adsorption (%) at pH=7-8**			**Chromium adsorption (%) at pH=2-3**			**Lead adsorption (%) at pH=6-7**		
	20cm	**40cm**	**80cm**	**20cm**	**40cm**	**80cm**	**20cm**	**40cm**	**80cm**
2	ND*	97.27	88.17	ND*	95.43	84.57	ND*	99.66	96.87
4	99.99	97.24	88.15	ND*	95.41	84.53	ND*	99.60	96.81
6	99.99	97.21	88.07	ND*	95.40	84.52	ND*	99.57	96.76
8	99.99	97.15	88.04	99.99	95.34	84.48	ND*	99.47	96.72
10	99.98	97.12	87.99	99.99	95.29	84.43	99.99	99.44	96.61
12	99.98	97.01	87.93	99.99	95.25	84.37	99.99	99.32	96.57
14	99.98	96.97	87.83	99.99	95.16	84.32	99.99	99.27	96.48
16	99.98	96.83	87.76	99.98	95.06	84.20	99.99	99.15	96.34
18	99.97	96.74	87.64	99.98	94.99	84.13	99.99	99.04	96.27
20	99.97	96.62	87.55	99.98	94.91	84.01	99.99	98.92	96.13
Average value	99.98	97.02	87.91	99.99	95.22	84.36	99.99	99.34	96.56

ND-Not detected*

MOSC media adsorption experiment for the flow rate of 100 ml per minute showed the average removal efficiency of Cd at 20 cm, 40 cm and 80 cm from the base of the column as 98.15%, 92.14% and 84.49% respectively. Similarly for chromium it was 97.90%, 85.43% and 78.95% and in the case of lead, 98.66%, 96.80% and 94.91% respectively (Table 2).

The same experiment was repeated for a flow rate of 150 ml per minute at optimum pH conditions and there was some variation of percentage of removal of heavy metals present in water (Table 3).

Table 2 Experiment at flow rate of 100 ml/min and at various heights from the base of the column - adsorption of cadmium, chromium and lead at optimum pH for MOSC

Initial metal concentration (mg/L)	**Cadmium adsorption (%) at pH=7-8**			**Chromium adsorption (%)nat pH=2-3**			**Lead adsorption (%) at pH=6-7**		
	20cm	**40cm**	**80cm**	**20cm**	**40cm**	**80cm**	**20cm**	**40cm**	**80cm**
2	98.56	91.73	84.89	98.25	85.71	79.32	99.10	97.24	95.36
4	98.43	91.64	84.81	98.20	85.68	79.28	99.01	97.15	95.29
6	98.41	91.57	84.74	98.14	85.63	79.24	98.95	97.17	95.23
8	98.33	91.51	84.68	98.07	85.58	79.10	98.86	96.98	95.14
10	98.24	91.39	84.57	97.99	85.47	79.02	98.74	96.88	95.02
12	98.16	91.34	84.48	97.90	85.39	78.93	98.63	96.77	94.93
14	98.05	91.22	84.36	97.77	85.38	78.83	98.53	96.67	94.51
16	97.91	91.13	84.25	97.69	85.27	78.70	98.38	96.52	94.68
18	97.78	99.01	84.12	97.55	85.15	78.60	98.24	96.38	94.54
20	97.64	90.84	83.98	97.44	85.02	78.47	98.13	96.23	94.37
Average value	98.15	92.14	84.49	97.90	85.43	78.95	98.66	96.80	94.91

Table 3 Experiment at flow rate of 150 ml/min and at various heights from the base of the column - adsorption of cadmium, chromium and lead at optimum pH for MOSC

Initial metal concentration (mg/L)	**Cadmium adsorption (%) at pH=7-8**			**Chromium adsorption (%) at pH=2-3**			**Lead adsorption (%) at pH=6-7**		
	20cm	**40cm**	**80cm**	**20cm**	**40cm**	**80cm**	**20cm**	**40cm**	**80cm**
2	88.43	84.61	80.83	86.12	79.82	75.62	96.11	95.64	94.27
4	88.32	84.52	80.74	86.04	79.74	75.54	95.99	95.52	94.13
6	88.24	84.44	80.62	85.93	79.61	75.45	95.88	95.43	94.02
8	88.12	84.31	80.53	85.85	79.35	75.31	95.74	95.29	93.92
10	88.01	84.22	80.39	85.71	79.22	75.24	95.63	95.16	93.77
12	87.86	84.08	80.26	85.59	79.12	75.10	95.51	95.02	93.63
14	87.74	83.92	80.14	85.48	78.96	74.98	95.36	94.89	93.46
16	87.57	83.79	79.99	85.34	78.82	74.91	95.08	94.71	93.32
18	87.43	83.63	79.81	85.19	78.63	74.67	95.03	94.56	93.15
20	87.24	83.44	79.64	85.01	78.50	74.46	94.85	94.36	92.97
Average value	87.90	84.10	80.30	85.63	79.18	75.13	95.52	95.06	93.66

MOSC adsorption study for a flow rate of 150 ml per minute has given the following results. The average removal efficiency of Cd at 20 cm, 40 cm and 80 cm from the base of the column was 87.90%, 84.10% and 80.30% respectively. For Cr, it was 85.63%, 79.18% and 75.13% and in the case of lead, 95.52%, 95.06% and

93.66% respectively (Table 3). Figure 6 shows the level chart of clay-polymer composite media column height and flow rate in the heavy metal removal efficiency of MOSC.

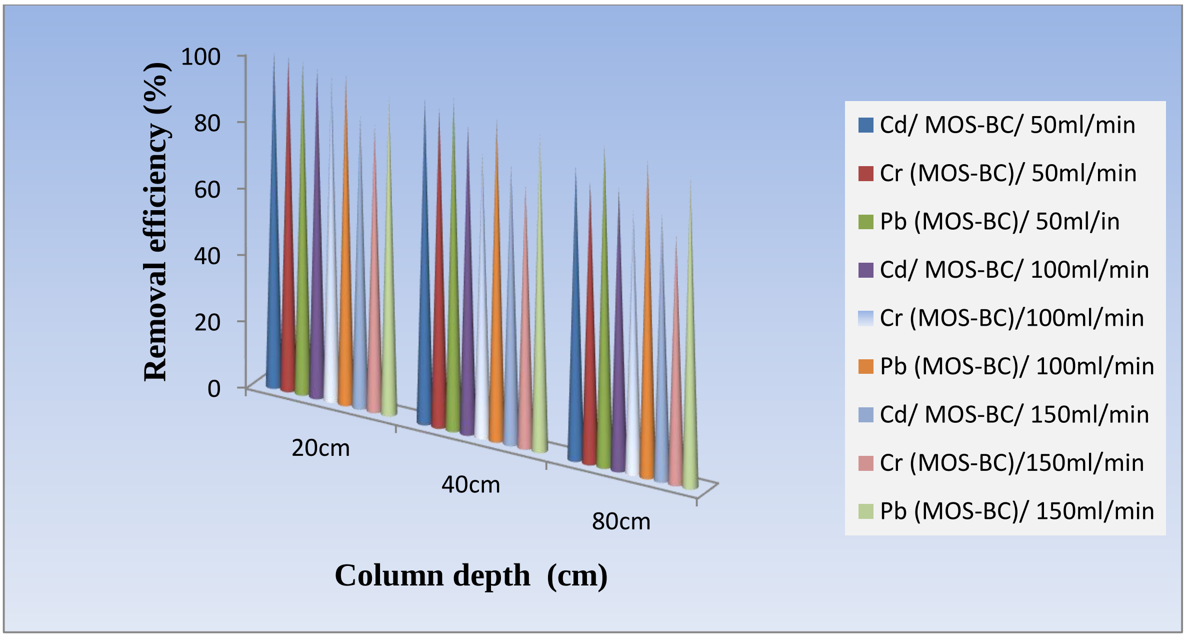

Fig. 6 Level chart of clay-polymer composite column height and flow rate in the heavy metal removal efficiency of MOSC

Figure 7 indicates the SEM of MOSC media before heavy metal removal. The SEM of MOSC after the heavy metal removal process of Cd, Cr and Pb are shown in Figure 8, 10 and 12 and corresponding EDX images are shown in Figure 9, 11 and 13.

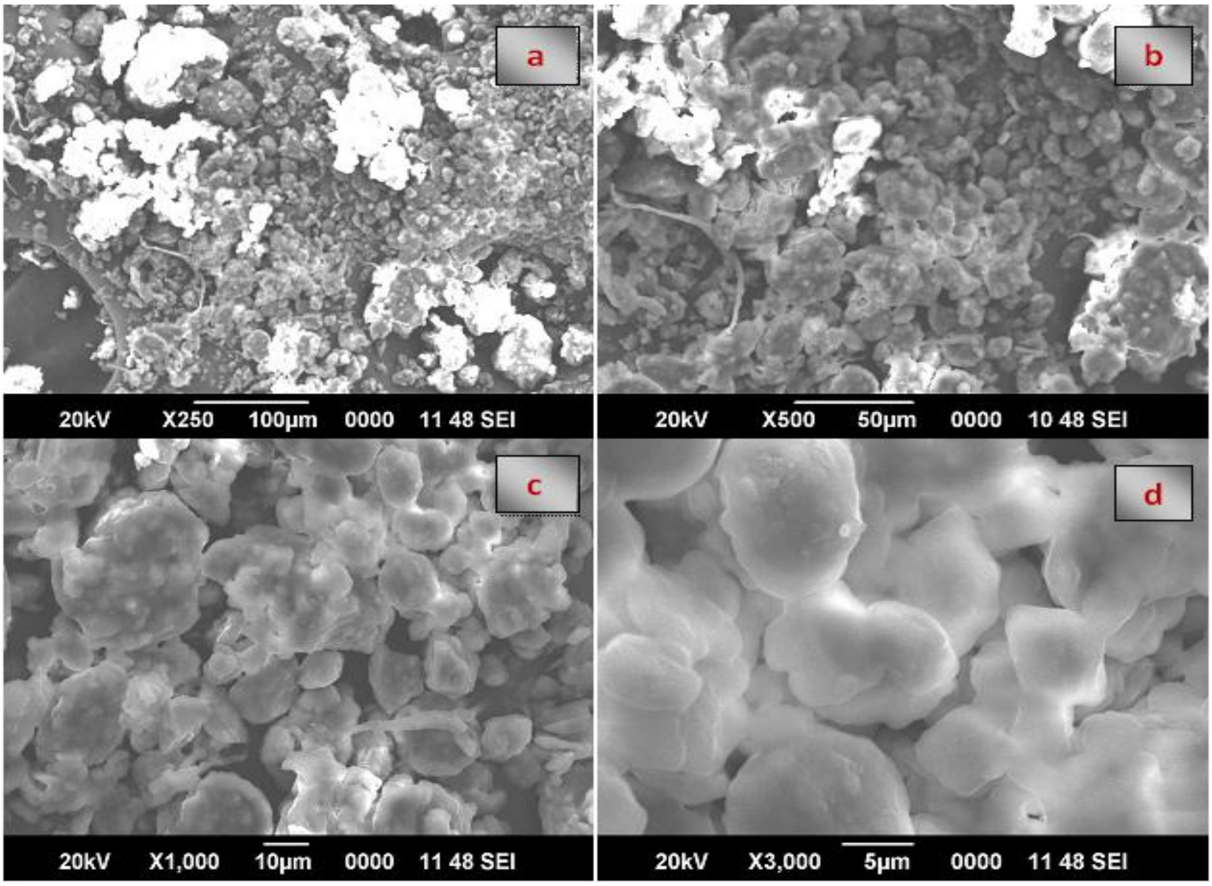

Fig. 7 Scanning electron micrographs of *Moringa oleifera* seed composite coagulant (MOSC) in the order of (a) 100 µm, (b) 50 µ m, (c) 10 µm and (d) 5 µm

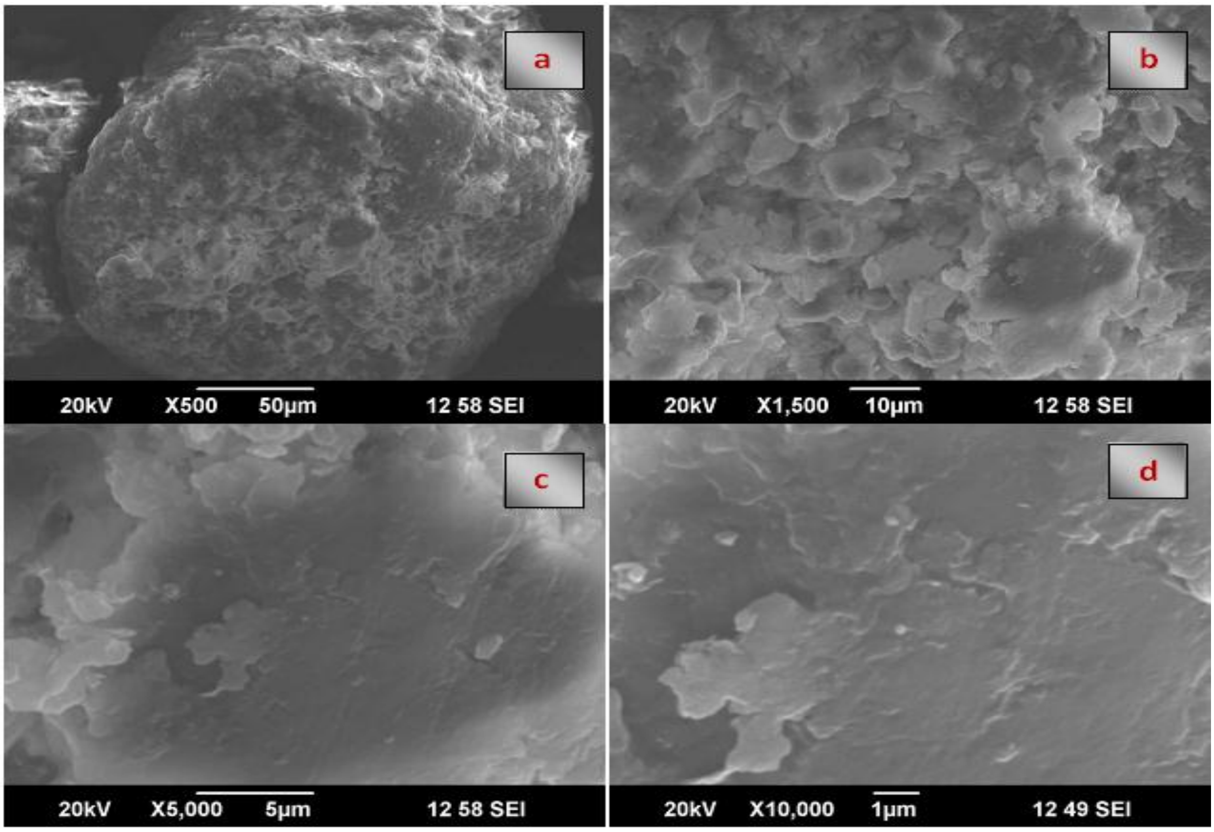

Fig. 8 SEM image of composite media after cadmium removal from the aqueous systems in the order of (a) 50 µm, (b) 10 µ m, (c) 5 µm and (d) 1 µm

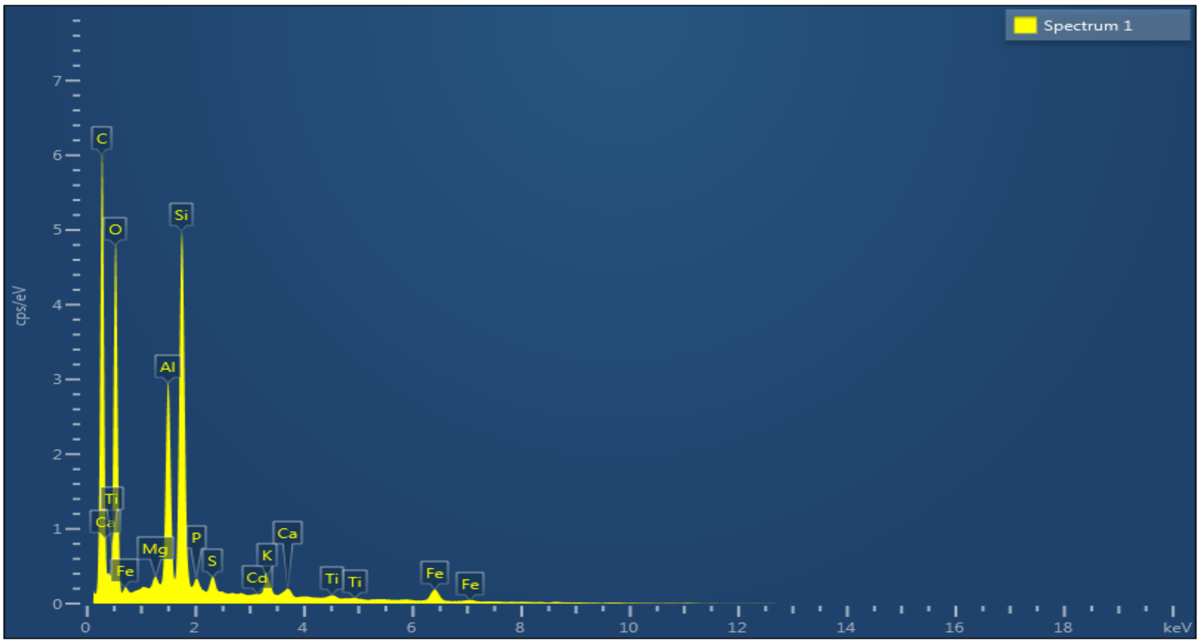

Fig. 9 EDX image of composite media after cadmium removal from the aqueous system

Figure 8 and 9 shows the SEM and EDX images of the composite media after cadmium ions removal. The high surface area with high surface site density of composite media can be potentially advantageous for the adsorptive removal of heavy metal ions.

The SEM-surface morphology (Figure 8) of metal ion loaded composite media was different compared to that of composite (Figure 7), supporting the Cd (II) adsorption onto clay-polymer media. At 1500 X magnification, an uneven surface texture along with lot of irregular surface format was observed. After adsorption, metal ion loaded composite media particles had granular, complex, uneven and porous surface textures that were not found in the composite. Adsorption of Cd (II) on to the clay-polymer surface was further confirmed by EDX analysis (Figure 9).

Figure 10 and 11 show the SEM and EDX images of the composite media after chromium ions removal. The SEM-surface morphology (Figure 10) of metal ion loaded composite media was different compared to that of composite (Figure 7), supporting the Cr(VI) adsorption onto clay-polymer media.

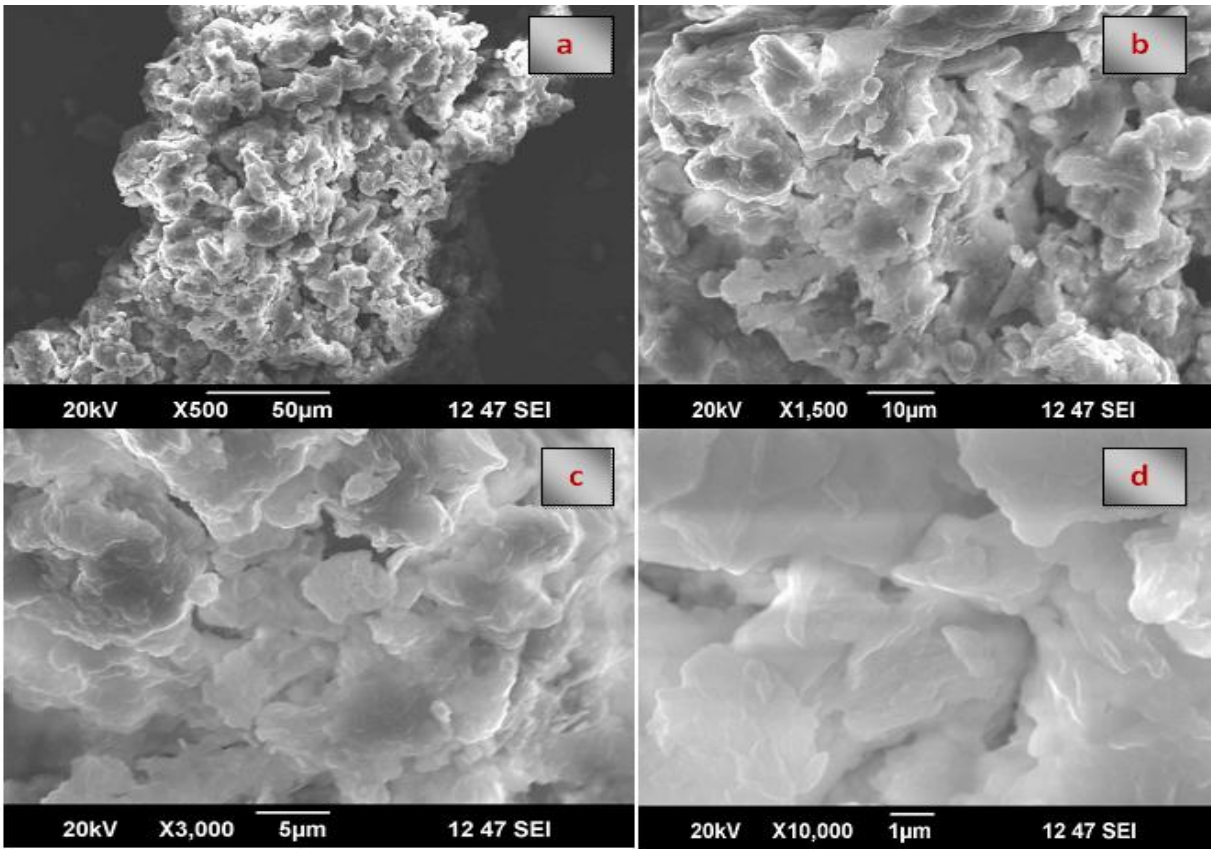

Fig. 10 SEM image of composite media after chromium removal from the aqueous systems in the order of (a) 50 μm, (b) 10 μ m, (c) 5 μm and (d) 1 μm

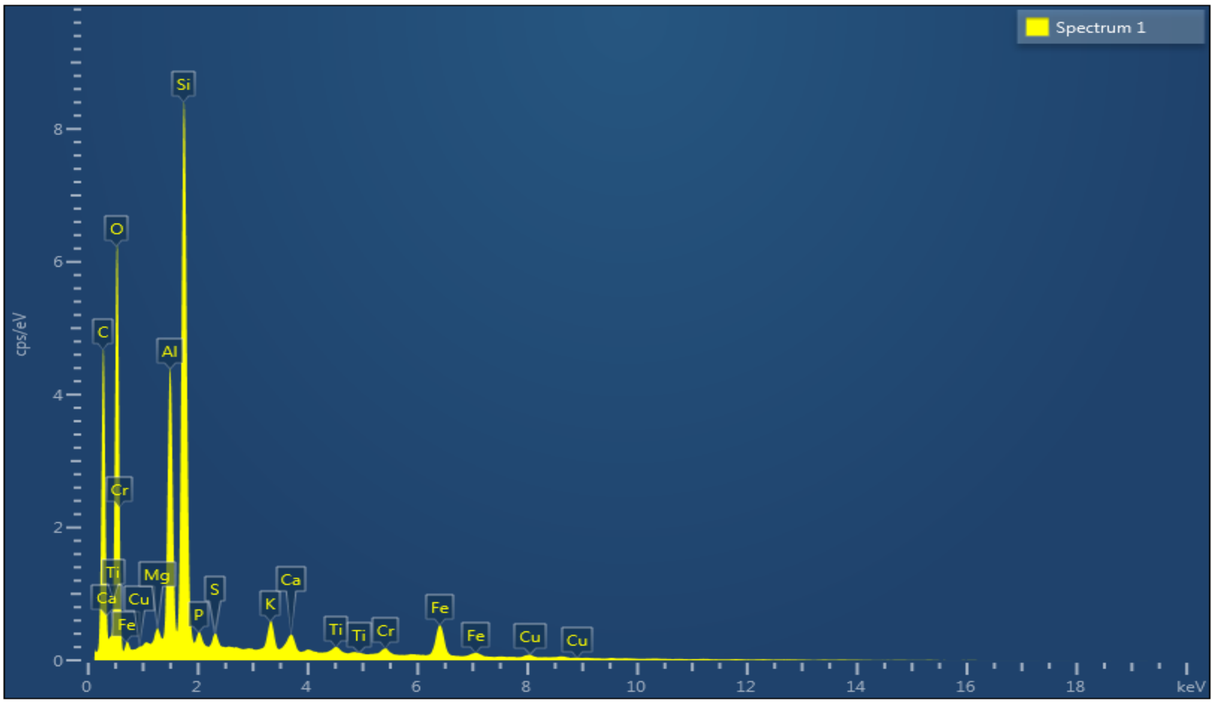

Fig. 11 EDX image of composite media after chromium removal from the aqueous systems

It is evident from analysis that the surface areas of composite are uneven, heterogeneous with pores on the surfaces. At 500 X magnification, an uneven surface texture along with lot of irregular surface format was observed. The change in morphology indicated the accumulation of chromium ions concentration onto clay-polymer surface areas (Figure 10). After adsorption, metal ion loaded composite media particles have granular, complex, uneven and porous surface textures that were not found in the composite. Further, pores facilitate the good possibility for metal ions to be adsorbed.

Adsorption of Cr (VI) on to the clay-polymer surface was further confirmed by SEM-EDX analysis (Figure 9).

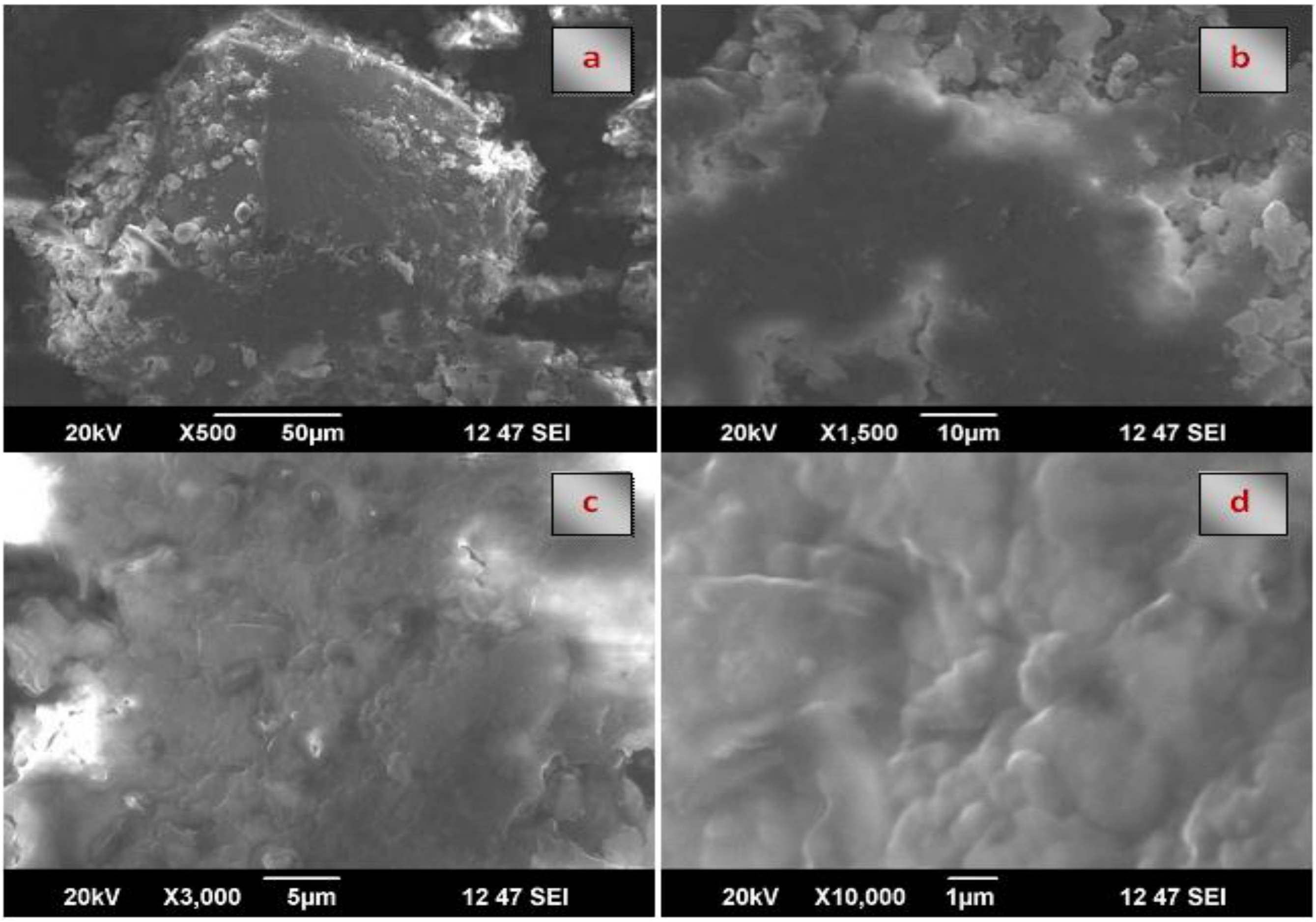

Fig. 12 SEM image of composite media after lead removal from the aqueous systems in the order of (a) 50 µm, (b) 10 µ m, (c) 5 µm and (d) 1 µm

Figure 10 and 11 shows the SEM and EDX images of the composite media after lead ions removal. A clear difference in the surface morphology (Figure 12) was observed for of metal ion loaded composite media to that of clay-polymer composite (Figure 7), supporting the Pb(II) adsorption onto composite media. SEM image of the clay-polymer composite had shown a distinct crystalline pattern with large spherical clusters type morphology whereas metal ion loaded composite media showed many aggregated small particles with dense agglomerated, etched dendrite type morphology.

Adsorption of Pb (II) on to the clay-polymer surface was further confirmed by EDX analysis (Figure 13). Similar results were obtained for green composites studied by different researchers, as shown in Table 4.

The results of the study point to the chemical interactions or complexed surface interactions between the homogeneous surface functional groups of clay-polymer composite media and the metal ions causing chemisorption.

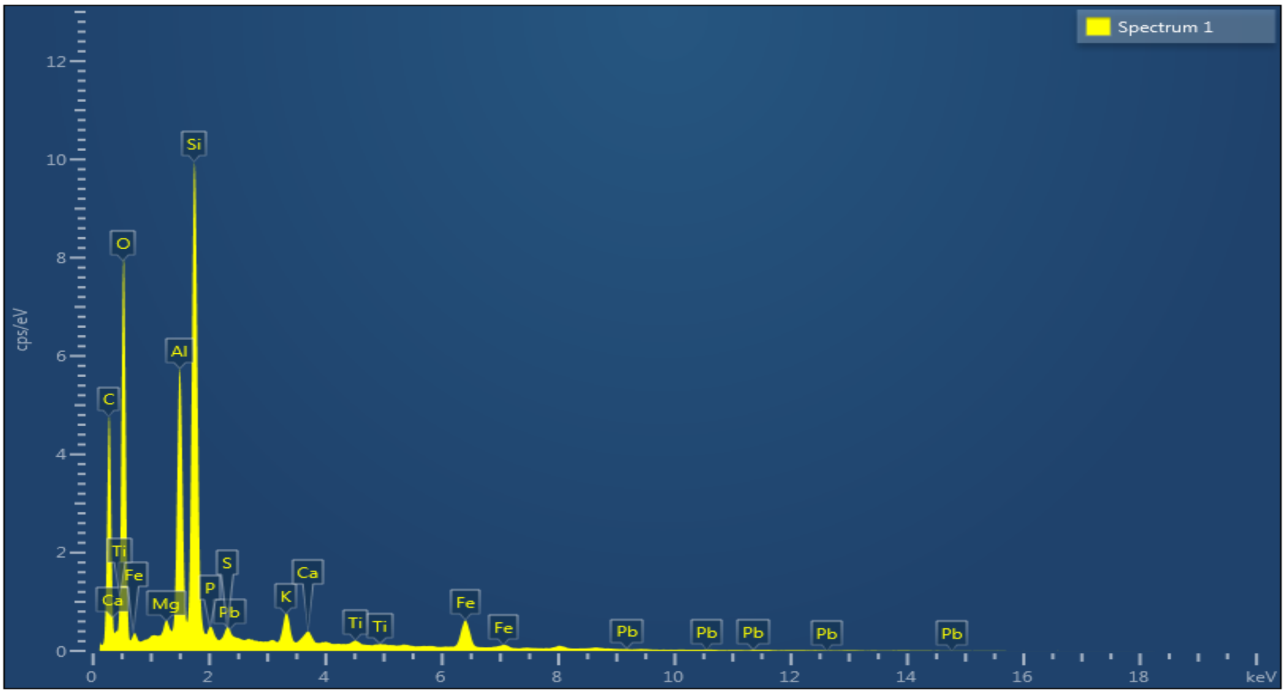

Fig. 13 EDX image of composite media after lead removal from the aqueous systems

Table 4 Comparison of maximum efficiency of various clay-polymer composites for heavy metal removal

Sl.No	**Contaminants in drinking water sources**	**Type of clay-polymer composite**	**Efficiency**	**Effecting variable**	**Value of the effecting variable**	**Reference**
1	Copper	Bentonite polyacrylamide composite	97%	pH	7	Zhao et al. 2010 [37]
2	Cr(VI)	Polymer- Clay	76.3-100%	pH	2	Sallam et al. 2017 [38]
3	Cr(VI)	chitosan/clay nanocomposite	93.5%	pH	3	Pandey and Mishra, 2011 [39]
4	Cr(VI)	Chitosan/ halloysite clay	90%	pH	3	Padmavthy et al. 2017 [40]
5	Chromium	chitosan-alumina	97.7%	pH	2	Masheane et al. 2017 [41]
6	lead	poly(acrylic acid)/ bentonite nanocomposite	99.6 %	time	<30min	Rafiei et al. 2016 [42]
7	lead	Nanochitosan/ kaolin clay	85%	pH	6	Kanchana et al, 2012 [43]
8	Cadmium lead	Polyvinyl alcohol-modified Kaolinite Clay	76% 97%	pH	6-7	Unuabonah et al. 2008 [44]
9	cadmium chromium lead	MOSC (Composite Media)	99.97-100% 99.98-100% 99.99-100%	pH	7-8 2-3 6-7	Present study

Conclusion

By the adsorption filtration studies using clay-polymer composite media of *Moringa oleifera* seed and bentonite clay, the heavy metals removal for a particular flow rate of 50 ml per minute at optimum pH was possible. The average removal efficiency of cadmium, chromium and lead at 20cm from the base of the column were 99.98% (pH range 7 to 8), 99.99% (pH range 2 to 3) and 99.99% (pH range 6 to 7) respectively. So, clay-polymer composites media adsorption using MOSC is suitable for drinking water treatment. During these processes, the metals interact physico-chemically with the composite to form clay-polymer-metal exfoliated complexes. The major advantages of the processes are the more shelf life of clay-polymer media, high regeneration efficiency and easier sludge disposal.

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