Novel and highly efficient functionalized bentonite for elimination of Cu^{2+} and Cd^{2+} from aqueous wastes

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ABSTRACT

The aim of this study was to synthesize novel and highly efficient functionalized material (BNMPTS) for selective elimination of Cu^{2+} and Cd^{2+} from aqueous waste. The detailed insights of solid/solution interactions were investigated by X-Ray photoelectron spectroscopic analyses. The grafting of silane caused for significant decrease in specific surface area of bentonite from 41.14 to 4.65 m^2/g . The functionalized material possessed significantly high sorption capacity (12.59 mg/g for Cu^{2+} and 13.19 mg/g for Cd^{2+}) and selectivity for these cations. The material showed very high elimination efficiency at a wide range of pH ~ 2.0 to 7.0 for Cu^{2+} , ~ 3.0 to 10.0 for Cd^{2+} and concentration (1.0 to 25.0 mg/L) for Cu^{2+} and Cd^{2+} . A rapid uptake of these two cations achieved an apparent equilibrium within 60 minutes of contact. The increased level of background electrolyte concentrations (0.0001 to 0.1 mol/L) did not affect the elimination efficiency of these two cations by BNMPTS. Moreover, the common coexisting ions did not inhibit the removal of these toxic ions. Furthermore, high breakthrough volumes i.e., 1.4 and 3.69 L for Cu^{2+} , 2.6 and 6.64 L for Cd^{2+} was obtained using 0.25 and 0.50 g of BNMPTS respectively in a fixed-bed column operations.

Keywords: Fixed bed column, Functionalized bentonite, Heavy metal ions, Sorption mechanism, X-ray photoelectron spectroscopy

1. Introduction

Water is a basic requirement for the survival of human beings and the supply of clean water is greatly required for healthy life; however, the shortage of clean water is a serious concern worldwide. The contamination of water bodies with several toxic heavy metal ions is a widespread concerns for environmentalists due to its distinctive physico-chemical properties such as non-biodegradability, high toxicity, and persistence in nature. The natural phenomena such as soil and rock erosions are partly responsible for contamination of aquatic environment; however, the anthropogenic activities are greatly contaminating the water bodies by variety of toxic heavy metal ions [1–5]. Among the toxic heavy metals, Cr, Pb, Fe, Cu, Ni, etc are excessively discharged into the environment through human activities.

Copper is an essential element in the human body at trace level but becomes toxic at higher concentration levels. The toxicity of copper includes liver and kidney dysfunction, abdominal and intestinal anxiety, anaemia, etc. [6, 7]. The presence of copper generates free reactive oxygen species in blood which seemingly dam-

ages DNA, proteins and lipids [8]. Therefore, because of its toxic nature the regulatory bodies demonstrated that the maximum contamination level of Cu in potable water is 1.5 mg/L [9]. On the other hand, cadmium (Cd) is another potential heavy metal often occurs in wastewaters. Cadmium toxicity causes nausea, *itai itai* disease, salivation, diarrhoea, respiratory problems, skeletal malformation, hypertension and renal calculi, etc. In some enzymes, zinc (II) ions are readily replaced by cadmium (II) ions, thereby disturbing the enzyme activity in bio-systems. Additionally, the cadmium is known to be a potential carcinogen hence, the IARC has classified Cd^{2+} as category 1 human carcinogen [10, 11]. The maximum contamination level of cadmium in drinking water was prescribed as low as 0.003 mg/L [9].

The decontamination of water bodies from heavy metal toxic ions is proposed by different methods which greatly includes with adsorption, membrane filtration, coagulation, reverse osmosis etc. These methods are having its own merits and demerits in terms of the operational cost, procedure, subsequent environmental impact etc. However, among these methods, the adsorption is considered to be simple and cost-effective since it offers the possible

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utilization of naturally abundant materials for the removal of various water pollutants [12, 13].

Clay minerals are natural filter media eliminating a variety of pollutants from aqueous media. Clay minerals possessed a large number of exchangeable cations which could play an important role in the adsorption process [14, 15]. These materials are ubiquitous and relatively low in cost as compared to the activated carbon commonly used as filter media for water purification [16]. Previous reports indicated that clay and clay-based materials are highly effective in removing toxic heavy metals from aquatic environments [17–19]. Bentonite is abundant clay having layered phyllosilicates. Similar to other clay minerals, bentonite possesses exchangeable cations and distinct porous structure which makes bentonite a suitable and efficient adsorbent material [20, 21]. The adsorption ability of bentonite is primarily defined by its pore structure and the cation exchange capacity (CEC) [22]. However, the use of pristine bentonite in real water treatment showed inherent limitations including the selectivity of materials, the swelling nature of clay and most importantly the settling capacity of solids. Therefore, the intended modifications of the clay materials were previously reported which overcome partly the limitations of clay minerals for its greater use in water decontamination studies [23–29]. Surfactants are commonly employed for the surface modification of clay minerals; however, the surfactant loaded clay materials showed its limitations since the surfactant molecules easily desorb and making secondary pollution of water bodies [30]. Therefore, grafting/incorporation of organosilanes with the clay minerals showed an impetus for researchers since the silane grafted composite materials possessed significantly enhanced stability. Moreover, the selective introduction of functional group through specific silanes enables the selectivity of materials for targeted pollutants in aqueous wastes that enhances greater applicability of materials for wider applications in various waste water treatment strategies [11, 24]. It was reported previously that the reaction conditions, surface hydroxyl group concentration and silane characteristics play a vital role in successful silylation of clay minerals [24]. Therefore, the present communication is intended to functionalize the bentonite with the thiol group (-SH) using the 3-mercaptopropyltrimethoxysilane (MPTS) molecules using a simple one step process. Further, the functionalized material was employed for the removal of copper (II) and cadmium (II) under batch and column reactor studies. The mechanistic aspects involved in the sorption of copper (II) and cadmium (II) by the surface of functionalized bentonite was extensively studied. Further, the efficient use of functionalized natural clay in the dynamic reactor operations could possibly enable the scaling up of the technology for real treatment of aqueous wastes.

2. Materials and Methods

2.1. Materials

Bentonite (BN) as mined at Bhuj, Gujarat, India was collected and utilized in the studies. The pristine bentonite (particle size of 0.15 mm) was thoroughly washed using purified water and then employed for further use. 3-mercaptopropyletrimethoxy silane (Sigma

Aldrich, USA), CdSO_4 , and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Kanto Chemical Co. In., Japan), oxalic acid glycine (Daejung Chemicals and Metals Co. Ltd., Korea) were utilized. Moreover, manganese (II) chloride, ethylenediaminetetraacetic acid, nickel chloride and sodium phosphate are procured from Duksan Pure Chemicals Co. Ltd., Korea. Magnesium sulfate heptahydrate and calcium chloride dihydrate powder were purchased from Samchun Pure Chem. and Metals Co. Ltd., Korea.

2.2. Methodology

2.2.1. Grafting of silane with bentonite

3-mercaptopropyletrimethoxy silane was grafted with the bentonite network using slightly modified method [31, 32]. Briefly, 30 g of bentonite was dispersed in 600 mL of toluene. The suspension was refluxed under stirring for 30 min at 60°C under nitrogen atmosphere. 30 mL of 3-mercaptopropyletrimethoxy silane was then added dropwise to this suspension and it was further refluxed for 48 h. The suspension was carefully filtered and the solid was thoroughly washed by toluene (20 mL) followed by ethanol (50 mL). The material was dried at 100°C for 24 h. The silane grafted bentonite was carefully stored in a sealed polyethylene bottle and named as BNMPSTs.

2.2.2. Characterizations

The FT-IR data of pristine bentonite (BN) and functionalized bentonite (BNMPSTs) were obtained by using FT-IR (Affinity-1 Shimadzu, Japan) machine. The surface images of BN and BNMPSTs were taken by the SEM (FE-SEM; S-4700, Hitachi, Japan). Energy-dispersive X-ray spectroscopic analysis (EDAX) was employed to obtain the elemental composition of BN and BNMPSTs. The X-ray diffraction results were obtained using the XRD machine (PANalytical, Netherland). BET Analyzer (Model-1201) was utilized to measure the specific surface area determination of silids. Moreover, the X-ray photoelectron spectroscopy (XPS) (Model: ESCALAB-250Xi+) analyses were conducted to obtain greater insights of the interaction of sorbate ions with BNMPSTs. Further, the pH_{PZC} of bentonite and BNMPSTs were obtained following the known method which was reported previously [33].

2.2.3. Batch reactor operations

The flow-chart showing the experimental design of the present research work is shown in Fig. S1. The stock solutions (100.0 mg/L) of each copper (II) sulphate pentahydrate and cadmium (II) sulphate were prepared by dissolving an appropriate amount of copper (II) and cadmium (II) in purified water. Further, the required experimental concentrations of copper (II) and cadmium (II) were obtained by successive dilution of stock solutions. Batch reactor operations in the removal of copper (II) or cadmium (II) by solids were carried out using 60 mL polyethylene bottles. The pH dependent adsorption studies was performed by taking 50.0 mL of 10.0 mg/L copper (II) and 5.0 mg/L cadmium (II) solutions in different polyethylene bottles and the pH of each solutions were adjusted with drop wise addition of 0.1 mol/L HCl/NaOH solutions. Further, 0.1 g of solid (BN or BNMPSTs) was introduced in each bottles and bottles were tightly closed. These experimental bottles were kept in the shaking incubator (KUJKE, Shaking Incubator, Korea; Model 36-SIN-125) and solution mixtures were shaken for 24 h

at $25 \pm 1^\circ\text{C}$. The solution mixtures were then filtered by syringe filters ($0.45 \mu\text{m}$). Filtrates were subjected for measurement of sorbate concentrations using the atomic absorption spectrometer (AAS) (Model AA240FS, Varian, Australia). The blank sorbate concentration was also obtained and hence, the percentage removal of these cations was computed.

Similarly, the concentration dependence studies were conducted varying the metal ion concentrations from 1.0 to 25.0 mg/L at pH 4.0 and 5.0 for Cu(II) and Cd(II), respectively. The remaining adsorption experiments were performed as described previously and the percentage removal of these ions as a function of sorbate concentration is computed. The time dependent adsorption was carried out using Cu (II) and Cd(II) concentrations 10.0 mg/L (pH 4.0) and 5.0 mg/L (pH 5.0), respectively. The removal of Cu(II) and Cd(II) as a function of time is obtained. The detailed procedure was described previously [15]. The Background electrolyte dependent elimination of these two cations was studied by adding accurate amounts of NaCl in sorptive solution as to obtain the NaCl concentrations of 0.0001, 0.001, 0.01 and 0.1 mol/L. The pH of Cu(II) and Cd(II) was maintained to 4.0 and 5.0, respectively. The percentage removals of these two cations were obtained as a function of background electrolyte concentrations. The competitive sorption was extensively studied in presence of several co-anions (ethylenediaminetetraacetic acid, glycine, oxalic acid and phosphate) and co-cations (Mg^{2+} , Mn^{2+} , Ni^{2+} and Ca^{2+}). The adsorption experiments were conducted using the co-ions concentrations of 50.0 mg/L at 25°C by keeping Cu^{2+} and Cd^{2+} concentrations 10.0 mg/L at pH 4.0 and 5.0 mg/L at pH 5.0, respectively.

2.2.4. Fixed bed column reactor operations

Column studies were conducted employing a glass column (length 30 cm and inner diameter 1 cm). The glass beads were used having the diameter of 1 mm. The column was packed with 0.25 g or 0.5 g of BNMPST solid. The BNMPST material was safely placed in the middle of the column and 1.0 g of sand was kept below and above to the BNMPST solid. The remaining space in the column was packed with glass beads. Cu^{2+} (10.0 mg/L) or Cd^{2+} (5.0 mg/L) solution was pumped upward using the peristaltic pump having a flow rate of 1.0 mL/min. A fraction collector was used to collect the effluent volume. Effluent was filtered by $0.45 \mu\text{m}$ filter and the filtrate was subjected for the analysis of Cu(II) or Cd(II) concentrations using the AAS. The loading capacity of BNMPST was obtained by modelling the breakthrough data with non-linear Thomas equation which is reported previously [7].

3. Results and Discussions

3.1. Characterization of the Materials

The FT-IR spectra of pristine bentonite and functionalized bentonite (BNMPST) are illustrated in Fig. S2(a). A prominent vibrational peak appeared at wavenumber $3,365 \text{ cm}^{-1}$ which was due to the stretching vibrations of O-H of the silanol group. Weak vibrational bands appeared at 2913 and $2,837 \text{ cm}^{-1}$ were assigned as stretching vibrations of $-\text{CH}_3$ and $-\text{CH}_2$, respectively [32, 34]. The methoxy group ($-\text{OCH}_3$) of MPTS possessed a characteristic vibration at $2,914 \text{ cm}^{-1}$ [32, 35]. A stretching vibrational peak at $2,550 \text{ cm}^{-1}$ was due

to the sulfhydryl group of MPTS [36]. Further, C-H deformation and C-S stretching vibrations of the sulfhydryl group of MPTS were observed at 682 and $1,402 \text{ cm}^{-1}$, respectively [37]. These results confirmed that MPTS is bonded with the bentonite network. Further, the XRD peaks of bentonite and BNMPST solids are given in Table S1. There is no significant change in the peak positions after the incorporation of organosilane. The prominent peaks obtained at 2 theta values of 20.95, 26.78, 36.68, 50.26, 60, and 68.36 indicated the presence of quartz in the clay sample [38, 39].

The BET method is employed to obtain the N_2 adsorption/desorption isotherms for BN and BNMPST solids (Fig. S2(b)). Fig. S2(b) exhibited type IV isotherm having H3 type hysteresis loop which indicates the mesoporous structure of materials [40]. Further, the pristine bentonite showed relatively a wider hysteresis loop and the pore size and pore volume were $80.92 \text{ \AA}$ and $0.070 \text{ cm}^3/\text{g}$, respectively. The pore size and pore volume of bentonite are notably changed and BNMPST material possessed $237.91 \text{ \AA}$ and $0.027 \text{ cm}^3/\text{g}$ of pore size and pore volumes, respectively. The BET specific surface area of BN and BNMPST were obtained as 41.14 to $4.65 \text{ m}^2/\text{g}$, respectively. The surface area of bentonite clay was considerably decreased after the grafting of MPTS since the silane appeared to occupy the places within the galleries of bentonite. A significant reduction in the surface area of smectite after functionalization with MPTS was reported previously [34]. Moreover, a similar decrease in surface area of bentonite was observed with the modification of bentonite by hexadecyl trimethyl ammonium (HDTMA) [39]. The immobilization of MPTS onto sepiolite caused for a significant decrease in surface area of clay [36, 41] and the surface area of SBA-15 modified with mercapto- or amino-propyl had resulted in the reduction of specific surface area of the material [42].

The SEM micrograph of BN is displayed in Fig. 1(a) whereas that of BNMPST is shown in Fig. 1(b). The BN and BNMPST showed heterogeneous and disordered surface structures. Moreover, it is clearly visible from the SEM images that the pristine bentonite possessed more porosity and the porosity is drastically reduced after the grafting of MPTS molecules with the bentonite. This observation

Fig. 1. Scanning electron microscopic images of (a) pristine bentonite (BN); and (b) BNMPST and EDX analysis of (c) pristine bentonite (BN); and (d) BNMPST.

is in line with the textural properties obtained by the BET surface area results. Furthermore, EDX analyses were performed for BN (Fig. 1(c)) and BNMPTS (Fig. 1(d)). The EDX analytical graph showed that the major elemental composition of bentonite included with Si, Al, O and Fe along with Na and K elements at lesser extent. It is noteworthy to observe that the EDX spectrum of BNMPTS was contained with a considerable amount of sulphur which was not observed in pristine bentonite. This indicated that the mercapto (-SH) group was successfully incorporated to bentonite and possibly formed a stable bonding on bentonite surface. Similar results were reported in which the sulphur composition corresponding to the mercapto (-SH) group were observed with kaolinite [32, 35, 43].

3.2. Batch Reactor Studies

3.2.1. pH dependence studies

Percentage elimination of Cu^{2+} and Cd^{2+} by pristine bentonite and BNMPTS material at various pH values is shown in Fig. 2(a) and 2(b). It is interesting to observe that the grafting of MPTS onto bentonite clay has enabled to increase the percentage removal of these two toxic ions and almost 100% of Cu^{2+} was removed within the pH range ~ 2.0 to 7.0 using BNMPTS. Moreover, a high percentage (*Ca* 99%) of Cd^{2+} was successfully removed within pH ~ 3.0 to 10.0 . The pH dependent study revealed that BNMPTS possessed high affinity towards Cu^{2+} and Cd^{2+} which showed potential applicability of the material in the remediation of aqueous waste containing these toxic contaminants. The pH_{pzc} of the BNMPTS was determined and found to be 7.73. This indicated that BNMPTS possessed net positive charge at pH lower than 7.73 and it is having net negative charge above pH 7.73. Besides, the speciation of Cu^{2+} (Fig. S3(a)) shows that copper exists as Cu^{2+} species up to pH 5.5. Between pH 5.0-7.0, Cu^{2+} exists as insignificant

of $\text{Cu}(\text{OH})^+$ species with a maximum of 1.4% only. Further, Cu^{2+} starts to form insoluble tenorite species at pH > 5.5 . Almost 100% of Cu^{2+} was removed beyond pH 5.5 and this could be due to both adsorption and co-precipitation of Cu^{2+} onto the surfaces of BNMPTS material [15]. On the other hand, the speciation of Cd^{2+} (Fig. S3(b)) shows that Cd^{2+} (ionic species) exists up to pH 8.8 and insoluble $\text{Cd}(\text{OH})_2(\text{s})$ primarily exists above this pH. In between *Ca* pH 8.7, about 5% of $\text{Cd}(\text{OH})^+$ species exists. Therefore, cadmium (II) is predominantly present as cationic (Cd^{2+}) species within the studied pH region. The high percentage of Cu^{2+} and Cd^{2+} are removed even at acidic conditions or below the pH_{pzc} of the BNMPTS. Therefore, all the remaining sorption experiments were performed at pH 4.0 and 5.0 for Cu^{2+} and Cd^{2+} , respectively. The results indicated that the Cu^{2+} /or Cd^{2+} are bound with strong chemical forces rather than the weak physical forces. The available -SH or -OH groups, perhaps, take part predominantly in the bond formation onto the surface. Additionally, the dense brushes of the silanes are present on the surface of BNMPTS which traps the Cu^{2+} and Cd^{2+} efficiently and this significantly enhances the sorptive elimination of these pollutants in aqueous wastes at a wide range of pH (Fig. 2(c)).

3.2.2. Time dependent elimination of Cu^{2+} and Cd^{2+}

Time dependent elimination of Cu^{2+} and Cd^{2+} using BNMPTS are illustrated graphically in Fig. S4(a). BNMPTS showed very fast and rapid initial uptake of these two cations and about 95% of these two toxic ions were removed within 5 minutes of contact. The percentage removal was gradually slowed down and apparent sorption equilibrium was reached within 30 minutes of contact for both the metals cations. The results confirmed that the BNMPTS possessed high affinity towards the Cu^{2+} and Cd^{2+} and the active sites on BNMPTS solid were readily accessible to these toxic ions

Fig. 2. Sorptive removal of (a) Cu^{2+} ; (b) Cd^{2+} as a function of pH using the BN and BNMPTS ($[\text{Cu}^{2+}]$: 10.0 mg/L; $[\text{Cd}^{2+}]$: 5.0 mg/L at 25°C); (c) Schematic of sorption of Cu^{2+} and Cd^{2+} by the BNMPTS solid.

[36, 44]. This further reaffirmed that the dense brushes of silanes available on BNMPPTS material forms strong chemical bonds with these cations and rapid removal of Cu^{2+} and Cd^{2+} were occurred using the BNMPPTS material. Further, the kinetics was conducted for pseudo-first order (PFO) and pseudo-second order (PSO) models using the known kinetic equations as given elsewhere [45]. Fig. S4(b) and (c) showed apparent simulation of PFO and PSO models employing experimental results. The uptake capacity and rate constants are optimized for possible minimum value of least square sums. The results are returned in Table S2. PSO model relatively fitted well to kinetic data for the sorption of Cu^{2+} and Cd^{2+} by BNMPPTS solid. Further, the removal capacity was found to be 4.13 and 2.03 mg/g respectively for Cu^{2+} and Cd^{2+} using BNMPPTS solid. The well-fitting of PSO model suggested that the chemical interactions are predominantly involved at the solid/solution interface [46]. The removal of Cu^{2+} using bentonite coated with Fe_3O_4 magnetite nanoparticles and Cd^{2+} using 3-MPA@PMNPs were also followed PSO model than PFO model and showed that the interaction of sorbates species with adsorbent is chemical in nature [38, 47].

3.2.3. Influence of initial metal concentrations

The elimination efficiency of Cu^{2+} and Cd^{2+} by BNMPPTS at varied concentrations of adsorbates are given in Fig. S5. It is observed that BNMPPTS material was able to attain very high removal efficiency for Cu^{2+} and Cd^{2+} even at high concentrations of respective ions. Further, increasing the concentrations of metals from 1.0 to 25.0 mg/L did not show significant impact on the percentage

removal of these ions. It is noted that at the concentration of 25.0 mg/L, BNMPPTS was able to remove 96 and 93% of Cu^{2+} and Cd^{2+} , respectively. These findings revealed that the high uptake capacity of BNMPPTS for Cu^{2+} and Cd^{2+} and affinity of these cations towards the composite material.

It is further observed that increasing the concentration of Cu^{2+} and Cd^{2+} from 1.0 to 25.0 has caused to increase the amount of Cu^{2+} from 0.493 to 11.955 mg/g and Cd^{2+} from 0.418 to 11.592 mg/g, respectively.

The concentration dependent data are utilized to obtain the Langmuir and Freundlich adsorption isotherms [15]. The Langmuir monolayer sorption capacity (q_0), Langmuir constant (b), Freundlich constants (K_f and $1/n$) for BN and BNMPPTS are obtained and given in Table S3. It is observed that the sorption of Cu^{2+} and Cd^{2+} by the BNMPPTS material followed Langmuir sorption isotherm model better than Freundlich adsorption isotherm since higher R^2 value is obtained for Langmuir adsorption isotherm. Similar results are reported in which the removal of Cd(II) by dopamine-functionalized meso-structured silica (DMOS) and Cu(II) by mercapto functionalized palygorskite (MPAL) followed Langmuir adsorption isotherm [48, 49]. Previously, it was also reported that the adsorption of Cu(II) and Zn(II) onto natural bentonite (NB) and modified bentonite (MB) followed Langmuir adsorption isotherm indicated homogenous distribution of adsorption sites on the solid surfaces and the formation of monolayer adsorbate species onto the sorbent surface [50]. Furthermore, the affinity of BNMPPTS towards Cu^{2+} and Cd^{2+} was shown by higher values of Langmuir constant (b). The Freundlich constant ($1/n$) has frac-

Table 1. Maximum Adsorption Capacity of Various Adsorbents for Cd (II) and Cu(II)

Sl. No	Adsorbents	Concentration range (mg/L)	pH	Adsorption capacity (mg/g)	References
Cd(II)					
1	AS-APTES	2–30	5	8.475	[11]
2	Mesoporous Silica (AMS)	4.6–47.6	6.5	2.75	[10]
3	Magnetic- <i>Chlorella vulgaris</i>	1.00–30.27	4.5	13.157	[52]
4	Bamboo charcoal	20–100	-	12.08	[53]
5	Superparamagnetic Fe_3O_4 @ FePO_4 nanoparticles	1–200	7	13.51	[54]
6	Porous resin	20–500	7	3.506	[55]
7	Iron-oxide immobilized sand	1–20	4.5	0.528	[7]
8	BN	1–25	5	3.57	This study
9	BNMPPTS	1–25	5	13.19	This study
Cu(II)					
10	Mesoporous Silica	1.91–13.51	5	3.619	[56]
11	Activated bentonite	1–20	5	3.787	[57]
12	CIB-EDGE	100–2,000	4	10.52	[58]
13	Humic acid modified bentonite	50–700	5	10.33	[59]
14	Sodium alginate composite gel	200	4	6.783	[60]
15	Nanoclay	10–50	8	7.53	[61]
16	Coconut residue	5–100	7	2.76	[62]
17	BN	1–25	4	4.15	This Study
18	BNMPPTS	1–25	4	12.59	This Study

AS-APTES- activated sericite functionalized with 3-aminopropyltriethoxy silane

CIB-EDGE -Chitosan immobilized on bentonite and ethylene glycol diglycidyl ether

tional values which showed the heterogeneous surface of the material and the available sites for adsorption is distributed exponentially. Similarly, the higher level of adsorbate removal is indicated by K_f values and good adsorption intensity is denoted by lesser value of $1/n$ [51]. Comparison for maximum adsorption capacity of various adsorbents for Cd(II) and Cu(II) are given in Table 1, respectively. The adsorption capacity of various sorbents are different due to the variation in physico-chemical properties of adsorbents as well as the experimental factors such as pH, temperature, ionic strength, concentration range, etc [11]. However, it is interesting to observe that BNMPTS showed fairly high adsorption capacity for Cu(II) and Cd(II) which is comparable or even higher than several similar adsorbents reported previously.

3.2.4. Effect of Background electrolyte concentrations

Removal of pollutants from water is generally impacted by the presence of background electrolytes present in aqueous wastes. However, this relies on the concentration and nature of the electrolytes [11]. Therefore, the elimination of Cu^{2+} and Cd^{2+} were performed at varied concentrations of background electrolyte (NaCl) and results are shown in Fig. 3. Fig. 3 showed that a thousand times increase in background electrolyte concentrations could not affect the elimination efficiency of Cu^{2+} and Cd^{2+} by BNMPTS. These findings again showed that the modified bentonite has a

Fig. 3. Removal efficiency of Cu^{2+} and Cd^{2+} at different concentrations of NaCl using BNMPTS ($[\text{Cu}^{2+}]$: 10.0 mg/L (pH: 4.0); $[\text{Cd}^{2+}]$: 5.0 mg/L (pH: 5.0) at 25°C).

Fig. 4. Cu^{2+} and Cd^{2+} removal by BNMPTS solid in presence of several co-existing (a) cations; and (b) anions ($[\text{Cu}^{2+}]$: 10.0 mg/L (pH: 4.0); $[\text{Cd}^{2+}]$: 5.0 mg/L (pH: 5.0); [Co-existing ions]: 50.0 mg/L at 25°C).

strong affinity towards these metal ions and suggests that Cd^{2+} ions are aggregated onto BNMPTS solid through the strong chemical bonds, possibly, through the -SH or -OH functional groups which leads the 'inner-sphere' complexation at solid surface [10, 11]. Similarly, the percent removal of Cu^{2+} by walnut (*Juglans regia*), hazelnut (*Corylus avellana*), and almond (*Prunus dulcis*) is negligible when the concentration of KNO_3 was increased from 0.01 to 0.1 mol/L [63].

3.2.5. Effect of Co-existing ions

The percent elimination of Cu^{2+} and Cd^{2+} using BNMPTS was studied in presence of the selected cations (Mg^{2+} , Mn^{2+} , Ca^{2+} and Ni^{2+}) and anions (oxalic acid, glycine and phosphate) and the results are given in Fig. 4(a) and 4(b). The presence of EDTA significantly suppressed the removal of Cu^{2+} and Cd^{2+} by BNMPTS. This is because EDTA is forming stable complexes with metal ions and the complex species are not bound with the solid surface [64, 65]. On the other hand, other cations or anions did not affect the elimination efficiency of Cu^{2+} and Cd^{2+} . Therefore, the findings further showed the selectivity and the efficiency of BNMPTS towards Cu^{2+} and Cd^{2+} in presence of these co-existing cations/anions. Tamez et al. [66], found that the presence of sodium, potassium and calcium or magnesium did not affect significantly the binding of Cu^{2+} and Cd^{2+} onto the Fe_3O_4 solid. Hence, only a small decrease in percentage removal of these ions was recorded in presence of Mg^{2+} (3,000 mg/L). Similarly, the elimination of Cu(II) and Pb(II) by non-living green algae was not affected significantly in the presence of several anions except EDTA. The presence of 1.0 mmol/L EDTA had caused to suppress significantly the removal efficiency of copper and lead by the non-living green algae [67]. Similarly, nitrate salts of Na, K and Mg showed insignificant influence on the elimination of Cd(II) by brown, green, and red seaweeds. But uptake of cadmium was suppressed at calcium level of 1.62 mmol/L to 80% and further decreased to 65% at 3.24 mmol/L [68]. The removal of Cd^{2+} , Cu^{2+} , Pb^{2+} and Hg^{2+} by ZnS and FeS nanomaterials was 99% in mixed metal cation solutions in presence of 60 fold concentrations of Ca^{2+} and Mg^{2+} . Hence the presence of other cations have negligible or no effect on the toxic metal removal using metal-sulfide nanomaterials [69]. In other study, the elimination of Cd^{2+} by MnO_2 loaded D301 showed no significant effect in presence of several cations (Na^+ , K^+ and Ca^{2+} , or Mg^{2+}) and anions (Cl^- , NO_3^- , SO_4^{2-} and PO_4^{3-}) except of PO_4^{3-} [70]. The

presence of EDTA on the sorption of Cd^{2+} and Zn^{2+} by apatite showed a decrease in the uptake of Cd^{2+} and Zn^{2+} due to the formation of $[\text{CdEDTA}]^{2-}$ and $[\text{ZnEDTA}]^{2-}$ complexes [71].

3.3. Fixed Bed Reactor Operations

The breakthrough column results are shown in Fig. 5. The functionalized material showed complete breakthrough volume at 1.4 and 3.69 L for Cu^{2+} , 2.6 and 6.64 L for Cd^{2+} while using 0.25 g and 0.50 g of BNMPSTs, respectively. Furthermore, the known Thomas equation was exploited in order to estimate the loading capacity of BNMPSTs by performing the non-linear least square fitting of breakthrough column results. The constants K_T and loading

Fig. 5. Breakthrough curves obtained for the removal of Cu^{2+} and Cd^{2+} using BNMPSTs material ($[\text{Cu}^{2+}]$: 10.0 mg/L (pH: 4.0); $[\text{Cd}^{2+}]$: 5.0 mg/L (pH: 5.0), Flow rate: 1 mL/min).

capacity (q_0) are presented in Table 2. The loading capacity obtained for BNMPSTs are relatively high at least for the Cu^{2+} and Cd^{2+} . This eventually infers the useful applicability of BNMPSTs for efficient elimination of aqueous waste containing copper and cadmium [39, 45].

3.4. Adsorption Mechanism

Previous reports have shown that an enhanced uptake of Cu^{2+} was achieved using mercapto functionalized silica aerogel [72], Poly(vinyl alcohol)/silica (PVA/silica) membranes [73], electrospun CeO_2 nanofiber [74] and palygorskite [49]. Similarly, the removal of Cd^{2+} was successfully succeeded with mercapto functionalized silica [75, 76], palygorskite [77], attapulgite [78], sepiolite [79], zinc based metal organic framework [80] and coal gangue [81]. It was assumed that the copper/cadmium may undergo chemisorption on the surface of mercapto functionalized surface and consequently forming an 'inner-sphere complexes' at adsorbent surface. Several researchers have reported that the incorporated mercapto group participates in chemisorption of copper and cadmium [74, 80, 81]; whereas few researchers reported that the sorption of toxic ions proceeds through hydroxyl group instead mercapto group [49, 78]. Hence, in order to ascertain the mechanistic pathway of Cu^{2+} and Cd^{2+} sorption onto synthesized hybrid, the BNMPSTs was analysed by XPS results as obtained before and after the adsorption of these cations. The wide scan XPS spectra are shown in Fig. S6 (a)–(c). The XPS results of BNMPSTs loaded with Cu^{2+} and Cd^{2+} confirmed the distinctive electron peaks of $\text{Cu}2p$ and $\text{Cd}3d$. The doublet peaks at 933.3 and 957.3 eV binding energies are due to the $\text{Cu}2p(1/2)$ and $\text{Cu}2p(3/2)$ electrons. Similarly, the binding energy peaks at 405.7 and 412.4 eV are due to the $\text{Cd}3d(3/2)$ and $\text{Cd}3d(5/2)$ electrons. This evidently showed that Cu^{2+} and

Table 2. The Loading Capacity and Thomas Rate Constants in the Elimination of Cu^{2+} and Cd^{2+} by BNMPSTs

BNMPSTs	Metals	Thomas constants		Least square sum (s^2)
		q_0 (mg/g)	K_T (L/min/mg)	
0.25 g	Cu^{2+}	28.87	8.14×10^{-4}	1.0×10^{-2}
	Cd^{2+}	19.71	1.0×10^{-4}	1.9×10^{-2}
0.5 g	Cu^{2+}	32.03	3.6×10^{-4}	9.2×10^{-3}
	Cd^{2+}	35.09	2.8×10^{-4}	2.0×10^{-1}

Fig. 6. XPS spectra of (a) O1s scan of BNMPSTs before and after the sorption of Cu^{2+} and Cd^{2+} , (b) S2p scan of BNMPSTs before and after the sorption experiment.

Cd^{2+} are sorbed onto the surface of BNMPTS material.

Further, the alteration in binding energy of O1s with and without loading of Cu^{2+} and Cd^{2+} with BNMPTS are illustrated as in Fig. 6(a). It is shown that the O1s peak was slightly shifted from 530.0 to 531.2 eV and 530 to 531.3 eV with the loading of Cu^{2+} and Cd^{2+} , respectively. This inferred that Cu^{2+} and Cd^{2+} are bound through the -OH group of BNMPTS [82, 83]. Moreover, the binding energy of S2p electrons was obtained at 163.14 eV (Fig. 6(b)) and this peak is attributed to the disulfide bond [49]. This binding energy remains almost the same after the loading of Cu^{2+} /or Cd^{2+} which suggests that the mercapto group is not participating in the sorption of these two toxic ions. Previously, Wang et al. [78] showed the role of disulfide in sorption of cadmium by mercapto-functionalized attapulgite (MATP) using density functional theory (DFT) calculations and found that disulfide did not play significant role in Cd adsorption. Therefore, insight mechanistic study revealed that adsorption of copper (II) or cadmium (II) mainly proceeded through hydroxyl groups present on the functionalized material and consequently forming an 'inner sphere complexes' at the surface of solid. Further, the XPS results indicated that Cu^{2+} and Cd^{2+} are substantially sorbed onto BNMPTS and atomic percentage of Cu and Cd in the used BNMPTS solids were recorded as 0.87 and 0.45% respectively.

4. Conclusions

3-mercaptopropyltrimethoxy silane (MPTS) was grafted onto the bentonite surface and it was reaffirmed with the FT-IR and SEM/EDX analyses. The structural and textural properties of clay (BN) and functionalized clay (BNMPTS) were characterized by the XRD and BET analyzers. The silane grafting caused a significant decrease in the specific surface area i.e., from 41.14 to 4.65 m^2/g obtained for BN and BNMPTS, respectively. The functionalized bentonite (BNMPTS) was enabled to remove a very high percentage (almost 100%) of Cu^{2+} and Cd^{2+} at a wide range of pH. The maximum sorption capacities were found to be 12.59 and 13.19 mg/g for Cu^{2+} and Cd^{2+} , respectively. The sorption reaction is rapid and an apparent equilibrium is reached within 30 minutes of contact and the kinetic data is fitted well to the PSO model. Increasing the concentration of background electrolyte and the presence of co-ions generally did not affect the removal efficiency of these two cations by BNMPTS except the presence of EDTA. Furthermore, the maximum loading capacities of Cu^{2+} and Cd^{2+} on to the column packed with BNMPTS were found to be 32.03 and 35.09 mg/g , respectively. The insight mechanism study performed using XPS analyses revealed that sorption of Cu^{2+} and Cd^{2+} mainly proceeded via the -OH group present at the terminal of BNMPTS. The study therefore, implied that MPTS functionalized bentonite is a potential solid material to be employed efficiently in the elimination of Cu^{2+} and Cd^{2+} in aqueous wastes.

Author Contributions

RM (Ph.D. Student) performed all the experiments in the laboratory.

L (Assistant Professor) helped in drafting the article. DT (Professor) formulated the problem and finalized the manuscript. The data explanation and necessary corrections in the manuscript are made by him.

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