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$SnCl_2$ Treated Red Mud as an Effective Adsorbent for the Removal of Toxic Molybdate Ions from Industrial Wastewater

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Molybdate removal from wastewaters from industries, mining and nuclear power stations, is an important task in the water remediation methodologies. This oxyanion of molybdenum is difficult to be removed and its presence in aquatic environment is detrimental to aquatic life and endogenous human beings due its high toxicity and bio-accumulation nature. In present investigation, $SnCl_2$ treated red mud (TRM) and zirconium alginate beads doped with TRM (TRM-Zr.alg) are observed to have good affinity for molybdate ions. Hence, these materials were investigated as adsorbents and various extraction conditions *viz.*, pH, contact time, dosage of TRM and TRM-Zr.alg, initial molybdate concentration and temperature are optimized for the maximum removal of molybdate ions. The optimized conditions were pH: 2.5; dosage: 2.0 g/L for TRM and 2.25 g/L for TRM-Zr.alg; contact time: 45 min for TRM and 60 min for TRM-Zr.alg; temperature: 30 ± 1 ºC and rpm: 300. Interferences of co-ions in the solutions were investigated and the spent TRM and TRM-Zr-alg were also nvestigated for their regeneration and reuse. The endothermic and spontaneity of sorption process can be inferred from the negative ΔG and positive ΔH values and further, the high values of ΔH indicate the sorption mechanism is not 'physisorption' but more inclined towards ion-exchange and/or some sort of surface complex formation between molybdate and adsorbents. The sorption process was analyzed and observed that Freundlich model well explains, indicating the heterogeneous surface and multilayer adsorption. The kinetics of adsorption is explained by pseudo-second order model. The methodology developed was successfully applied to treat industrial and mining effluents samples. The novelty of the present investigation is that red mud, a waste material, is explored for its inherent potentials as adsorbent for extracting the highly toxic molybdate ions from wastewater.

Keywords: Molybdate removal, Red mud, Zirconium alginate beads, Tin(II) chloride, Regeneration, Applications.

INTRODUCTION

Removal of molybdate ions from the industrial and mining effluents is one of the major environmental issues [1]. The molybdate being an oxyanion of heavy metal, is very difficult to be removed by the conventional methods. Other well-known industries for the intensive utility of molybdenum salts are paints and pigments, polymers, retardants for flame and catalysts [2]. Effluents from the mining of molybdenum-based ores, nuclear reactors wastewater and solid-waste municipal incinerator are other sources of contamination [3,4].

Traces of molybdate helps the growth of plants but it turns to be a potential pollutant when it crosses the allowed limits. The molybdate consumption through water causes kidney ailments, anaemia, orthopaedic problems and even death. The maximum allowed limit of molybdenum in industrial wastewater is percribed 350 µg/L as per WHO recommendations [2].

Of the various methods proposed for heavy metal remediation, based on precipitation and flocculation [5,6], ion exchange [7] and adsorption [8], adsorption methods are promising from the view point of economy and simplicity. Goethite, α-FeOOH and akageneite, β-FeOOH and maghemite were investigated as sorbents for molybdate removal from the wastewaters [9-11]. The main drawback of using these hydroxides as adsorbents is that they form gels and the filtration becomes difficult. To overcome this, hydroxides of various metals are loaded onto active carbons, aluminium silicates, zeolite and polymers and using them as sorbents for water remediation for molybdate ions [10,12]. Loessial soil and slag waste [13], activated carbon [14], pyrite [10] and zeolite-supported magnetite [15] are employed as adsorbents for the removal of molybdate ions from wastewater. The use of nanoparticles as an adsorbent is a new development and it is interesting the researchers [16,17]. But the disadvantages are that the nanoparticles may undergo 'agglomeration' and further, the separation of particles is difficult.

Red mud is a waste generated while extracting aluminium from bauxite ore. It consists of many metal oxides and adsorbent properties of red mud are attributed to them. By treating red mud with suitable redox or complexing agents, the 'morphology and nature' of functional groups of the red mud may be altered. This may, at times, results in the enhanced sorption nature for the treated red mud towards specific ions of interest. This method of tailor making the nature of red mud may be used for and the affinity for the specific ions.

Several investigations are reported using red mud or modified red mud as an adsorbent for the removal of Pb^{2+} [18], fluoride [19,20], dyes [21,22], organics [23] and phosphate [24] from wastewaters. The drawback of red mud is due to its gelling nature and this renders the separation difficult, thus high-speed centrifuges are needed. In present work, stannous chloride ($SnCl_2$) treated red mud was investigated as adsorbent for the removal of molybdate with a view that the reduction might change the nature of functional gropes resulting enhanced adsorption. To overcome the gelling effect and to make the easy filtration, the treated red mud was doped in Zr-alginate beads. Thus $SnCl_2$ threated red mud and Zr-alginate beads doped with treated red mud, were investigated as adsorbents for the removal of molybdate ions from the wastewater.

EXPERIMENTAL

Analytical grade reagents (AR) chemicals were used and simulated solutions of molybdate were prepared using sodium molybdate heptahydrate ($Na_2MoO_4·7H_2O$). Red mud was obtained from Vedanta Aluminium Ltd., India and composed of ferric oxide, aluminium oxide, titanium dioxide, silicon dioxide, soda, calcium oxide, vanadium trioxide and phosphorus pentoxide.

$SnCl_2$ treated red mud (TRM): Red mud was washed with distilled water, for a number of times, until the washing were neutral. Then the material was dried at 110 ºC for 2 h in a hot air-oven. Then the material was cooled in a desiccator and well-grounded to a particle size (> 75 μ) and then about 20.0 g of material was taken in a 250 mL round bottom flask with water condenser set-up. Then 100 mL of 0.1 N $SnCl_2$ solution was added, pH was adjusted to 2.0 and heated for 2 h. After the completion of condensate heating, the materials was filtered and washed with distilled water until the red mud was free from the Sn^{2+} ions. The complete removal of $SnCl_2$ ions was assessed by testing the filtrate with $AgNO_3$ for chloride ions. When the test was negative, then it indicated that the red mud was free from $SnCl_2$. Then the material was dried in hot-air oven at 110 ºC for 2 h, cooled in a desiccator and preserved in coloured bottle.

Treated red mud immobilized in zirconium alginate beads (TRM-Zr.alg): Added sodium alginate (3.0 g) in 100 mL of distilled water was slowly heated to 70 ºC with constant vigorous stirring until a homogeneous solution was resulted. Then, 5.0 g of treated red mud was added and stirred for 1 h to have a highly dispersed treated red mud in Na-alginate solution. The solution was cooled and added dropwise to the previously cooled 3.0% $ZrOCl_2$ solution. Beads doped with treated red mud were formed. They were digested at room temperature for overnight for complete development beads. The beads were filtered, washed and dried at 80 ºC for 1 h in hot air-oven.

The TRM and 'TRM-Zr-alg' were investigated for their absorptivity for molybdate ions using simulated solutions of molybdate.

Extraction studies: Batch modes of extraction were employed [6,25]. In brief, 100 mL of simulated molybdate solution of known concentration was taken into a 250 mL iodine flask. To this solution, accurate weighed TRM or TRM-Zr.alg were added and then the pH (initial) was adjusted to the required values. Then the mixture of solutions was agitated in mechanical shakers for desired time at 300 rpm. After completion of equilibration time, the adsorbent was removed by filtration quantitatively. The filtrate was analyzed for the molybdate content by AAS method using Shimadzu atomic absorption spectrophotometer [2].

Percentage of extraction of molybdate and the adsorption capacity of TRM and TRM-Zr.alg were assessed by using eqns. 1 and 2 [26]:

$$\text{Removal (\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

$$q_e = \frac{C_o - C_e}{m} \times V \quad (2)$$

where m = mass of TRM or TRM-Zr.alg (g), V = volume of simulated molybdate solution (L), C_o = initial molybdate solution concentration and C_e = final molybdate solution concentration (mg/L).

Extraction of molybdate as a function of pH, dosage of TRM or TRM-Zr.alg, equilibration time, initial concentration of molybdate and temperature was investigated. In these investigations, the aimed parameter was increasingly varied while all other parameters were maintained at constant optimum values to assess the effect of aimed parameter on the extraction of molybdate. Further, the effect caused by various co-anions on the molybdate was also investigated.

RESULTS AND DISCUSSION

Effect of extraction conditions:

pH: The effect of initial pH of solution on the molybdate adsorption was studied by varying initial pH of the solution from 1 to 10 and the results are depicted in Fig. 1. In pH range 2 to 4, both the adsorbents show good molybdate adsorption. Increasing the pH of solution above pH 4, the adsorption was decreased. The maximum extraction of 80.2% for TRM and 91.0% for TRM-Zr.alg were observed at pH 2.0. The good adsorption molybdate in acidic pHs may be explained from the view point of pHzpc values. The evaluated pHzpc values for TRM and TRM-Zr.alg were 5.0 and 6.0 respectively (Fig. 2).

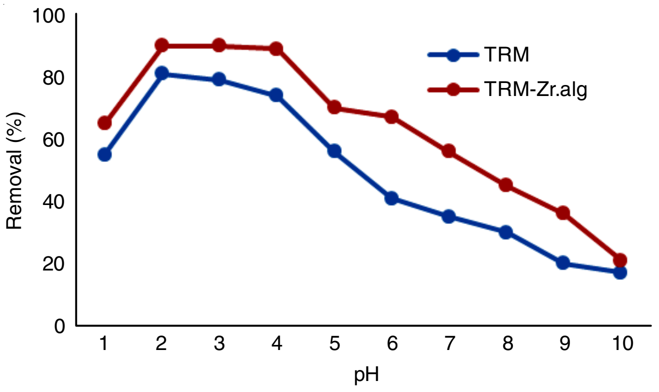

Fig. 1. Effect of pH on the removal of molybdate ions

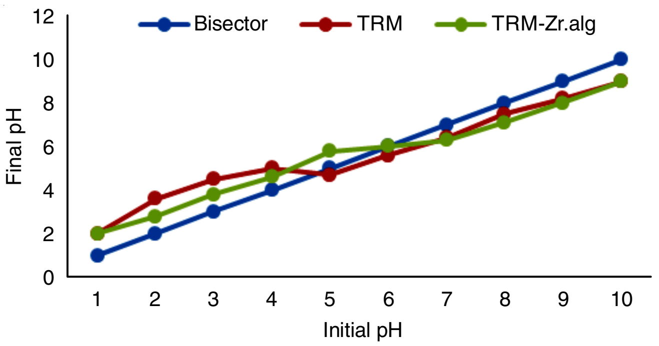

Fig. 2. Evaluation of pHzpc

At these values, the surface of the adsorbents were neutral. Above these values, the sorbent surface acquired negative charge while below these values, the surface was protonated, resulting surface positive charge. Molybdate being an anion, has shown good adsorption at low pHs of solutions due to positively charged surface of the adsorbents. When the pH of solution was above pH$_{zpc}$ (5.0 for TRM and 6.0 for TRM-Zr.alg), the negatively changed molybdate was repelled by the negatively changed surface of the adsorbent, resulting low extractions.

Dosage of TRM/TRM-Zr.alg: By varying the TRM/TRM-Zr.alg dosages from 0.25 to 3.0 g/L, molybdate extraction was investigated and the results are presented in Fig. 3. Molybdate adsorption was increased initially but the proportionality was not observed at moderate and high dosages and in fact, a steady state was resulted when their dosages were 2.0 g/L for TRM and 2.25 g/L for TRM-Zr.alg.

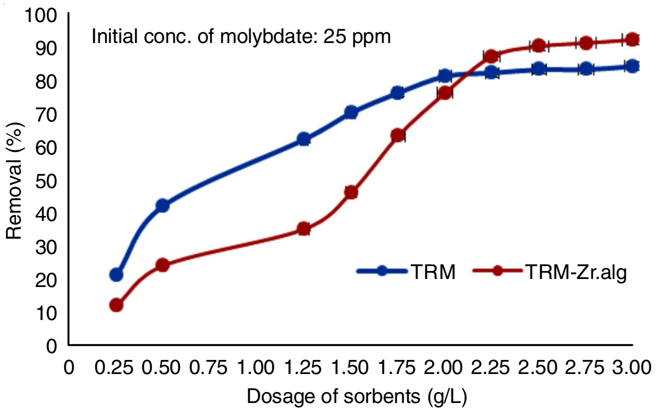

Fig. 3. Effect of dosage of TRM/TRM-Zr.alg on molybdate removal

With increase of dosage, active sites were increased and hence, good adsorption of molybdate was expected as the dosage was increasing. This proportionally was obeyed at low concentrations of TRM and TRM-Zr.alg but not at moderate or high concentrations. The aggregations of particles of adsorbents and blocking or clogging of pathways for molybdate ions to reach the inner active sites, may be the reasons for the loss of proportionality of adsorption with increase in dosage of adsorbents.

Equilibration time: Molybdate adsorption was investigated by varying the agitation time from 15 min to 120 min and the results are presented in Fig. 4. At low equilibration times, the molybdate adsorption was linearly increased with progress of time but the adsorption was slowed and proportionality was not observed and eventually a steady state was resulted after 45 min with TRM and 60 min with TRM-Zr.alg as adsorbents. As the adsorbents dosage was fixed, only a certain number of active sites were available. With progress of time, these sites were increasingly used up and hence, rate of molybdate adsorption was slow down and eventually when all the sorption active sites were used-up, a steady state was resulted [18].

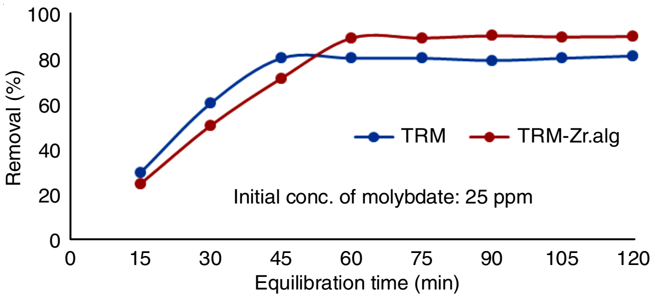

Fig. 4. Effect of equilibration time on the removal of molybdate ions

Initial concentration: The effect of molybdate concentration on the adsorptivity of molybdate was investigated by changing the molybdate concentration from 5 to 50 mg/L. The results are presented in Fig. 5. It could be observed that % removal was decreased with the increase in initial concentration of molybdate ions. This observations could be accounted from the fact that the demand for number active sites increased as initial concentration of molybdate was increased. But for a fixed adsorbent dosage, (2.0 g/L for TRM and 2.25 g/L for TRM-Zr.alg), the active sites were fixed. Hence, sufficient number of active sites were not available to meet the increasing demand. This resulted in the fall of adsorptivity.

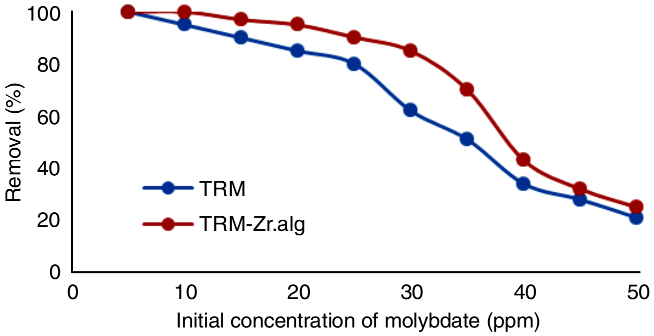

Fig. 5. Effect of initial Mo(V) concentration on molybdate removal

Further, the variations in the adsorption capacities of TRM and TRM-Zr.alg were also investigated and the results are presented in Fig. 6. The variations of adsorption capacity (q_e) with the change in molybdate ions initial concentration were interesting to observe. The q_e values almost linearly increased with progressive increase in molybdate concentration from 5 mg/L to 25 mg/L for TRM and 30.0 mg/L for TRM-Zr.alg. But when the initial concentration of molybdate ions was further increased, the q_e values were decreased.

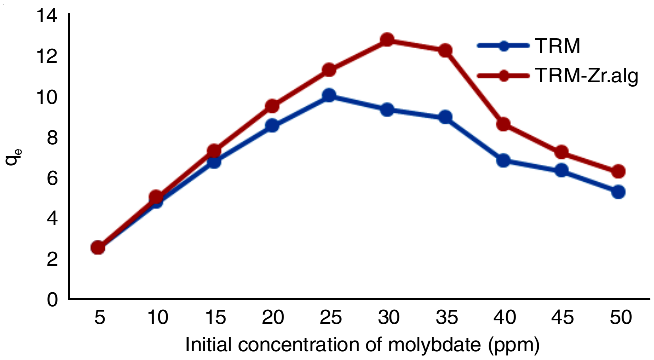

Fig. 6. Variation of adsorption capacities of adsorbents with initial Mo(VI) concentration

Of the various factors that governs the adsorption, the rate of diffusion of molybdate ions towards the surface of the adsorbents is an important factor. The molybdate concentration throughout the agitating solution is not same. The molybdate concentration on the surface of the adsorbent differ from the molybdate concentration in the core of the solution. This difference in concentrations, forces or drifts the molybdate ions towards the surface of the adsorbents. If the concentration gradient is more or more, the diffusion of molybdate ions is also more and more. Hence, with increase in molybdate concentration, the concentration gradient is more and hence more diffusion and thereby resulting the increase in adsorption capacity. But when the concentration increases more than an optimum level (25 mg/L with TRM and 30 mg/L with TRM-Zr.alg), the q_e values fall and this signal that diffusion mechanism is less significantly controlling the adsorption mechanism [27].

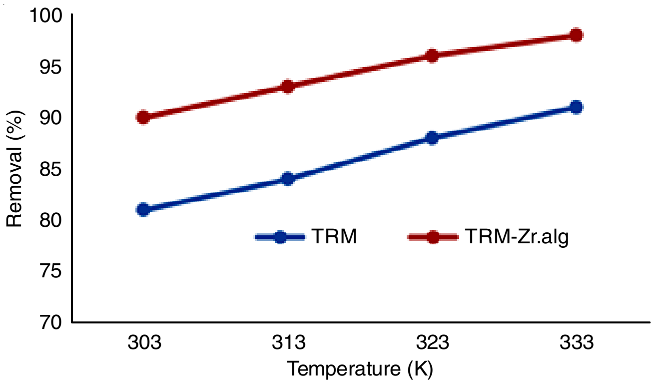

Fig. 7. Effect of solution temperature on molybdate removal

Temperature: The effect of solution temperature on the molybdate adsorption was studied by changing temperature from 303 to 333 K and results are presented in Fig. 7. It could be inferred that as the temperature was increased, the molybdate adsorption was also increased. With increase in temperature, the surface functional groups of TRM and TRM-Zr.alg acquire more vibrational kinetic energies and this results in the decrease of density of surface layers of the said adsorbents and consequently, the surface is more porous to allow the penetration of molybdate ions. Further, the increase in temperature increases the diffusion of molybdate ions towards the sorbent surface. These factors facilitates the enchantment of molybdate adsorption [28].

Interference studies: The effect of two fold excess co-anions on the adsorptivities of TRM and TRM-Zr.alg for molybdate was investigated and the results are depicted in Fig. 8. It was found that nitrate, bicarbonate, sulphate and chloride have almost not interfered but fluoride, phosphate, arsenate and antimonate have marginal interference.

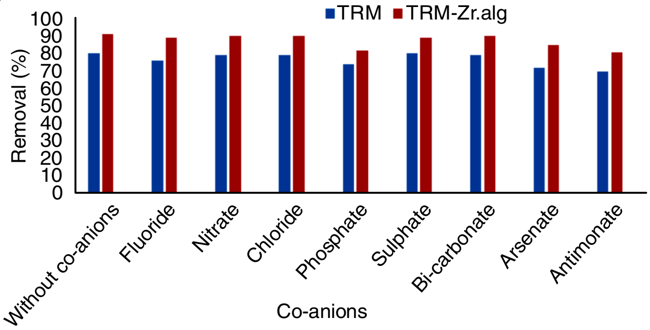

Fig. 8. Effect of co-anions on molybdate removal

Sorption nature

Thermodynamic parameters: Thermodynamic parameters *viz.* Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were evaluated by adopting eqns. 3 and 4 [29]:

$$\Delta G = - RT \ln K_d \tag{3}$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{4}$$

where, R = gas constant (8.314 J mol^{-1} K^{-1}) and T = temperature (K).

Through van't Hoff plots, ($\ln K_d$ *vs.* 1/T), the parameters were assessed and the values are presented in Table-1.

TABLE-1
EVALUATED THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF Mo(VI) ONTO THE ADSORBENTS

Adsorbents	ΔH (kJ/mol)	ΔS (J/mol)	ΔG (kJ/mol) 303 K	ΔG (kJ/mol) 313 K	ΔG (kJ/mol) 323 K	ΔG (kJ/mol) 333 K	R^2
TRM	25.30	240.05	-50.20	-53.30	-56.50	-58.30	0.9880
TRM-Zr.alg	32.54	267.20	-53.91	-55.91	-57.70	-60.20	0.9775

The negative ΔG values indicate that the adsorption is spontaneous and increase of negative values with increase in temperature signal the favourability of sorption at the elevated temperatures [30]. The positive ΔH values for the molybdate ions adsorption, 25.30 kJ/mol for TRM and 32.54 for TRM-Zr.alg indicate the endothermic nature and the magnitudes indicate that the sorption is not electrostatic (physisorption) in nature and it may sort be either ion-exchange and/or surface complex formation between the functional groups of TRM/TRM-Zr.alg and molybdate ions [31]. The positive sign and magnitude of ΔS values (240.05 J/mol for TRM and 267.20 J/mol for TRM-Zr.alg) indicated a high degree of disorder at the surface and liquid interface. This is a favourable factor for driving the molybdate ions to crossover the boundary-barrier and thereby resulting enhanced molybdate ions adsorption.

Adsorption isotherms: The nature of molybdate adsorption was evaluated by adopting the following linear models as per eqns. 5-8 [32-35]:

Freundlich:

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \tag{5}$$

Langmuir:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}} C_e \tag{6}$$

Temkin:

$$q_e = B \ln K_T + B \ln C_e \tag{7}$$

Dubinin and Radush:

$$\ln q_e = -\beta\varepsilon^2 + \ln q_m \tag{8}$$

The evaluated parameter are presented in Table-2. From the correlation coefficient (R^2) values, the better fit model falls in the order: Freundlich model > Langmuir model > Temkin model > Dubinin-Radushkevich (D-R) model for the adsorption of molybdate both on TRM and TRM-Zr.alg.

Kinetics of adsorption: The kinetics of adsorption were evaluated according to the eqns. 9-12 [19,30,36,37]:

Pseudo 1st order:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{9}$$

Pseudo 2nd order:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} - \left(\frac{1}{q_e}\right)t \tag{10}$$

Elovich equation:

$$\log\left[\log\left(\frac{c_i}{c_i - q_t m}\right)\right] = \log\frac{k_o}{2.303V} + \alpha \log t \tag{11}$$

Bangham's pore diffusion model:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{12}$$

The parameters evaluated are presented in Table-3. The R^2 values fall in the order: Pseudo 2nd order < Pseudo 1st order < Elovich < Bangham's pore diffusion model. Thus, pseudo 2nd order model explains well the molybdate ions adsorption.

Recycling of spent TRM and TRM-Zr.alg: For having cost effectiveness, the spent sorbents were tried to be regenerated by various eluents comprising of acids, alkalies and salt solutions of varying concentrations. It was observed that 0.1 N NaOH was effective in regenerating the sorbents. In brief, 20.0 g of spent TRM and TRM-Zr.alg was added to 100 mL of 0.1 N NaOH and digested for overnight at room temperature. Then the material was filtered and thoroughly washed with distilled water until the washings were neutral. The material was dried at 110 ºC, cooled and stored in brown bottles. Thus, regenerated material was employed for treating molybdate polluted water. The regeneration and reuse were repeated. It was interesting to note that the adsorbents retained their sorption capacity up

TABLE-2
EVALUATED ISOTHERM PARAMETERS FOR THE Mo(VI) ADSORPTION ONTO THE ADSORBENTS

Adsorbents		Freundlich	Langmuir	Temkin	Dubinin-Radushkevich
TRM	Slope	0.270	0.180	0.771	-9.9
	Intercept	1.700	0.305	6.122	2.2
	R^2	0.989	0.961	0.801	0.789
		1/n = 0.270	R_L = 0.09	B = 0.77	E = 6.8 kJ/mol
TRM-Zr.alg	Slope	0.189	0.121	1.100	-3.9
	Intercept	2.654	0.152	6.900	2.4
	R^2	0.990	0.970	0.870	0.880
		1/n = 0.170	R_L = 0.06	B = 1.112	E = 7.6 kJ/mol

TABLE-3
EVALUATED KINETIC PARAMETERS FOR THE Mo(VI) ADSORPTION ONTO THE ADSORBENTS

Adsorbent	Models				
	Parameter	Pseudo first order	Pseudo second order	Elovich model	Bangham's pore diffusion
TRM	Slope	0.026	0.081	3.234	0.670
	Intercept	1.345	2.967	4.702	2.523
	R^2	0.964	0.990	0.890	0.802
TRM-Zr.alg	Slope	0.034	0.058	0.840	0.745
	Intercept	1.445	2.465	8.213	3.456
	R^2	0.960	0.989	0.942	0.920

TABLE-4
APPLICATIONS: TREATING OF INDUSTRIAL EFFLUENTS FOR Mo(VI) REMOVAL WITH THE METHODOLOGIES DEVELOPED USING 'TRM' AND 'TRM-Zr.alg' AS ADSORBENTS

Samples	Mo(VI) concentration (mg/L)			Extraction (%)		Mo(VI) concentration (mg/L)			Extraction (%)	
	Initial (C_i)*	Final (C_e*)		With TRM	With TRM-Zr.alg	Initial (C_i)*	Final (C_e*)		With TRM	With TRM-Zr.alg
		With TRM	With TRM-Zr.alg				With TRM	With TRM-Zr.alg		
	A: Industrial effluents					B: Mining wastewater				
1	1.3	0.0	0.0	100	100	7.0	0.0	0.0	100	100
2	2.6	0.0	0.0	100	100	8.9	0.0	0.0	100	100
3	3.1	0.0	0.0	100	100	10.5	1.2	0.9	88.5	91.4
4	3.8	0.0	0.0	100	100	16.7	2.1	1.4	87.4	91.6
5	4.5	0.0	0.0	100	100	19.0	3.0	1.6	84.2	91.5
6	5.0	0.0	0.0	100	100	20.0	4.0	2.3	80.0	88.5
7	5.3	0.0	0.0	100	100	22.0	4.6	2.7	79.1	87.7

*Average value of five estimations; S.D: ± 0.23; Optimum conditions: pH: 2.5; dosage: 2.0 g/L for TRM and 2.25 g/L for 'TRM-Zr.alg'; contact time: 45 min for TRM and 60 min for 'TRM-Zr.alg'; rpm: 300; Temp: 30 °C.

to 3 cycles in the case of TRM and 4 cycles with TRM-Zr.alg (Fig. 9).

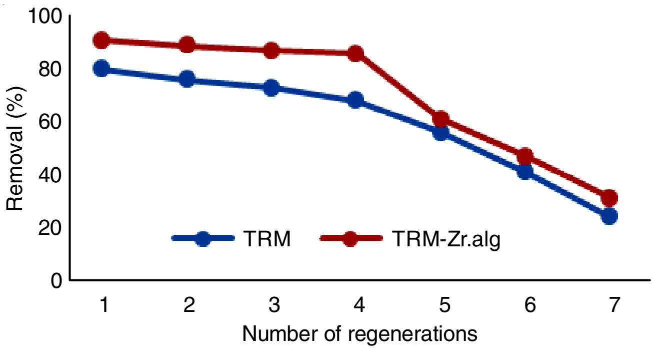

Fig. 9. Regeneration *vs.* % removal

Applications: Wastewater samples were collected from industries and mining located in Ethiopia and in Chennai, India and analyzed for molybdate content. Then the samples were treated with TRM and TRM-Zr.alg at the optimum extractions conditions. The results are presented from Table-4 and it may be inferred that the methodology developed is highly successful.

Comparison: The developed sorbents TRM and TRM-Zr.alg were compared with the sorbents already reported in the literature with respect to pH and sorption capacities. The data is presented in Table-5. It may be inferred that the TRM and TRM-Zr.alg have the adsorption capacities more than many sorbents *hitherto* reported.

Conclusion

The waste water from many industries, mining and nuclear power stations contains toxic oxyanions of molybdate and its removal is essential. Stannous chloride treated red mud (TRM) and zirconium alginate beads doped with TRM (TRM-Zr.alg) are observed to have strong adsorptivities for the molybdate ions. Hence, these materials were investigated as adsorbents for the removal of toxic molybdate ions from watewaters. Various extraction conditions *viz*., pH, contact time, dosage of TRM and TRM-Zr.alg, initial molybdate concentration and temperature are investigated and optimized for the maximum adsoptivity of molybdate ions. Interferences of co-ions were investigated and the spent TRM and TRM-Zr-alg were investigated for their regeneration and reuse.

TABLE-5
COMPARISON OF TRM AND TRM-Zr.alg AS ADSORBENTS WITH ALREADY REPORTED ADSORBENTS IN THE LITERATURE FOR TREATING Mo(VI)

Sorbent	Optimum pH	Adsorption capacity (mg/g)	Ref.
Pyrite	3-5	15.3	[1]
Desulfurization steel slag	3-4.5	4.38	[13]
Nano-magnetic $CuFe_2O_4$	3.0	30.58	[4]
Zeolite-supported magnetite	3.0	18.0	[15]
NaOCl-oxidized multiwalled carbon nanotubes	7.0	22.73	[16]
TRM	2.5	23.0	Present work
TRM-Zr.alg	2.5	32.3	

Thermodynamic parameters are evaluated. The negative ΔG and positive ΔH values revealed the endothermic and spontaneity of sorption. Further the high ΔH values indicate the mechanism of sorption is either ion-exchange and/or surface complex formation between functional groups of TRM and TRM-Zr.alg and molybdate ions. Of the various isotherm models studied, Freundlich model explain well the sorption process, reflecting heterogeneous surface and multilayer adsorption. The kinetics of adsorption is well explained by pseudo 2nd order model. The methodology developed in this investigation is successfully applied to treat industrial and mining effluents samples. The inherent merit of the present investigation is that red mud, a waste material, is put to better use by developing a methodology for the removal of toxic molybdate ions from wastewater.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. B.C. Bostick, S. Fendorf and G.R. Helz, *Environ. Sci. Technol.*, **37**, 285 (2003);
https://doi.org/10.1021/es0257467

2. M. Kurian, *FlatChem*, **30**, 100307 (2021); https://doi.org/10.1016/j.flatc.2021.100307
3. K. Bourikas, T. Hiemstra and W.H. Van Riemsdijk, *J. Phys. Chem. B*, **105**, 2393 (2001); https://doi.org/10.1021/jp002267q
4. Y.J. Tu, T.S. Chan, H.W. Tu, S.L. Wang, C.F. You and C.K. Chang, *Chemosphere*, **148**, 452 (2016); https://doi.org/10.1016/j.chemosphere.2016.01.054
5. N.A.A. Qasem, R.H. Mohammed and D.U. Lawal, *npj Clean Water*, **4**, 36 (2021); https://doi.org/10.1038/s41545-021-00127-0
6. M. Kumar, A. Seth, A.K. Singh, M.S. Rajput and M. Sikandar, *Environ. Sustain. Indic*., **12**, 100155 (2021); https://doi.org/10.1016/j.indic.2021.100155
7. S.A. Cavaco, S. Fernandes, M.M. Quina and L.M. Ferreira, *J. Hazard. Mater.*, **144**, 634 (2007); https://doi.org/10.1016/j.jhazmat.2007.01.087
8. G.V. Krishna Mohan, A. Naga Babu, K. Kalpana and K. Ravindhranath, *Int. J. Environ. Sci. Technol.*, **16**, 101 (2019); https://doi.org/10.1007/s13762-017-1593-7
9. M. Rovira, J. de Pablo, L.I. Casas, J. Gimenez, F. Ciarens and X. Martinez-Llado, Sorption of Molybdenum(VI) on Synthetic Magnetite, Sorption of Molybdenum (VI) on Synthetic Magnetite, In: Scientific Basis for Nuclear Waste Management XXIX, Materials Research Society Symposium Proceedings, Materials Research Society, vol. 932, pp. 12-16 (2006).
10. N. Xu, C. Christodoulatos and W. Braida, *Chemosphere*, **62**, 1726 (2006); https://doi.org/10.1016/j.chemosphere.2005.06.025
11. N. Xu, C. Christodoulatos and W. Braida, *Chemosphere*, **64**, 1325 (2006); https://doi.org/10.1016/j.chemosphere.2005.12.043
12. A. Afkhami, T. Madrakian and A. Amini, *Desalination*, **243**, 258 (2009); https://doi.org/10.1016/j.desal.2008.04.028
13. J.J. Lian, S.G. Xu, N.B. Chang, C.W. Han and J.W. Liu, *Environ. Eng. Sci.*, **30**, 213 (2013); https://doi.org/10.1089/ees.2011.0441
14. D. Pirouz, G. Hossein, K. Morteza and R. Mohammad, *World Appl. Sci. J.*, **7**, 230 (2009).
15. B. Verbinnen, C. Block, D. Hannes, P. Lievens, M. Vaclavikova, K. Stefusova, G. Gallios and C. Vandecasteele, *Water Environ. Res.*, **84**, 753 (2012); https://doi.org/10.2175/106143012X13373550427318
16. Y.C. Chen and C.Y. Lu, *J. Ind. Eng. Chem.*, **20**, 2521 (2014); https://doi.org/10.1016/j.jiec.2013.10.035
17. H. Sadegh, G.A.M. Ali, V.K. Gupta, A.S.H. Makhlouf, R. Shahryari-Ghoshekandi, M.N. Nadagouda, M. Sillanpää and E. Megiel, *J. Nanostruct. Chem.*, **7**, 1 (2017); https://doi.org/10.1007/s40097-017-0219-4
18. S.L. Narayanan, G. Venkatesan and V. Potheher, *Int. J. Environ. Sci. Technol*., **15**, 1687 (2018); https://doi.org/10.1007/s13762-017-1513-x
19. N. Babu, *J. Environ. Chem. Eng.*, **6**, 906 (2018); https://doi.org/10.1016/j.jece.2018.01.014
20. G. Lv, L. Wu, L. Liao, Y. Zhang and Z. Li, *Appl. Clay Sci*., **74**, 95 (2013); https://doi.org/10.1016/j.clay.2012.10.004
21. G.V. Krishna Mohan and N. Babu, *Der Pharma Chem.*, **18**, 403 (2016).
22. F. Zhang, Y. Yin, C. Qiao, Y.-N. Luan, M. Guo, Y. Xiao and C. Liu, *Adsor.. Sci. Technol*., **2021**, 7694783 (2021); https://doi.org/10.1155/2021/7694783
23. R.V. Busto, M. Gonçalves and L.H.G. Coelho, *Water Sci. Technol.*, **74**, 1283 (2016); https://doi.org/10.2166/wst.2016.309
24. Y. Wang, Y. Yu, H. Li and C. Shen, *J. Environ. Sci.*, **50**, 79 (2016); https://doi.org/10.1016/j.jes.2016.04.025
25. A.R.K. Trivedy, Pollution Management in Industries, Environmental Publications, Karad, India, Ed.: 2 (1995).
26. A.S. Eltaweil, I.M. Mamdouh, E.M.A. El-Monaem and G.M. El-Subruiti, *ACS Omega*, **6**, 23528 (2021); https://doi.org/10.1021/acsomega.1c03479
27. S. Ravulapalli and R. Kunta, *J. Fluor. Chem.*, **193**, 58 (2017); https://doi.org/10.1016/j.jfluchem.2016.11.013
28. W.K. Biftu, M. Suneetha and K. Ravindhranath, *Biomass Convers. Biorefin.*, (2021); https://doi.org/10.1007/s13399-021-01568-w
29. S. Pala, W.K. Biftu, M. Suneetha and K. Ravindhranath, *Int. J. Environ. Anal. Chem.*, (2021); https://doi.org/10.1080/03067319.2021.1927004
30. C. Fan and Y. Zhang, *J. Geochem. Explor.*, **188**, 95 (2018); https://doi.org/10.1016/j.gexplo.2018.01.020
31. C. Sun, C. Li, C. Wang, R. Qu, Y. Niu and H. Geng, *Chem. Eng. J.*, **200-202**, 291 (2012); https://doi.org/10.1016/j.cej.2012.06.007
32. H.M. Freundlich, *J. Phys. Chem.*, **57**, 1100 (1906).
33. I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918); https://doi.org/10.1021/ja02242a004
34. M.J. Temkin and V. Pyzhev, *Acta Physiochim USSR*, **12**, 217 (1940).
35. M.M. Dubinin, *Dokl. Akad. Nauk SSSR*, **55**, 327 (1947).
36. Y.S. Ho and G. McKay, *Process Biochem.*, **34**, 451 (1999); https://doi.org/10.1016/S0032-9592(98)00112-5
37. Y.S. Ho, J.C.Y. Ng and G. McKay, *Sep. Purif. Methods*, **29**, 189 (2000); https://doi.org/10.1081/SPM-100100009