Asian Journal of Chemistry; Vol. 34, No. 6 (2022), 1391-1400

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2022.23636

Simultaneous Removal of Molybdate and Chromate Ions from Industrial Wastewater using Biosorbents Derived from Stems of *Murraya koenigii*: Thermodynamics, Isothermal and Kinetic Investigations

Goriparthi Aparna Devi[1], Kunta Ravindhranath[1,*], Sneha Latha Pala[1], Sudhakar Miriyala[1] and Wondwosen Kebede Biftu[1,2]

[1]Department of Chemistry, Koneru Lakshmaiah Education Foundation, Green Fields, Vaddeswaram-522502, India
[2]R&D Directorate, Ethiopian Radiation Protection Authority, Addis Ababa, Ethiopia

*Corresponding author: E-mail: ravindhranath.kunta@gmail.com

Received: 26 November 2021; *Accepted*: 21 January 2022; *Published online*: 18 May 2022; AJC-20797

The removal of molybdate and chromate from industrial wastewater is one of the major tasks of water remediation methods. The disposal of ill-treated effluents containing these toxic heavy metal oxyanions into aqueous environment, effects aquatic life, ecosystems and endogenous the human life. The adsorptive methods available so far are to removal either molybdate or chromate ions and not their simultaneous removal. In the present investigation, a bioadsorbent derived from *Murraya koenigii* plant has the potential to remove both molybdate and chromate ions simultaneously at pH 2.5. The adsorbent was characterized using XRD and FTIR besides the assessment of conventional physico-chemical parameters. Various extraction conditions were investigated and optimized using simulated solutions of individual as well as mixtures of molybdate and chromate ions. The optimum conditions for simultaneous removal are: pH: 2.5; dosage of adsorbent: 2.5 g/L; contact time: 120 min; rpm: 300; temp.: 30 ± 1 ºC. The extraction was marginally effected by common co-ions. The adsorbents can be regenerated and reused for three cycles. Thermodynamic parameters revealed that the adsorption of molybdate and chromate onto the surface of the adsorbent is endothermic and spontaneous. Further, the magnitude of ΔH values and IR data confirmed that the nature of adsorption is 'ion exchange and/or a sort of surface complex formation'. Kinetics of adsorption was analyzed by various models and of them, pseudo-second-order model explains well. Of the various isotherm models analyzed, Langmuir model fits well and thereby indicating the homogeneity surface of the adsorbent and unform distribution of active sites. The developed method was applied to treat real wastewater samples collected from industrial and mining effluents and found to be highly effective. The novelty of the present investigation is that a simple and effective bioadsorbent is developed for the simultaneous removal of highly toxic molybdate and chromate ions from the industrial wastewaters.

Keywords: Water remediation methods, Bioadsorbents, *Murraya koenigii*, Molybdate ions, Chromate ions.

INTRODUCTION

The toxicity caused by the contamination of natural water with heavy metal ions released from inadequately treated industrial effluents, is one of the major environmental problems [1]. This threat is progressively increasing with each passing day with the raise of industrialization and increase in mining activity. Of these, the oxyanions of heavy metal ions especially chromate and molybdate ions become a major water quality management problem throughout the world [2,3].

Molybdenum is widely used as an alloying metal in many metallurgical process especially in the production of stainless steel and ferrous alloys. It is used in the synthesis of pigments, styrene-based polymers, flame retardants and catalysts in high temperature chemical reactions [3]. Mining, wastewater from nuclear reactors and leachings from the municipal solid-waste incinerator are other important source of molybdate contamination [4,5]. The huge quantities of wastewater from these sources contain threatening proportions of molybdate ions. Molybdate at trace levels is essential for the growth of plants and organisms but it is detrimental to human beings at elevated concentrations especially to the people depending upon the well water in the vicinity of afore said sources [3]. The toxicity of molybdate is well studied and its consumption causes anaemia, kidney and liver problems, deformities in bones and joints and even death. The permissible limit of molybdenum in industrial effluents is fixed as 350 μg/L by WHO [3]. Chromate is another common contaminant in the effluents of industries based on leather, paints, mining, metal plating, *etc*. It causes various ailments in human beings namely nausea, skin ulcers, liver and kidney problems, lungs cancer, *etc*. [6]. As per WHO, chromium permissible limit is 50 ppb if not 'nil' for drinking water [7].

Both chromium and molybdenum are present in the effluents from many industries related to ferrous alloys, mining of ores, nuclear power stations, *etc*. Stringent norms have been imposed on industries in many western developed countries to control these potential contaminants of water. Thus treating the effluents from industries and mines to remove molybdenum and chromate before disposing the effluents into environment is essential.

Different water remediation methods based on precipitation and flocculation [8,9], ion exchange [10] and adsorption [11] are reported for the removal of molybdate and chromate ions. Of these, adsorption methods are promising, economical and involve less complicated procedures. Iron hydroxides such as goethite (α-FeOOH), akageneite (β-FeOOH) and maghemite (γ-Fe_2O_3) are investigated as adsorbents for the removal of chromate and/or molybdate [12-16]. These hydroxy oxides form gels and thereby, rendering the separation process difficult. By loading the hydroxides of various metal ions on the matrixes of active carbon, zeolite, aluminium silicates, polymeric structures and employing such composites as adsorbents for the water remediation are found to be effective for the removal of many anionic pollutants [13-16]. Such innovative approaches are proving to be effective and simple.

Employing nanoparticles as adsorbents is another important development but it suffer from the fact that the particles may undergo 'agglomeration' and the separation of non-magnetic particles become difficult. Further, the synthesis of nanoparticles involves the use of toxic materials as 'capping or stabilizing' agent. In this contest, biomaterials or their derivatives are interesting researchers as adsorbents. For the removal of molybdate from polluted water, some investigations using NaOCl oxidized multiwalled carbon nanotubes [17], loessial soil and slag waste [18], granular activated carbon [19], pyrite [20] and zeolite-supported magnetite [21] as adsorbents are reported. Many adsorbents are developed for the removal of chromate based on biomaterials *e.g.* pineapple leaves [22], leaves of *Salvadora persico* and *Caesalpinia bonduc* plants [23], agricultural biowastes [24], hazelnut shell [25], *Chenopodium album* and *Eclipta prostrate* plant materials [26], spent coffee grounds [27], peanut shell [28] and active carbon of *Lantana camara* plant [29]. Further, calcium alginate beads doped with nano-ZrO_2 and activated carbon of *Annona reticulate* plant [30] and green synthesized nano mixed (Al-Fe-Zr) oxide [31], have also been used as adsorbents for the removal of chromate ions.

Thus biosorbents are proving to be simple, effective and moreover they are based on renewable materials. It may be observed from the review that most of these methods are devoted to remove either molybdate or chromate ions and not both at a time when they co-exist in the mining and industrial wastewater So, developing low-cost adsorbents based on biomaterials possessing high adsorption capacities towards molybdate and chromium ions, is an important aspect of water remediation methods.

The major problem in adopting biomaterials as adsorbents, is the identification of biomaterials having both affinity for molybdate and chromate ions. In present investigation, many biomaterials are probed to assess their adsorptive nature for molybdate and chromate ions and observed that the activated carbon derived from stems of *Murraya koenigii* plant is effective for the removal of both ions at pH 2.5.

EXPERIMENTAL

Analytical grade chemicals were procured from the reputed commercial sources and used as such. Simulated solutions of molybdate and chromate solution (25 mg/L) were prepared using A.R. $Na_2MoO_4·7H_2O$ and $K_2Cr_2O_7$, respectively.

Preparation of active carbon (MKAC)

Synthesis of active carbon: Using *Murraya koenigii* plant stems as precursor, active carbon was generated by digesting the stems with conc. H_2SO_4. The distilled-water washed stem pieces were half-dried under sunlight and digested for overnight by immersing the material in conc. H_2SO_4. Then the material was transferred to round bottomed flask (fitted with a condenser set-up) and needed quantity of conc. H_2SO_4 was added. Then the material was heated for nearly 1 h until the complete conversation of the biomaterial to carbon. Thus, produced activation carbon was filtered and thoroughly washed with deionized water until the washings were neutral to litmus paper. Then the material was dried at 110 ºC for 2 h, pulverized and sieved through 75 μm mesh (ASTM). Thus, generated activated carbon was named as 'MKAC' in lieu with *Murraya koenigii* active carbon.

Characterization of MKAC: Sorbent was characterized for it various physico-chemical properties namely, moisture (%), ash (%) [32], particle size (μ) [33], iodine number (mg/g), apparent density (g/mL) and BET analysis (surface area (m^2/g) [34] as per the standard procedures available in the literature. The results are presented in Table-1.

TABLE-1
PHYSICO-CHEMICAL CHARACTERISTICS OF MKAC

Parameter	Value	Ref.
Moisture (%)	3.2	BIS (1989)
Ash (%)	2.88	[32]
Particle size (μ)	30.2	[33]
Iodine number (mg/g)	623	ASTM D4607-94 (2006)
Apparent density (g/mL)	0.226	BIS (1989)
BET analysis	Before sorption: 468.9	[34]
Surface area (m^2/g)	After sorption: 201.8	

The sorbent nature of the MKAC was assessed by XRD and FTIR. MKAC samples 'before and after' adsorption of molybdate and chromate ions were subjected to these investigations. The XRD analysis was done using PAN analytical X-ray diffract meter using Cu$K\alpha$ source at 1.54 Å. FTIR spectra of MKAC were noted 'before and after' the adsorption of molybdate and chromate ions using BRUKER ALFA FTIR spectrophotometer (KBr pellet method) in the range 4000-500 cm^{-1}.

Batch methods: Batch experiments [35] were carried at by varying initial pH of solutions, sorbent dose, time of equilibration, initial adsorbate (molybdate/chromate) concentrations, temperature, *etc*. The method adopted for optimizing these parameters was as follows:

General procedure: To 100 mL of simulated solutions of molybdate (25.0 mg/L) or chromate (25.0 mg/L), varying amounts of MKAC were added and the initial pHs of the solutions were adjected in the range 2 to 10. The solutions were agitated using a shaking machine at 300 rpm for varying periods. After completion of the equilibration times, the solutions were filtered and the filtrates were assayed for the residual molybdate and chromate amounts using AAS methods [3]. Extraction conditions were optimized by varying the aimed parameter while keeping other parameters at constant optimum levels.

For investigating the effect of co-ions (that can possibly co-exit) on the adsorptivity of MKAC for molybdate and chromate ions, synthetic solutions comprising of two-fold excess of chloride, sulphate, carbonate, carbonate, fluoride and oxyanions like AsO$_3^-$ and SbO$_4^{3-}$ were prepared and subjected to the extraction investigations with MKAC as adsorbent at the optimum conditions. Percentage of extraction of molybdate or chromate ions and the adsorption capacity of MKAC were assessed by using the equations [36]:

$$\text{Removal (\%)} = \frac{C_o - C_i}{C_o} \times 100$$

and

$$q_e = \frac{C_o - C_e}{m} \times V$$

where m = mass of adsorbent (g), V = volume of simulated molybdate or chromate solution (L), C_0 and C_e are respectively the initial and final concentration of molybdate or chromate solutions (mg/L).

Recycling procedure for spent MKAC: Spent MKAC (50 g) was soaked in 150 mL of 0.1 N HCl and digested at room temperature for overnight. The MKAC was filtered and washed with distilled water for neutrality. Then the material was dried in oven at 105 ºC and reused as adsorbent. The process of regeneration and reuse were repeated for a number of cycles.

RESULTS AND DISCUSSION

Physico-chemical parameters: Various parameters of the synthesized MKAC were assessed by adopting standard procedures. The findings are presented in Table-1. The high iodine value imply the greater degree of unsaturation of MKAC. BET surface areas is observed to be decreased after the adsorption of molybdate and chromate. This indicates the adsorbates, molybdate and chromate ions are 'onto' the surface of MKAC.

XRD analysis: XRD spectrum of MKAC was recorded before and after adsorption of molybdate and chromate ions are presented in Fig. 1. Before spectrum, two prominent peaks at 2θ values 22.4º (002) and 44.4º (101) pertaining graphite carbon were observed. The former peak is quite broad and indicative of the presence of non-graphitized carbon. This results in endowing porous nature to the active carbon. These structural features import more surface area to the adsorbent and thereby, provide more conducive nature for the penetration of adsorbates (molybdate and chromate) deeper into the matrix of the adsorbent.

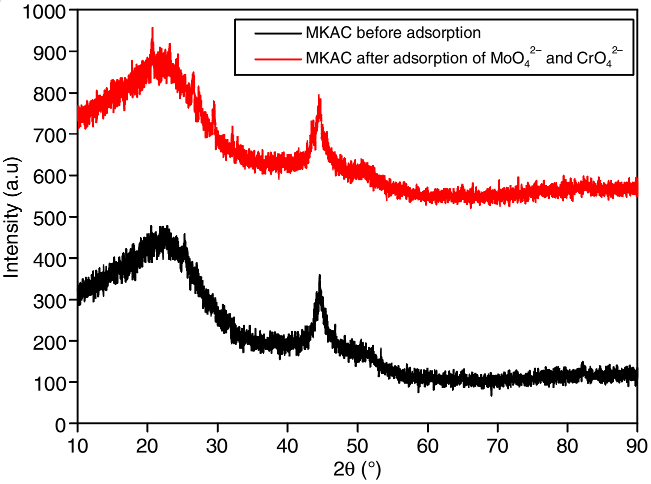

Fig. 1. XRD spectra of MKAC: before and after adsorption of molybdate and chromate

The XRD spectrum observed for the after adsorption of molybdate and chromate ions, in addition of peaks at 22.4º and 44.4º, sharp peaks appeared at 26.4º, 25.3º, 29.4º. Further, there is a change in the intensities and width of the bands at 22.4º and 44.4º. These changes may be due to the structural changes caused by the adoption of molybdate and chromate onto the surface of MKAC.

FTIR analysis: The MKAC spectra 'before and after' adsorption of molybdate and chromate ions are presented in Fig. 2. Before adsorption, the peaks pertaining to -OH (3211-3106 cm^{-1} br.), ester or aromatic nature (1616, 1399 cm^{-1}), C-O (1131 cm^{-1} *str*.), -SO$_3$H (1017 cm^{-1}) and various =C-H (823, 706, 652, 628, 605 cm^{-1} def.) are observed. After adsorption of molybdate and chromate ions, marked spectral changes were observed. The broad band of -OH is shifted to 3229-3099 cm^{-1}; ester or aromatic peaks have moved to 1616 and 1406 cm^{-1}. The emphatic change appeared with respect C-O- band. The single large peak at 1126 cm^{-1} has been changed to a number

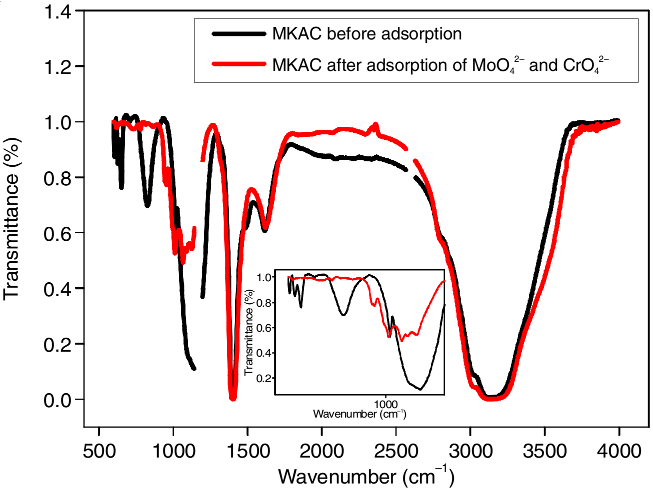

Fig. 2. FTIR spectra of MKAC before and after adsorption of molybdate and chromate

peaks at 1126, 1090, 1067 and 1011 cm^{-1} with varying intensities, which indicated the molybdate and chromate ions are bounded to the surface of MKAC through a sort of surface complex formation involving '-C-O-' groups. The new peaks appeared at 954 and 942 cm^{-1} may be due to Mo-O-O- or Cr-O-O-. The peaks pertaining to defamation of =C-H/-C-H or mono and disubstitutions in aromatic rings of activated carbon appeared at 815, 779, 664, 655, 636 and 619 cm^{-1}. All these changes in the spectral characteristics are indicative of adsorption of molybdate and chromate ions onto the surface of MKAC.

Effect of extraction conditions

pH effect: It is investigated by varying the pH from 2 to 10 but keeping constant the other parameters. Fig. 3 indicates that the adsorption of molybdate as well as chromate, is more at low solution pH values and it decreases with increase in pH. The percentage removal for molybdate was decreased from 82% at pH: 2.5 to 24% at pH: 10 and in the case of chromate the decrease is from 90.2% at pH: 2.5 to 10% at pH:10.

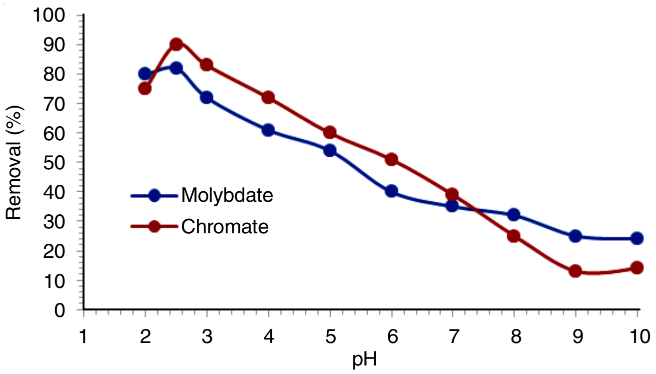

Fig. 3. Effect of pH on the removal of molybdate and chromate (conc. of each ion: 25 mg/L)

The maximum adsorption for both the ions were observed at pH: 2.5. It is a noteworthy finding as it helps us to investigate further to develop a method for the simultaneous removal of molybdate and chromate ions at the common pH 2.5. These observations may be explained from the view point of pH$_{zpc}$ values. At pH$_{zpc}$, the surface positive charges of the sorbent balance the negative charges, resulting neutral surface. Below the pH$_{zpc}$, the surface is charged positively and above negatively. The pH$_{zpc}$ of the MKAC is evaluated (Fig. 4) and found to be 6.0. So, if the surrounding solution pH is 6.0, the surface of MKAC is neutral. With increase of pH of the solution, the surface of MKAC acquires negative charge but with decrease of pH, the surface acquires positive charge. The positive charge is due to 'protonation' of function groups while negative charge is due to the dissociation of the functional groups. As the chromate and molybdate ions are anions (negatively charged), they are more adsorbed by MKAC when its surface is positively charged. Hence, at low pH of 2.5, the percentage removal of both the ions are more. With the increase of pH of surrounding solution, the surface of MKAC acquires negative charge and hence, the negatively charged molybdate as well as chromate are repelled by the negatively charged surface of MKAC. This result in the low absorptivity of MKAC for both the ions at high pH.

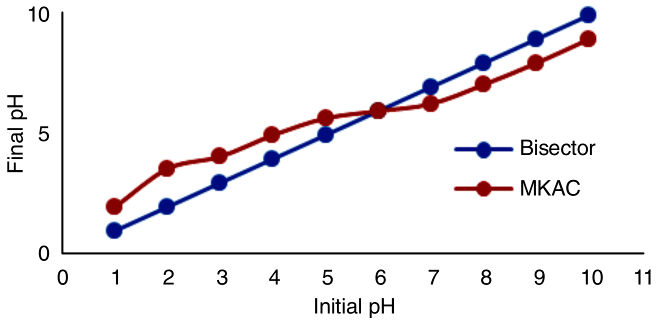

Fig. 4. Evaluation of pH$_{zpc}$

Dosage of MKAC: By varying the MKAC dosage from 0.25 to 34.0 g/L (but keeping constant the other extraction conditions), the adosorptivities of MKAC for molybdate and chromate ions were investigated.

At low concentrations of MKAC, an increase in percentage removal of molybdate or chromate ions is linearly (nearly) proportional to the MKAC dosage. But at moderate concentrations, the proportionality is lost and at high concentrations, a steady state is resulted with no further increase in the absorptivity of MKAC for the said two ions. The optimum dosage observed were 1.5 g/L for chromate and 2.0 g/L for molybdate (Fig. 5).

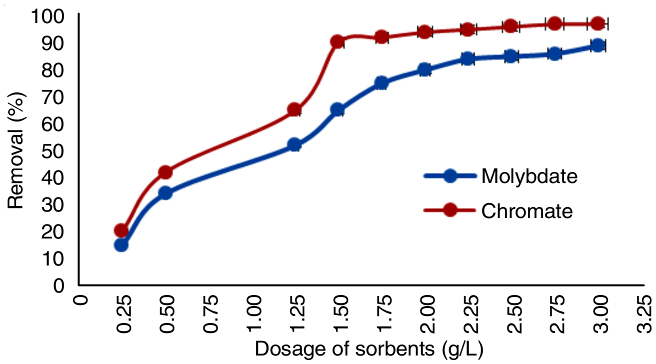

Fig. 5. Effect of dosage of MKAC (initial conc. of molybdate/chromate: 25 ppm)

As the dosage increases, active sites are increased and so, proportional increase in the extraction is expected. But the adsorptive behaviour is not in accordance with the expectations. The reason may that at high concentrations, the MKAC particles are getting aggregated. The aggregations, on one hand reduces the availability of active sites and on the other 'clogs' the pathways for ions to approach the inner laying active sites. As a consequence of these, the proportionality between 'adsorptivity' and 'dosage' is lost and after certain stage, an equilibration state is resulted.

Agitation time: By varying the time of agitation from 15 min to 150 min, the changes in the percentage of extraction by MKAC for molybdate and chromate ions, were investigated (Fig. 6). The other extractions conditions maintained constant were pH: 2.5; MKAC dosage: 2.0 g/L for molybdate ions and 1.5 g/L for chromate ions; initial molybdate or chromate concentrations: 25.0 mg/L; rpm 300 and temp. 303 K. Adsorption is rapid and linearly proportional to time initially but with time,

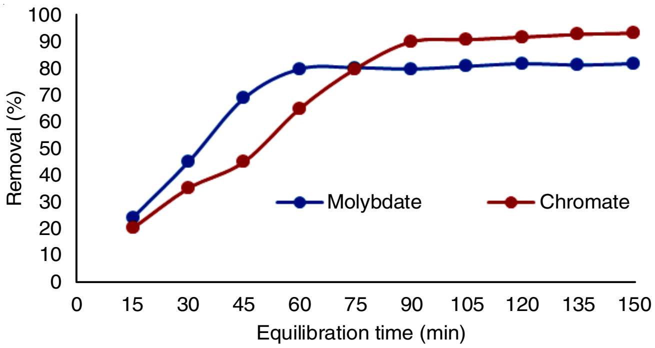

Fig. 6. Effect of equilibration time on % removal of molybdate/chromate (initial conc. of ions: 25 ppm)

the adsorption is mellowed and proportionality with time is not observed. After a certain agitation time, a steady state is resulted. Only a marginal increase in the percentage removal of molybdate or chromate ions was observed after 60 min or 90 min, respectively. These observations are similar to the expectations. As the adsorbent used is fixed (2.0 mg/L for molybdate and 1.5 g/L for chromate), a fixed number of active site are available for adoption process. In the earlier timings of agitation, the availability of active sites for sorption process, is more and so, good adsorption is observed. But as the time progresses, the active sites are used up and hence, adsorption is slowed. A steady state is resulted when all the active sites are exhausted due to the adsorption of molybdate and chromate ions: 60 min for chromate and 90 min for molybdate.

Initial concentration of adsorbates: The adsorptivity of MKAC is markedly influenced by the initial concentration of molybdate or chromate ions. Investigations were done by changing the initial concentrations of molybdate or chromate ions from 5 to 50 mg/L to assess the effect of initial concentrations on the adosptivity of MKAC.

It can be inferred from Fig. 7 that percentage removal is decreased as the initial concentration is increased. The decrease is observed from 100% to 21% for molybdate ions and 100% to 25% for chromate ions as the initial concentration of molybdate or chromate, is increased from 5 to 50 mg/L. A decrease in the % of extraction, is as per expectations. As fixed amounts of MKAC was used (1.5 g/L for chromate ions and 2.0 g/L for molybdate ions), only a fixed number of active sites are available. But with progressive increase in the initial concentration of molybdate or chromate ions, the demand for active sites is increased. But as only a limited number of active sites are available, the % of extraction is decreased.

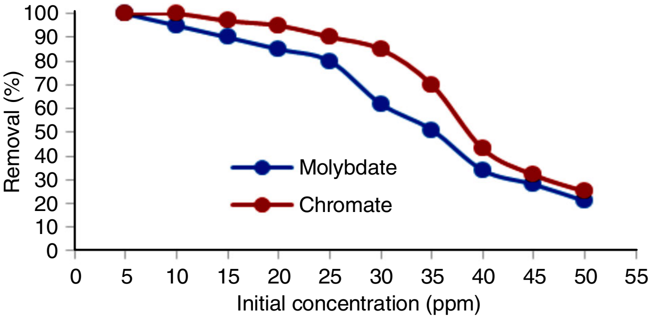

Fig. 7. Initial conc. *vs.* % removal

It is interesting to note that the variations of q_e, adsorption capacity, as the initial concentrations of molybdate or chromate ions are changed (Fig. 8). The adsorption capacity of MKAC for molybdate is increased as the concentration of molybdate is increased from 5 to 25 mg/L but on further increase of molybdate concentration, the q_e values are decreasing. In the case of chromate adsorption by MKAC, the q_e values are increased as the concentration of chromate is increased from 5 to 30 mg/L and then onwards, the q_e values are decreased with further increase in the chromate concentration.

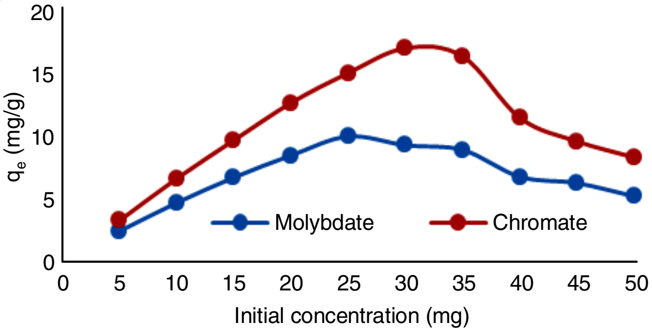

Fig. 8. Initial concentration *vs.* sorption capaity (q_e)

The concentration of molybdate or chromate ions is not uniform thorough out the mixture of solutions. The concentration of the said ions varies from bulk of the solution to the layers of solution near to the surface of the sorbent. This is similar to concentration gradient and it effects the diffusion of adsorbate ions towards the surface of the adsorbent. With increase in the initial concentration of adsorbate, the concentration gradient is more and thereby causing the molybdate or chromate ions to drift or diffuse more towards the adsorbent surface. This results in the increase of sorption capacity with increase in the initial concentration. But at high concentrations, the diffusion mechanism is not markedly contributing to the adoption capacity, resulting the lowering of adsorption capacity [36].

Effect of solutions temperature: The solution temperature on the adsorption equilibrium was investigated by varying the temperature from 303 to 333 K. Percentages of extractions of molybdate as well as chromate ions, have shown increasing trend with increase in temperature (Fig. 9). At high solution temperatures, surface functional groups on the MKAC surface, acquire enhanced vibrational kinetic energy. This results in the decrease of density of surface layers of MKAC and thereby, the hidden active sites at low temperatures are open at enhanced solution temperatures. Further, the molybdate or chromate ions acquire more migrational energies with enhancement in the solution temperature. Due to these, molybdate or chromate ions penetrate more into the MKAC matrix, resulting enhancement in adsorption [36].

Interference studies: Natural water contains many co-ions. Their effect on the adsorptivities of MKAC for molybdate and chromate ions was investigated. For this purpose, simulated molybdate and chromates solutions (25 mg/L) having two-fold excess of various common co-ions, were prepared. The solutions were subjected to the treatment with MKAC at the

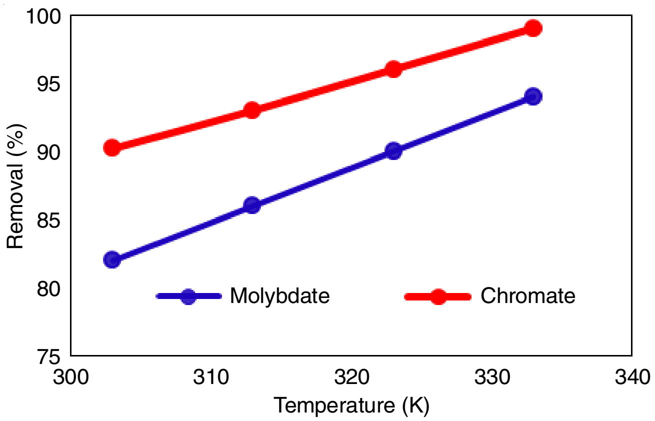

Fig. 9. Temperature *vs.* % removal

optimum conditions *viz.* pH: 2.5, sorbent dosage: 1.5 g/L for molybdate ions and 2.0 g/L for chromate ions; time of agitation: 60 min for chromate ions and 90 min for molybdate ions; temp.: 303 K; rpm: 300.

It is interesting to note that even two-fold excess of Ca^{2+}, Mg^{2+}, Al^{3+}, Zn^{2+} and Fe^{2+} ions have not effected the percentage of extraction of molybdate and chromate with MKAC at the optimum conditions evaluated in this investigation and in fact, the extraction has been marginally enhanced.

Among the anions interference, chloride, sulphate, nitrate and bicarbonate have almost not interfered in the extraction. However, fluoride (75%; 84%), phosphate (73%; 82%), arsenate (68%; 80%) and antimonate (66%; 79%) have affected marginally the extraction of molybdate as well as chromate ions (80%; 90.2%).

Simultaneous extraction of molybdate and chromate ions: At pH 2.5, MKAC has shown good adsorption for both molybdate and chromate ions. This promotes to investigate the possibility of simultaneous removal of both ions at pH 2.5. Hence, simulated binary mixtures of molybdate and phosphate of different compositions were prepared and subjected to the treatment by MKAC. The extraction conditions were optimized *viz.* pH 2.5; sorbent dosage: 2.5 g/L; time of agitation: 120 min; temp: 303 K; rpm: 300. It may be noted that adsorbent dosages and time of agitations are to be enhanced for simultaneous removal than for individual ions. The results are presented in Table-2.

Evaluation of thermodynamic parameters: Thermodynamic parameters, *viz.* Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were assessed adopting the equations [37]:

$$\Delta G = -RT \ln K_d$$

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

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

To evaluate these factors, van't Hoff plot, ln K_d *vs.* 1/T, was drawn (Fig. 10). The assessed parameters are presented in Table-3. It is interesting to note that the ΔG values are more negative with the enhancement in solution temperature. This signifies that the adoption of molybdate and chromate ions onto 'MKAC' is spontaneous and is more favoured with the increase in solution temperature [38].

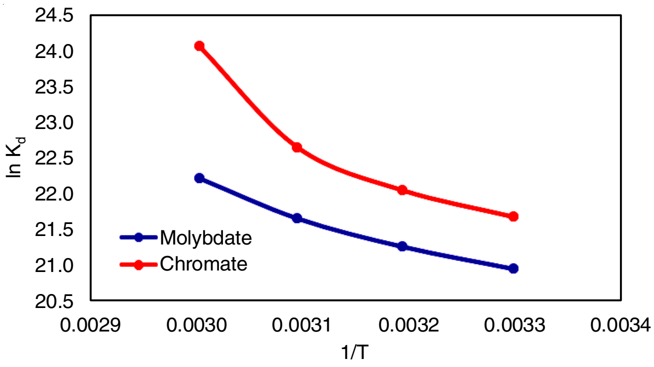

Fig. 10. Van't Hoff plot

The ΔH values are 35.259 kJ/mol for molybdate ions adsorption and 64.854 kJ/mol for chromate ions adsorption. The positive sign indicates that the sorption is endothermic while their magnitude signifies that the adsorption is not mere

TABLE-2
SIMULTANEOUS MOLYBDATE AND CHROMATE REMOVAL*
Optimum conditions: pH: 2.5; dosage of MKAC: 2.5 g/L; Contact time: 120 min; rpm: 300; Temp.: 303 K)

Samples	Molybdate + chromate (mg/L)		Conc. after MKAC – sorption (mg/L)		Removal (%)	
	Molybdate	Chromate	Molybdate	Phosphate	Molybdate	Phosphate
1	2.5	2.5	Zero	Zero	100	100
2	5.0	5.0	Zero	Zero	100	100
3	7.5	7.5	Zero	Zero	100	100
4	10.0	10.0	Zero	0.10	100	98.7
5	15.0	15.0	2.4	1.5	84.0	90.0
6	20.0	20.0	3.5	2.3	82.5	88.5

*Average of five samples; S.D.: ± 0.26

TABLE-3
THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF MOLYBDATE AND CHROMATE ONTO MKAC

Adsorbate	ΔH (kJ/mol)	ΔS (J/mol)	ΔG (kJ/mol)				R^2
			303 K	313 K	323 K	333 K	
Molybdate removal	35.259	289.9	-52.58	-55.48	-58.37	-61.27	0.9739
Chromate removal	64.854	392.18	-53.97	-57.89	-61.82	-65.74	0.8961

electrostatic interactions but it may be due ion-exchange and/or a kind of surface complex formation [39].

The ΔS values are 289.9 J/mol for molybdate ions sorption and 392.18 J/mol for chromate ions sorption. The positive sign and magnitude indicated that there is high degree of disorder at the interface between MKAC and solution. In other words, turmoil is happened at the interface, which is a favourable condition for driving the molybdate and chromate ions to pass through the surface barrier existing at the solid and solution interface. This results in more adsorptivity for MKAC [40].

Evaluation of adsorption isotherms: The nature of adsorption on MKAC for molybdate and chromate ions were investigated by adopting linear models of various isotherms [37,41-44], which are

Freundlich:

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

Langmuir:

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

Temkin:

$$q_e = B \ln K_T + B \ln C_e$$

Dubinin-Radushkevich:

$$\ln q_e = -\beta\varepsilon + \ln q_m$$

The evaluated parameter values are shown in Table-4. From the correlation coefficient (R^2) values, it may be inferred that Langmuir as well as Freundlich models explains well the adoption of molybdate.

In the case of chromate the better fit model falls in the order: Langmuir model > Freundlich model > Temkin model > Dubinin-Radushkevich (DR) model. This indicates that Langmuir model is better fit model to explain the chromate sorption by MKAC. This signifies that surface of MKAC is uniform and the adsorption is homogenous as the sorbent sites are uniformly located. The evaluated R_L values indicated that the adsorption is favourable [37]. Further, the evaluated B values from DR model confirmed the same.

Evaluation of kinetics of adsorption: The kinetics of adsorption of molybdate and chromate ions onto the MKAC surface were evaluated as per the equations [36,45-48]:

Pseudo 1st order:

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

Pseudo 2nd order:

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

Bangham's pore diffusion model:

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

Elovich equation:

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

The assessed parameter are given in Table-5. The R^2 values for molybdate adsorption falls in the order: Pseudo 2nd order >. Pseudo 1st order model > Elovich model > Bangham's pore diffusion model. In the case of chromate adsorption, the R^2 values fall in the order: Pseudo 2nd order >. Bangham's pore diffusion model > Elovich model > Pseudo 1st order model. Thus, pseudo 2nd order model is better fit model to explain the kinetics of adsorption for molybdate as well as chromate adsorption.

Recycling of spent MKAC: The spent adsorbents are to be regenerated for devising cost effective methodologies. Hence, investigations were performed to regenerate and reuse the spent MKAC. For this purpose, various acids, bases and salt solutions

TABLE-4
EVALUATED ADSORPTION ISOTHERMS PARAMETERS ON MKAC

Adsorbate		Freundlich isotherm	Langmuir isotherm	Temkin isotherm	Dubinin-Radushkevich isotherm
Molybdate removal	Slope	0.265	0.175	0.768	-9.9
	Intercept	1.777	0.306	6.222	2.2
	R^2	0.959	0.959	0.571	0.587
		1/n = 0.265	R_L = 0.06	B = 0.768	E = 7.0 kJ/mol
Chromate removal	Slope	0.168	0.112	1.033	-4.2
	Intercept	2.374	0.141	6.816	2.5
	R^2	0.603	0.969	0.531	0.440
		1/n = 0.168	R_L = 0.05	B = 1.033	E = 2.9 kJ/mol

TABLE-5
EVALUATED KINETICS PARAMETERS OF THE ADSORPTION PROCESS ON MKAC

Models	Parameter	Pseudo 1st order	Pseudo 2nd order	Elovich model	Bangham's pore diffusion
Molybdate removal	Slope	0.024	0.076	3.152	0.509
	Intercept	1.248	2.506	4.485	2.484
	R^2	0.887	0.937	0.838	0.792
Chromate removal	Slope	0.013	0.045	6.127	0.733
	Intercept	1.357	2.465	14.103	2.786
	R^2	0.873	0.967	0.942	0.949

TABLE-6
APPLICATIONS: TREATMENT OF SAMPLES OF WASTEWATER COLLECTED FROM INDUSTRIES AND MINING USING MKAC AS ADSORBENT
(Optimum conditions: pH: 2.5; dosage of MKAC: 2.5 g/L; Contact time: 120 min; rpm: 300; Temp.: 30 ± 1°C)

Samples	Initial conc. (C_i)* (mg/L)				Final conc. (C_e)* (mg/L)				Extraction (%)			
	Molybdate		Chromate		Molybdate		Chromate		Molybdate		Chromate	
	A	B	A	B	A	B	A	B	A	B	A	B
1	0.8	1.6	1.2	2.4	Zero	Zero	Zero	Zero	100	100	100	100
2	1.0	2.3	2.4	3.2	Zero	Zero	Zero	Zero	100	100	100	100
3	1.3	1.0	2.8	4.2	Zero	Zero	Zero	Zero	100	100	100	100
4	2.1	3.6	3.0	3.9	Zero	Zero	Zero	Zero	100	100	100	100
5	–	4.4	4.5	–	Zero	Zero	Zero	Zero	100	100	100	100
6	3.2	-Nil-	–	7.2	Zero	Zero	Zero	Zero	100	100	100	100
7	–	4.9	5.6	5.6	Zero	Zero	Zero	Zero	100	100	100	100

*Average value of five estimations; S.D.: ±0.34; A = Industrial effluents; B: Mining wastewater

at different concentrations were used as extracting agents to remove molybdate and chromate ions from the adsorption active sites and thereby, regenerating the MKAC for further use. In present case, 0.1 N HCl was found to be effective. From Fig. 11, it can be inferred that up to three cycles, MKAC retained its capacity for the adsorption of molybdate and chromate ions with the marginal loss of adsorption capacity.

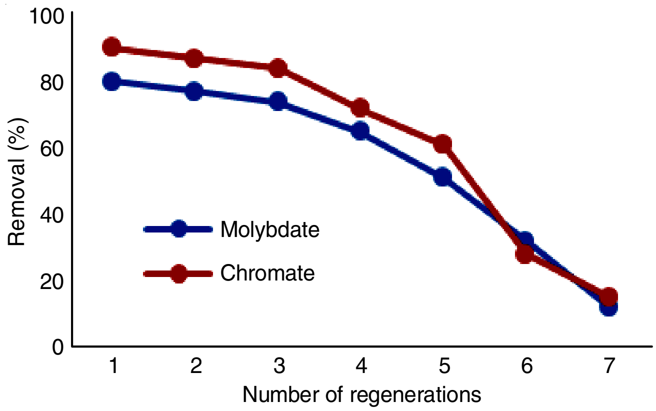

Fig. 11. Regenerations *vs.* % removal

Applications: Various wastewater samples were collected from different industries and minings located at different places in Ethiopia and Madras city, India. The samples were analyzed for the contents of molybdate and chromate ions. Then the samples were treated with MKAC as per the method developed in this investigation. From Table-6, it is inferred that MKAC is remarkably successful in removing molybdate and chromate ions from real wastewater samples.

Comparison: The present developed adsorbent, MKAC, is compared with the *hitherto* developed sorbents with respect to working pH and adsorption capacity. The data is summarized in Table-7. It may be inferred that most of the previous studies aimed to remove either molybdate or chromate from industrial water and not both at a time. The simultaneous removal of molybdate and chromate assumes importance in the treatment of wastewater from industries, mininges and nuclear power stations. The adsorption capacity of MKAC is more than many adsorbents reported and the emphatic novelty is its effectiveness in the simultaneous removal of molybdate and chromate ions from the wastewater samples.

Conclusion

Sulphuric acid generated activated carbon from stems of *Murraya koenigii* plant (MKAC) has the potential to remove both molybdate and chromate ions simultaneously at pH 2.5. The activated carbon has been characterized with respect to various physico-chemical parameters and also by adopting

TABLE-7
COMPARISON OF MKAC WITH ALREADY REPORTED ADSORBENTS

Adsorbent	Optimum pH	Mo(VI)/Cr(VI)	Ref.
Pyrite	pH 3- 5	15.3 mg/g (Mo)	[2]
Nano-magnetic $CuFe_2O_4$	3	30.58 (Mo)	[5]
Spent coffee grounds	2	22 (Cr)	[11]
Magnetite nanoparticles	2.5	19.2 (Cr)	[13]
NaOCl-oxidized multiwalled carbon nanotubes	7	22.73 (Mo)	[17]
Desulfurization steel slag	3-4.5	4.38 (Mo)	[18]
Zeolite-supported magnetite	3	18 mg/g (Mo)	[21]
Salvadora persica (ashes)	2	22.9 (Cr)	[23]
Caesalpinia bonduc plants (ashes)	2	19.6 (Cr)	[23]
Lantana camara plant ash	2	26.25 (Cr)	[29]
Red mud modi?ed by lanthanum (La-RM)	7	17.35 (Cr)	[49]
Magnetic MWCNTs	3	11.4 (Cr)	[50]
Carbon nanotubes	4	9 (Cr)	[51]
(nZVI)/Fe_3O_4 nanocomposites	8	29.43	[52]
MKAC	2.5	30.8 (Mo + Cr)	Present work

XRD and FTIR analysis methods. Various extraction conditions such as pH, dosage of MKAC, time of contact, initial concentration of adsorbates, temperature, *etc*. have been investigated and optimized using simulated solutions of individual and also mixtures of molybdate and chromate ions. Established optimum conditions for the simultaneous removal of chromate and molybdate ions were pH 2.5; dosage of MKAC: 2.5 g/L; contact time: 120 min; rpm: 300; temp.: 303 K. Interference caused by various co-ions has been investigated and observed that the adsorptivity of MKAC is least affected. The spent MKAC can be regenerated and reused upto three cycles. The adsorption mechanism is assessed by evaluating thermodynamic parameters, isothermal and kinetic models. The ΔG and ΔH values have revealed that the adsorption of molybdate and chromate ions onto MKAC is endothermic and spontaneous. The high values of ΔH indicate that the sorption is thorough ion-exchange and/or a kind of surface complex formation between surface functional groups of MKAC and molybdate or chromate ions. Of the various kinetic models analyzed for evaluating the sorption kinetics, pseudo 2nd order model is better fit to explain the kinetic of adsorption of molybdate and chromate ions by MKAC. The developed methodology was successfully applied to treat real wastewater samples collected from industrial and mining effluents and observed to be highly effective. The novelty of the present investigation is that a simple, effective and ecofriendly bioadsorbent is developed for the simultaneous removal of highly toxic molybdate and chromate ions from the industrial wastewater samples.

ACKNOWLEDGEMENTS

The authors are thankful to K L E F, Guntur and Andhra Pradesh for providing necessary facilities to pursue this research investigation.

CONFLICT OF INTEREST

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

REFERENCES

1. N. Goyal, S.C. Jain and U.C. Banerjee, *Adv. Environ. Res.*, **7**, 311 (2003); https://doi.org/10.1016/S1093-0191(02)00004-7
2. B.C. Bostick, S. Fendorf and G.R. Helz, *Environ. Sci. Technol.*, **37**, 285 (2003); https://doi.org/10.1021/es0257467
3. E. Weidner and F. Ciesielczyk, *Materials*, **12**, 927 (2019); https://doi.org/10.3390/ma12060927
4. K. Bourikas, T. Hiemstra and W.H. Van Riemsdijk, *J. Phys. Chem. B*, **105**, 2393 (2001); https://doi.org/10.1021/jp002267q
5. 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
6. R. Shrivastava, R.K. Upreti, P.K. Seth and U.C. Chaturvedi, *FEMS Immunol. Med. Microbiol.*, **34**, 1 (2002); https://doi.org/10.1111/j.1574-695X.2002.tb00596.x
7. A. Zhitkovich, *Chem. Res. Toxicol.*, **24**, 1617 (2011); https://doi.org/10.1021/tx200251t
8. A.K. Verma, R.R. Dash and P. Bhunia, *J. Environ. Manage.*, **93**, 154 (2012); https://doi.org/10.1016/j.jenvman.2011.09.012
9. S. Sharma and A. Bhattacharya, *Appl. Water Sci.*, **7**, 1043 (2017); https://doi.org/10.1007/s13201-016-0455-7
10. 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
11. S. De Gisi, G. Lofrano, M. Grassi and M. Notarnicola, *Sustain. Mater. Technol.*, **9**, 10 (2016); https://doi.org/10.1016/j.susmat.2016.06.002
12. G.P. Gallios and M. Vaclavikova, *Environ. Chem. Lett.*, **6**, 235 (2008); https://doi.org/10.1007/s10311-007-0128-8
13. P. Yuan, D. Liu, M.D. Fan, D. Yang, R.L. Zhu, F. Ge, J.X. Zhu and H.P. He, *J. Hazard. Mater.*, **173**, 614 (2010); https://doi.org/10.1016/j.jhazmat.2009.08.129
14. H.I. Adegoke, F.A. Adekola, O.S. Fatoki and B.J. Ximba, *Pol. J. Environ. Stud.*, **22**, 7 (2013).
15. N. Xu, C. Christodoulatos and W. Braida, *Chemosphere*, **64**, 1325 (2006); https://doi.org/10.1016/j.chemosphere.2005.12.043
16. A. Afkhami, T. Madrakian and A. Amini, *Desalination*, **243**, 258 (2009); https://doi.org/10.1016/j.desal.2008.04.028
17. Y.C. Chen and C.Y. Lu, *J. Ind. Eng. Chem.*, **20**, 2521 (2014); https://doi.org/10.1016/j.jiec.2013.10.035
18. 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
19. P. Derakhshi, H. Ghafourian, M. Khosravi and M. Rabani, *World Appl. Sci. J.*, **7**, 230 (2009).
20. N. Xu, C. Christodoulatos and W. Braida, *Chemosphere*, **62**, 1726 (2006); https://doi.org/10.1016/j.chemosphere.2005.06.025
21. 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
22. J. Ponou, J. Kim, L.P. Wang, G. Dodbiba and T. Fujita, *Chem. Eng. J.*, **172**, 906 (2011); https://doi.org/10.1016/j.cej.2011.06.081
23. Y.H. Rao and K. Ravindhranath, *Rasayan J. Chem.*, **10**, 1104 (2017); https://doi.org/10.7324/RJC.2017.1041829
24. U.K. Garg, M.P. Kaur, V.K. Garg and D. Sud, *J. Hazard. Mater.*, **140**, 60 (2007); https://doi.org/10.1016/j.jhazmat.2006.06.056
25. G. Cimino, A. Passerini and G. Toscano, *Water Res.*, **34**, 2955 (2000); https://doi.org/10.1016/S0043-1354(00)00048-8
26. A.N. Babu, G.K. Mohan and K. Ravindhranath, *Int. J. Chemtech Res.*, **9**, 506 (2016).
27. 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
28. Z.A. Al-Othman, R. Ali and M. Naushad, *Chem. Eng. J.*, **184**, 238 (2012); https://doi.org/10.1016/j.cej.2012.01.048
29. S. Ravulapalli and K. Ravindhranath, *Water Sci. Technol.*, **78**, 1377 (2018); https://doi.org/10.2166/wst.2018.413
30. W.K. Biftu and K. Ravindhranath, *Asian J. Chem.*, **33**, 281 (2021); https://doi.org/10.14233/ajchem.2021.22953
31. S.L. Pala, W.K. Biftu, M. Suneetha and K. Ravindhranath, *Int. J. Environ. Anal. Chem.*, (2021); https://doi.org/10.1080/03067319.2021.1927004
32. C. Namasivayam and K. Kadirvelu, *Bioresour. Technol.*, **62**, 123 (1997); https://doi.org/10.1016/S0960-8524(97)00074-6
33. A.N. El-Hendawy, S.E. Samra and B.S. Girgis, *Colloids Surf. A Physicochem. Eng. Asp.*, **180**, 209 (2001); https://doi.org/10.1016/S0927-7757(00)00682-8
34. S. Brunauer, P.H. Emmett and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938); https://doi.org/10.1021/ja01269a023
35. S. Ravulapalli and R. Kunta, *J. Fluor. Chem.*, **193**, 58 (2017); https://doi.org/10.1016/j.jfluchem.2016.11.013
36. M. Suneetha, B.S. Sundar and K. Ravindhranath, *J. Anal. Sci. Technol.*, **6**, 15 (2015); https://doi.org/10.1186/s40543-014-0042-1
37. A. Naga Babu, G.V. Krishna Mohan, K. Kalpana and K. Ravindhranath, *J. Anal. Methods Chem.*, **2017**, 4650594 (2017); https://doi.org/10.1155/2017/4650594

38. C. Fan and Y. Zhang, *J. Geochem. Explor.*, **188**, 95 (2018); https://doi.org/10.1016/j.gexplo.2018.01.020
39. 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
40. A.N. Babu, D.S. Reddy, G.S. Kumar, K. Ravindhranath and G.K. Mohan, *J. Environ. Manage.*, **218**, 602 (2018); https://doi.org/10.1016/j.jenvman.2018.04.091
41. I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918); https://doi.org/10.1021/ja02242a004
42. H.M. Freundlich, *Z. Phys. Chem.*, **57**, 1100 (1906).
43. M.J. Temkin and V. Pyzhev, *Acta Physiochim USSR*, **12**, 217 (1940).
44. M.M. Dubinin, *Dokl. Akad. Nauk SSSR*, **55**, 327 (1947).
45. W.K. Biftu, M. Suneetha and K. Ravindhranath, *Biomass Conv. Bioref.*, (2021); https://doi.org/10.1007/s13399-021-01568-w
46. Y.S. Ho and G. McKay, *Process Biochem.*, **34**, 451 (1999); https://doi.org/10.1016/S0032-9592(98)00112-5
47. Y.S. Ho, J.C.Y. Ng and G. McKay, *Sep. Purif. Methods*, **29**, 189 (2000); https://doi.org/10.1081/SPM-100100009
48. A.A. Atia, *Appl. Clay Sci.*, **41**, 73 (2008); https://doi.org/10.1016/j.clay.2007.09.011
49. Y.W. Cui, J. Li, Z.F. Du and Y.Z. Peng, *PLoS One*, **11**, e0161780 (2016); https://doi.org/10.1371/journal.pone.0161780
50. Z.N. Huang, X.L. Wang and D.S. Yang, *Water Sci. Eng.*, **8**, 226 (2015); https://doi.org/10.1016/j.wse.2015.01.009
51. M.A. Atieh, *Procedia Environ. Sci.*, **4**, 281 (2011); https://doi.org/10.1016/j.proenv.2011.03.033
52. X. Lv, J. Xu, G. Jiang, J. Tang and X. Xu, *J. Colloid Interface Sci.*, **369**, 460 (2012); https://doi.org/10.1016/j.jcis.2011.11.049