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Anionic reactive dye removal from aqueous solution using a new adsorbent—Sludge generated in removal of heavy metal by electrocoagulation

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Abstract

The present work investigates the potential of electrocoagulated metals hydroxide sludge (EMHS) generated during removal of Cr^{3+} using Al electrode for adsorption of Congo Red (CR) from aqueous solution. The effects of contact time, stirrer speed (to make the external mass transfer effect negligible), pH of the solution, initial concentration of adsorbate and adsorbent dose on dye removal have been investigated. The adsorption is highly pH dependent due to formation of various charged hydroxylated species [$Al(OH)^{2+}$, $Cr(OH)^{2+}$, etc.] of EMHS and as resonance of CR occurs at alkaline pH through involvement of free lone pair of electrons. Comparative COD reduction with diminution of color (measured spectrophotometrically) confirms successful removal of the adsorbate. Preferable fitting of Langmuir isotherm over Freundlich isotherm suggests monolayer coverage of adsorbate at the surface of adsorbent. The maximum adsorption capacity (q_m) increases from 271 to 513 mg/g when the initial pH is adjusted to 3.0 instead of 10.4. Comparison with literature reported values of q_m and n (Freundlich constant) with either CR as adsorbate or metal hydroxide adsorbent, establishes EMHS as an attractive adsorbent. In the pH range of 3–10, concentration of Cr^{3+} in the leachate remains below the discharge concentration of the same. FT-IR spectrum of dye-loaded sludge suggests that the dye removal is due to chemical interaction of CR and EMHS. The SEM image before and after the adsorption indicates that, CR was adsorbed at the surface of the adsorbent.

Keywords: Adsorption; Congo Red; COD reduction; Monolayer coverage; FT-IR spectrum; SEM micrograph

1. Introduction

One of the main problems associated with the treatment of textile dyeing plant wastewater is the removal of dyes. Discharge of dyes is objectionable not only for aesthetic reasons but also as many dyes and their degradation products are carcinogenic toward aquatic life and mutagenic for humans [1–3]. These are sources of water pollution and it is necessary to remove dye(s) from aqueous streams for safe disposal of effluent. Several techniques like chemical oxidation [4], coagulation [5], aerobic/anaerobic digestion [6], membrane separation [7,8] are conventionally used for removal of dye(s) from wastewater. Each of these methods has its limitations and advantages in application.

Various workers have recommended adsorption process for effective treatment of effluents containing coloring materials. Both granular or powdered activated carbon (AC) [9–13] and different low cost adsorbents (LCA) like coir pith [14], clay [15], bagasse, fly ash [16], mesoporous minerals [17], sawdust [18], alunite [19], banana peel [20], biomass [21,22] and others adsorbent like polymer [23], cotton [24] etc are used for removal of toxic dyes from effluent. Adsorption capacities of commercial AC for reactive dyes generally vary from 7.69 to 1179 mg/g [25]. However, AC has the disadvantage of high cost. Several workers have been investigated the suitability of waste metal hydroxide sludge from electroplating industry for removal of reactive dyes [26,27], catechol [28], etc. Reported adsorption capacity of metal hydroxide sludge generally varies from 44 to 60 mg/g with different reactive dyes as adsorbate [27]. High capacity–low cost adsorbents are still under development to reduce the adsorbent dose and minimize disposal problems.

Electrocoagulated metal hydroxide sludge (EMHS) is generated during removal of heavy metals by electrocoagulation (EC). Donald [29] reported that, EMHS is chemically inert, does not leach back contaminants. During removal of Cr^{3+} by EC by the authors in a separate study, about 4.7 g/l sludge is generated

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Nomenclature

C_0	initial Congo Red (CR) concentration (mg/l)
C_e	CR concentration in solution at equilibrium (mg/l)
k_1	Langmuir isotherm constant (l/mg)
k_2	Freundlich isotherm constant (mg/l)
n	Freundlich isotherm constant (g/l)
pH_{zpc}	pH at zero point charge
q_e	adsorbed CR per unit weight of EMHS at equilibrium (mg/g)
q_m	adsorption capacity corresponding to complete monolayer coverage (mg/g)
R^2	correlation coefficient
R_L	dimensionless equilibrium parameter for Langmuir isotherm

in bringing down to Cr^{3+} concentration from 1000 to 2 mg/l, using Al electrodes with 32.52 mA/cm^2 cell current density. Disposal/end use of this sludge is a paramount issue as this sludge has high toxic metal content. Main composition of the sludge is hydroxides of electrode metals and heavy metals [$M(OH)_n$, here M is Al or Cr]. Mole ratio of M^{3+} and OH^- generally varies from 2 to 2.5 [30] in the pH range 5–6. Our search did not reveal any literature on possible end use of EMHS such as adsorptive removal of toxic dye(s) from aqueous solution.

This investigation has therefore been carried out on adsorptive removal of Congo Red from aqueous solution by EMHS. The main objectives of the present work include: (i) performance of CR removal at different stirrer speed, initial pH of the solution, initial adsorbate concentration and adsorbent dose, (ii) reduction of COD during the contact between the phases, (iii) fitting of Langmuir and Freundlich isotherm model for the experimental equilibrium data, (iv) desorption study exploring the recovery of adsorbate, (v) study of leaching of Cr^{3+} from adsorbent to the aqueous phase and (vi) characterization of sludge and dye-loaded adsorbent by FT-IR and SEM.

2. Experimentation

2.1. Materials

Congo Red (Direct Red 28) was purchased from Loba Chemie Pvt. Ltd. (Mumbai, India). Physical and chemical properties of CR are shown in Table 1. Stock solution of CR was prepared by dissolving 1.0 g dye by in 1.0 l distilled water. Adsorption study was performed after appropriate dilution of stock solution. All other reagents used for this study were AR or GR grade.

Table 2
Characteristics of dried EMHS

Property name	Value
Average particle size (μm)	60.89
Al content (%)	14.27
Cr^{3+} content (%)	14.5
Chloride content (%)[a]	1.42
pH in aqueous suspension (0.16%)	6.80
Color	Deep cyan

[a] Energy dispersive X-ray analysis.

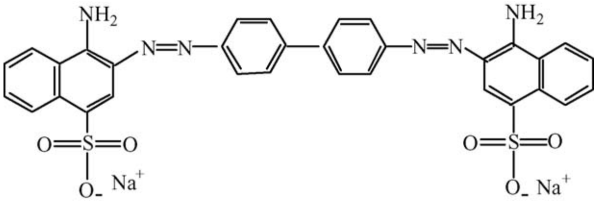
2.2. Adsorbent preparation

EMHS used for the adsorption study was obtained from electrocoagulation (EC) experiments with aluminum electrodes. The EC was performed with a solution of basic chrome sulfate [$Cr(OH)SO_4$, BCS] because most of the local tanneries use this salt for single bath chrome tanning operation [31]. The EMHS after EC was filtered, washed with distilled water to remove any unadsorbed metal ions and then oven dried at 103–105 °C for 12 h. The dried sludge was crushed in mortar and pestle and stored in desiccator. Particle size was analyzed using Malvern Particle Sizer (Model: 3601). X-ray diffraction pattern analysis was performed with a Philips diffractometer (Model: X'Pert Pro) equipped with a Co X-ray radiation source (40 kV, 30 mA). It shows that EMHS is amorphous in nature. Main components of EMHS are various monomeric and polymeric hydroxides of aluminum and chromium (III) [30]. Physiochemical properties of dried EMHS used as adsorbent for the present work are summarized in Table 2.

2.3. Adsorption studies

Adsorption experiments were carried out in a batch stirred cell at 30 °C by contacting 250 ml dye solution at desired concentration (100–300 mg/l). Solution was agitated with a magnetic stirrer of M/s Tarsons India Ltd. (Model: MC02). pH of the dye solution was adjusted to the desired initial value by addition of 0.1 (N) of acid (HNO_3) or alkali (NaOH) prior to addition of

Table 1
Physical and chemical properties of Congo Red

Structure	λ_{max} (nm)	MW	CI
	498	696.65	22120

EMHS. Effect of pH was studied by changing the initial solution pH from of 3.0 to 11.0. The adsorbent dose was varied from 0.05 to 0.4 g per 250 ml solution for an adsorption period of 60 min. During experiments samples were drawn at predetermined time intervals and centrifuged at 5000 rpm for 10 min for sludge separation. Supernatant was then analyzed spectrophotometrically for dye concentration after proper dilution and pH adjustment. The absorbance of CR changes in acidic pH. No change in absorbance is observed in pH range 7–12. Measurement of absorbance was performed on samples after bringing pH close to 8 by addition of alkali (0.1 N NaOH) or acid (0.1 N HNO_3). Preliminary trials experiments show that equilibrium was practically established within 4.0 h. To ensure that equilibrium condition is attained, experiments were conducted for an adsorption period of 12 h in a closed container. Isotherms were determined with 50 ml solutions by changing the initial dye content from 8.75 to 17.5 mg and adsorbent dose from 0.01 to 0.05 g.

2.4. Desorption studies

Dye-loaded adsorbent at equilibrium with initial adsorbate concentration of 100 mg/l, 0.1 g EMHS and solution pH of 7.0 was separated by filtration with Whatman filter paper and repeatedly washed with distilled water to remove any unadsorbed dye. Spent adsorbent was then mixed with equal volume of distilled water at different pH. The solution was agitated at 100 rpm for 20 min. Desorbed dye concentration was analyzed following the procedure stated in the next section.

2.5. Analysis

Concentration of CR in aqueous phase was determined spectrophotometrically. Appropriately diluted samples were scanned using SPEKOL-1200 UV spectrophotometer (Germany) at 498 nm. pH measurement of solution was performed using a digital pH meter of Toshniwal India Ltd. (Model: CL-46) make. Surface morphology of EMHS before and after adsorption was obtained from scanning electron microscope (SEM) of M/s JEOL, Japan (Model: JSM-5800). FT-IR spectra of the same samples were recorded using a spectrophotometer (FT-IR-1600, Perkin-Elmer). Atomic absorption spectrophotometer (Analyst-700 Perkin-Elmer, USA) was used for determination of the chromium and aluminum content in solution and sludge. COD of the samples were measured by “Open reflux method” of COD measurement [32]. Chemicals are used for determination of COD of AR/GR grade were procured from M/s E. Merck (India).

3. Results and discussion

3.1. Adsorption

3.1.1. Stirrer speed

Increase in agitation by increasing stirrer speed lowers the external mass transfer effect. Optimum stirrer speed was decided by varying it in the range 100–400 rpm to make the external mass transfer effect negligible prior to study the effect of others process parameters like pH, adsorbate concentration, etc. Effect of agitation was studied with 100 mg/l initial CR, pH of 7.0 and 0.1 g adsorbent (in 250 ml solution). By changing the stirrer speed from 100 to 200 rpm, the percentage removal of CR increased from 42.4 to 45.4 after 60 min of contact (Table 3). Only 0.7% higher removal was observed by further increment of stirrer speed from 200 to 400 rpm. It was therefore decided to conduct all further experiments at 200 rpm.

Table 3
Effect of stirrer (rpm) and contact time on adsorption of CR

Contact time (min)	Cumulative % removal		
	100 rpm	200 rpm	400 rpm
2.5	10.5	14.6	15.2
5	16.7	22.1	24.0
10	19.9	24.2	27.3
20	23.5	29.2	30.2
30	28.7	33.9	34.6
40	32.4	38.0	38.2
50	37.2	42.3	43.1
60	42.4	45.4	46.1

3.1.2. Effect of pH

Literature reports [27,33] that during adsorption of reactive dye(s) by metal hydroxide sludge in aqueous solution, pH plays an important role on removal mechanism and hence on removal efficiency. In the present work, pH dependency of CR adsorption on EMHS has also been studied. The results are shown in Fig. 1. At initial pH 7.0, 51.8% dye removal is observed after 60 min of adsorption. As pH decreases, removal increases sharply within first 10 min of adsorption. Almost complete removal is observed after 40 min with initial pH of 3.0. The same is reduced to 28.3% with initial pH value of 11.0. Adsorption increases appreciably as pH of solution decreases because charge density on both adsorbate and adsorbent depends on pH of the solution.

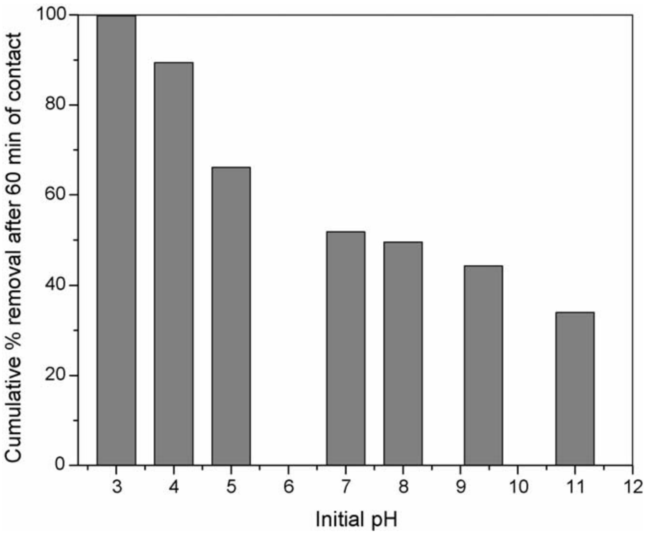


Fig. 1. Effect of pH on % removal of CR: initial CR concentration 100 mg/l, adsorbent dose 0.1 g and stirrer 200 rpm.

Under acidic pH, dye removal may be due to combined effect of (a) specific adsorption resulting from surface complexation reaction and (b) electrostatic attraction between the adsorbate and EMHS. (a) As indicated by Netpradit et al. [27], hydrolysis products of metal species in adsorbent readily adsorb anionic dye at the solution–particle interface than non-hydrolyzed metals ions due to surface complexation reaction. Different monomer and polymer hydroxides are formed depending on solution pH during hydrolysis reactions of metal (M = Al or Cr) species in sludge [34].

Bihydroxylated [$M(OH)_2{}^+$] or monohydroxylated [M $(OH)^{2+}$] species predominantly remains in solution along with other polymeric hydroxide species at lower pH. In the pH range 4–5 the hydroxo-complexes reorient to a bi-nuclear complex [$[M_2(H_2O)_8(OH)_2]^{4+}$] species having a high surface charge. They interact at in the solution as

$$M(OH)_2{}^+ + \text{dye–}SO_3\text{–Na} \leftrightharpoons [M(OH)_2\text{–}2(SO_3\text{–dye})]\,(\text{particle}) + Na^+ \tag{1}$$

$$M(OH)^{2+} + 2(\text{dye–}SO_3\text{–Na}) \leftrightharpoons [M(OH)\text{–}2(SO_3\text{–dye})\,(\text{particle})] + 2Na^+ \tag{2}$$

$$M(OH)_3{}^0 + m(\text{dye–}SO_3\text{–Na}) \leftrightharpoons [M(OH)_{3-m}\text{–}n(SO_3\text{–dye})]\,(\text{particle}) + mNa^+ + nOH^- \quad (m = 1\text{–}3) \tag{3}$$

$$[M_2(H_2O)_8(OH)_2]^{4+} + 4(\text{dye–}SO_3\text{–Na}) \leftrightharpoons [[M_2(H_2O)_8(OH)_2]\text{–}4(SO_3\text{–dye})]\,(\text{particle}) + 4Na^+ \tag{4}$$

(b) Congo Red is a sulfonated azo dye, anionic in nature. Highly positive hydroxide species have strong surface affinity towards oppositely charged CR. Due to London van der Waal's force of attraction removal is enhanced at lower pH values. At solution pH of 3, 10.4% higher removal is observed compared to initial pH of 4.0. Namasivayam and Sumithra [28] showed similar trend during adsorption of catechol on waste Fe(III)/Cr(III). Present observation slightly deviates from the results of Netpradit et al. [27] possibly due to inherent properties of different reactive dyes used.

At alkaline pH, monomeric anionic $M(OH)_4{}^-$ is the principal active component. In alkaline condition CR develops strong negatively charged surface as resonance occurs involving the free lone pair of electron on N of ($-NH_2$) group. This is shown in Fig. 2.

Due to electrostatic repulsion between adsorbate and adsorbent (both having high negative charge) lower removal is observed in alkaline pH. Still about 34% removal after 60 min of contact time at pH 11 occurs possibly due to exchange of anion of EMHS with CR (Eq. (5))

$$M(OH)_4{}^- + m(\text{dye–}SO_3\text{–Na}) \leftrightharpoons [M(OH)_{3-m}\text{–}m(SO_3\text{–dye})]\,(\text{particle}) + mNa^+ + (m+1)OH^- \tag{5}$$

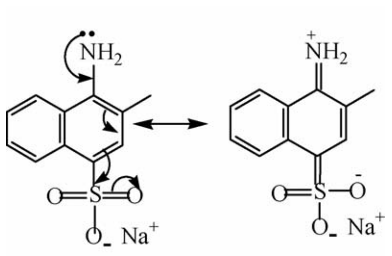


Fig. 2. Resonance structure of CR.

Acemioglu [35] reported similar trend. He reported that removal of CR by calcium-rich fly ash under alkaline pH decreases due to increase of negatively charged sites. The effect of pH on adsorption of CR can also be elucidated in term of pH_{zpc} of the adsorbent. The reported values of pH_{zpc} of $Al(OH)_3$ and $Cr(OH)_3$ are 8.35 and 7.7, respectively [36]. At pH below pH_{zpc} the net charge over adsorbent is positive. The removal of CR below pH_{zpc} is due to electrostatic attraction and/or anion exchange of adsorbent with CR.

Fig. 3 shows the change of pH during adsorption study. In case of initial pH value below or above 6.75 tend towards a final pH around 6.75. Mole ratio of M^{3+} and OH^- of an EMHS varies from 2.0 to 2.5 due to formation polymeric hydroxide species of M in the pH range 5.0–6.0 [30]. Under acidic pH, due to formation of primarily bihydroxylated and monohydroxylated species, this ratio drops below 2.0. Accumulation of OH^- is therefore reflected as pH elevation and due to its buffering nature pH remains close to the pH line 6.75. Similarly under alkaline pH, formation of tetra-hydroxylated species result in fall of pH due to consumption of hydroxyl ions from solution.

3.1.3. Effect of initial adsorbate concentration

Concentration of coloring agents is found to be different for different textile dyeing plant's effluent. Effect of initial CR concentration is therefore investigated for the present study. Fig. 4 shows the progress of cumulative % removal with time of contact

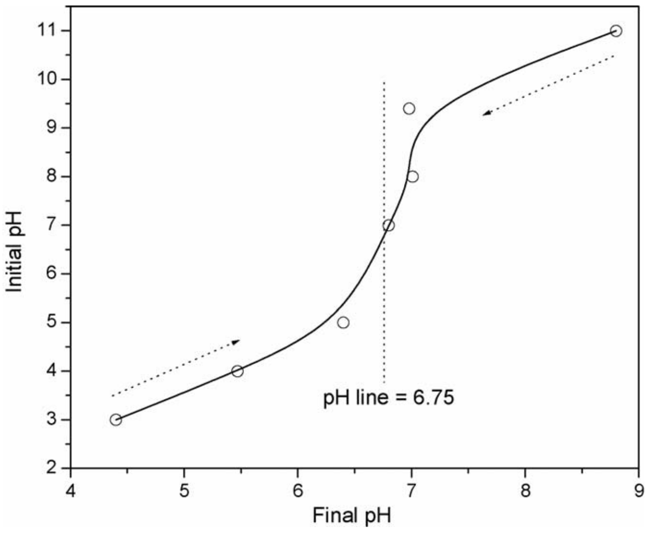


Fig. 3. Effect of initial pH on system pH after 60 min of adsorption.

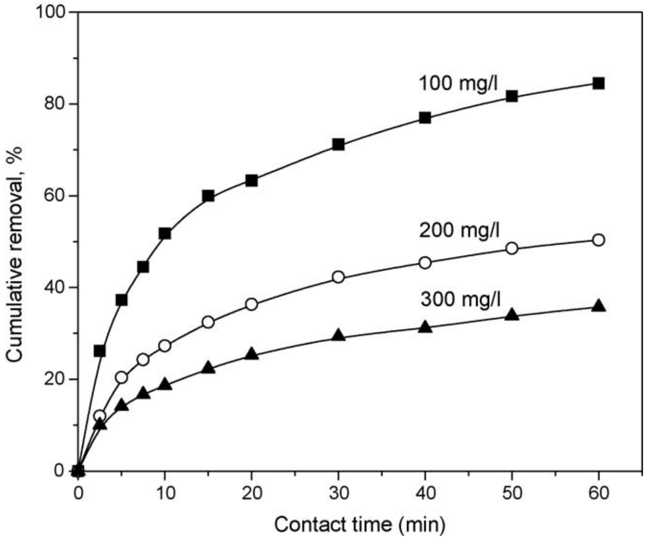


Fig. 4. Effect initial dye concentration on % cumulative adsorption: initial pH 7.0, adsorbent dose 0.2 g and stirrer 200 rpm.

at different initial CR concentration. Experiments were performed with 100, 200 and 300 mg/l initial CR. About 51.8% CR was adsorbed within 1st 10 min on EMHS with 100 mg/l CR. A similar trend is observed in case of 200 and 300 mg/l CR where 27.3 and 18.7% was removed in 10 min of contact time. Corresponding cumulative mass of CR removed were 64.75, 68.25 and 70.13 mg/g adsorbent. Higher removal at higher initial CR concentration is attributable to more effective contact with higher number density of CR molecules in solution [37]. After 60 min of contact removal increases to further 84.5, 50.4 and 35.8% as the process approaches toward the equilibrium.

3.1.4. Effect of adsorbent dose

Fig. 5 shows removal of CR on EMHS with contact time for different adsorbent doses of 0.05–0.4 g per 250 ml solution under identical operating conditions. At higher adsorbent dose, removal increases sharply within first few minutes of adsorption. For example, 22.1 and 65.5% removal is observed within initial 5.0 min of contact with 0.1 and 0.4 g of EMHS. This is attributed to the increase in available adsorption area with increase in adsorbent dose. At lower adsorbent dose, increase in removal is proportional to the increase in adsorbent dose. After 60 min of contact study 25.7% removal is noted with 0.05 g EMHS and the same is 51.8% with 0.1 g EMHS. At higher dose increase in removal of CR is less than proportional dose due to continuous depletion of CR molecules in aqueous phase.

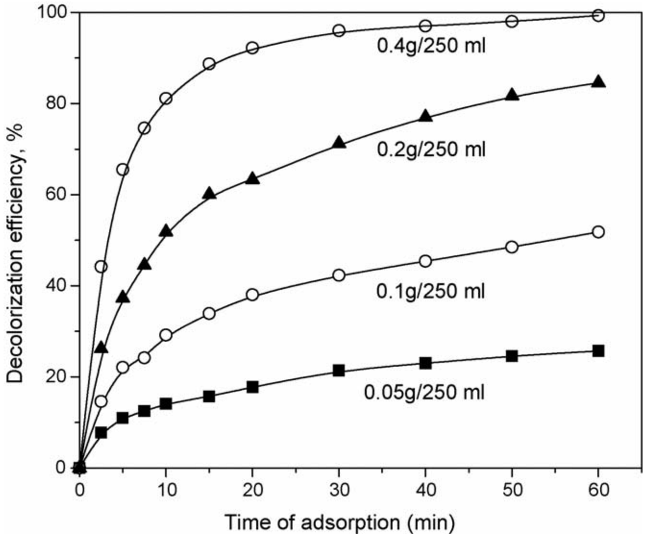


Fig. 5. Cumulative % adsorption at different doses of EMHS: initial CR concentration 100 mg/l, initial pH 7.0 and stirrer 200 rpm.

Diminution of color may be due to reduction of COD and/or formation of soluble organo-metallic complexes of reactive dyes. Complete removal of a dye is expected to reduce the COD most effectively. Reduction of COD of dye solution during adsorption study is shown in Fig. 6. For both the cases with 0.1 and 0.2 g adsorbent per 250 ml dye solution, % cumulative removal of COD and cumulative % diminution of color (measured spectrophotometertically) remains very close around the 45° line. This corroborates that color removal is proportional to reduction of COD in the present investigation and the process effectively removes CR from the liquid phase. It is therefore concluded that EMHS can be used effectively as an adsorbent for removal of anionic dye(s) from aqueous solution with high efficiency.

3.1.5. Adsorption isotherms

Langmuir and Freundlich isotherm are frequently used to describe the equilibrium behavior of an adsorption process. Eq. (6) shows the mathematical expression of Langmuir isotherm [38]

$$q_\mathrm{e} = \frac{k_1 q_\mathrm{m} C_\mathrm{e}}{1 + k_1 C_\mathrm{e}} \tag{6}$$

q_e is the equilibrium adsorption capacity (mg/g), C_e the liquid phase CR concentration at equilibrium (mg/l), k_1 the constant of the isotherm related to the energy of adsorption (affinity of adsorption) and q_m is the solid phase loading of adsorbate corre-

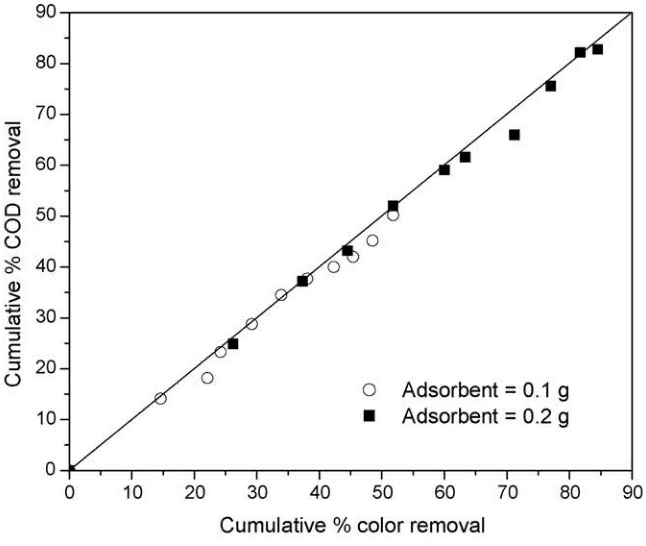


Fig. 6. COD reduction vs. color diminution.

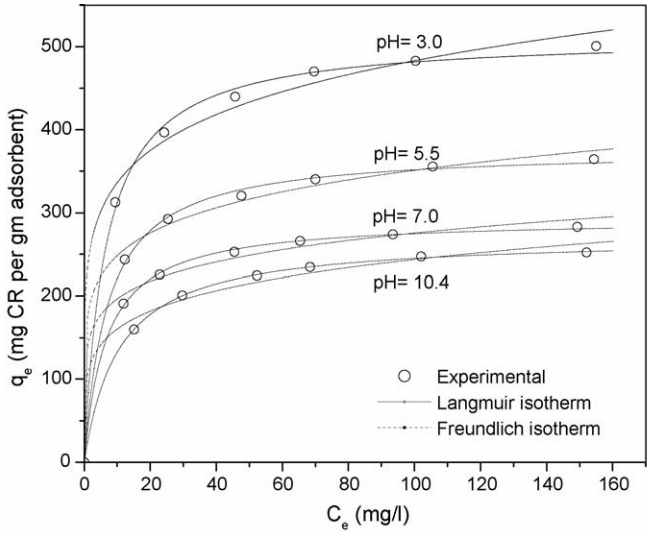


Fig. 7. Adsorption isotherm for different initial pH.

sponding to complete monolayer coverage of all available sites (maximum adsorption capacity). The expression of separation factor (R_L) in the non-dimensional form of Langmuir isotherm [38] is

$$R_L = \frac{1}{1+k_1C_0} \tag{7}$$

where C_0 is the initial CR concentration and R_L is the separation factor: $R_L > 1$ for unfavorable adsorption, $R_L = 1$ linear, and $0 < R_L < 1$ favorable adsorption.

Eq. (8) represents the Freundlich isotherm equation [38]:

$$q_e = k_2C_e^{1/n} \tag{8}$$

where k_2 and n are a measure of adsorption capacity and intensity of adsorption that have to be determined experimentally.

Constants of both isotherms were determined by least square fittings of experimental data. These fits are presented in Fig. 7. Best-fit constants for both Langmuir and Freundlich isotherm are summarized as isotherm equations in Table 4. The value of q_m (mg/g) is found to be increasing with decreasing the pH of solution. This indicates that EMHS removal is enhanced as discussed in Section 3.1.2 under acidic condition due to formation of various charged hydroxylated species.

The values of separation factor (R_L) based on Langmuir isotherm are found to vary in the narrow range of 0.018–0.039, indicate that adsorption of CR on EMHS is favorable.

Higher values of correlation coefficient (R^2) for Langmuir isotherm equation fitting is seen in Table 4 for all cases. This signifies that adsorption of CR on EMHS follows Langmuir isotherm and suggests that the dye adsorption is possibly due to monolayer coverage of dye molecule at the surface of EMHS. This observation is in agreement with the observations of Netpradit et al. [27]. They also reported better fit of Langmuir isotherm over Freundlich isotherm during removal of three anionic reactive dyes (RR1, RR120 and RR141) on waste metal hydroxide adsorbent. The value of maximum adsorption capacity (q_m) and intensity of adsorption (n) is compared to the values reported in literature for similar systems (Table 5). Comparative values of q_m clearly indicate that adsorption capacity of EMHS is much higher than the same reported in literature. Higher value of n (5.5–6.8) indicates favorable adsorption of CR on EMHS [27]. Adsorption capacity of adsorbents containing metal hydroxide of Al, Fe, Cr, etc. depend on its composition and metal hydroxide content. A major reason for higher adsorption capacity of our EMHS is its higher metal content compared to waste metal hydroxide sludge studied by other workers [28]. Lower adsorption capacity of other adsorbents not containing metal hydroxide is possibly due to inherent characteristics of different adsorbates or adsorbents.

3.2. Desorption

Desorption studies reveal the mechanism of adsorption. It also makes the process economically effective by simultaneous recovery of adsorbate and spent adsorbent. The % desorption at different pH is shown in Fig. 8. As pH of the solution increases % desorption increases as expected from adsorption study. Insignificant desorption of CR at pH of 3.0, again confirm that adsorption of dye is attributable to chemisorption. At neutral pH 7.0 about 10% desorption is observed. When pH of the solution is increased to 11, about 60% desorption takes place. This suggests that adsorption of CR on EMHS involves ion exchange between SO_3^- and OH^- as already discussed in Section 3.1.2.

3.3. Leaching of Cr^{3+} from EMHS

After completion of adsorption (Section 3.1.2) and desorption (Section 3.2) studies, the supernatant was analyzed for leached chromium concentration. This has been done to evaluate suitability of EMHS as adsorbent for removal of reactive anionic dye(s) from aqueous solution though the adsorbent contains toxic metal. Results are plotted in Fig. 9. For both the cases

Table 4
Langmuir and Freundlich isotherm equations

Initial pH	Final pH	Langmuir isotherm ($q_e = k_1q_mC_e/(1+k_1C_e)$)			Freundlich isotherm ($q_e = k_2C_e^{1/n}$)		
		k_1 with 95% confidence level limits	q_m with 95% confidence level limits	R^2	k_2 with 95% confidence level limits	n with 95% confidence level limits	R^2
3.0	4.41 ± 0.1	0.156 ± 0.025	512.7 ± 13.03	0.988	234.05 ± 36.8	6.35 ± 1.51	0.953
5.5	6.54 ± 0.1	0.142 ± 0.020	383.5 ± 8.25	0.989	175.77 ± 23.8	6.65 ± 1.42	0.959
7.0	6.80 ± 0.1	0.152 ± 0.013	292.9 ± 3.85	0.996	140.35 ± 21.1	6.82 ± 1.69	0.947
10.4	7.8 ± 0.1	0.096 ± 0.004	270.8 ± 2.25	0.999	105.65 ± 24.2	5.51 ± 1.63	0.927

Table 5
Maximum adsorption capacity (q_m) and intensity of adsorption (n) for different adsorbates and adsorbents

Adsorbate	Adsorbent	pH	q_m (mg/g)	n	Source
Congo Red	Fe(III)/Cr(III) hydroxide	–	44.0	1.93	[26]
Reactive Red 2			62.5	1.43	
Reactive Red 120	Metal hydroxide sludge	8.5	48.3	2.91	[27]
Reactive Red 141		56.2	3.36		
Catechol	Fe(III)/Cr(III) hydroxide	6.1	4.04	1.47	[28]
Congo Red	Biomass (*Azadirachta indica*)	6.7	0.072	6.11	[33]
Congo Red	Calcium rich fly ash	5.0	10.73	0.51	[35]
Congo Red	Coir pith	7.6	6.72	4.78	[37]
Congo Red	Fly ash	7.5	4.13	–	[39]
	Activated carbon		15.8		
Congo Red	Bagasse fly ash		11.9	3.47	
	Activated carbon (commercial grade)	7.0	0.64	4.27	[40]
	Activated carbon (laboratory grade)	1.88	2.93		
Congo Red	Biomass (*Aspergillus niger*)	6.0	8.19	–	[41]
Congo Red	Red mud	7.3	4.05	1.46	[42]
Congo Red	EMHS	7.0	293	6.82	Present work

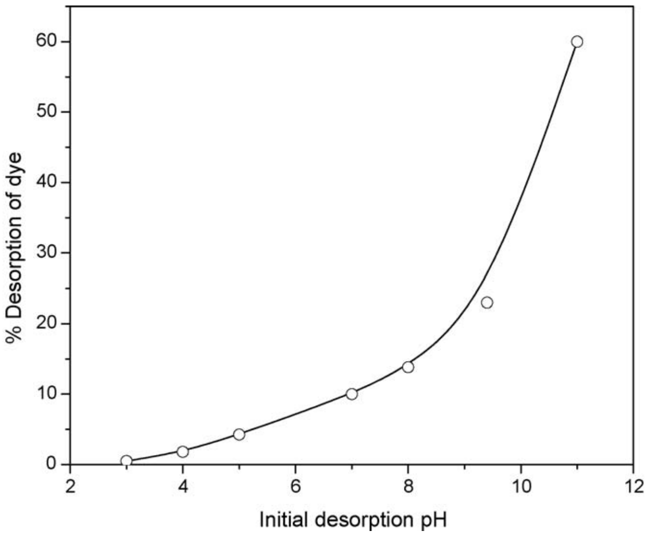


Fig. 8. Effect of pH on % desorption of CR.

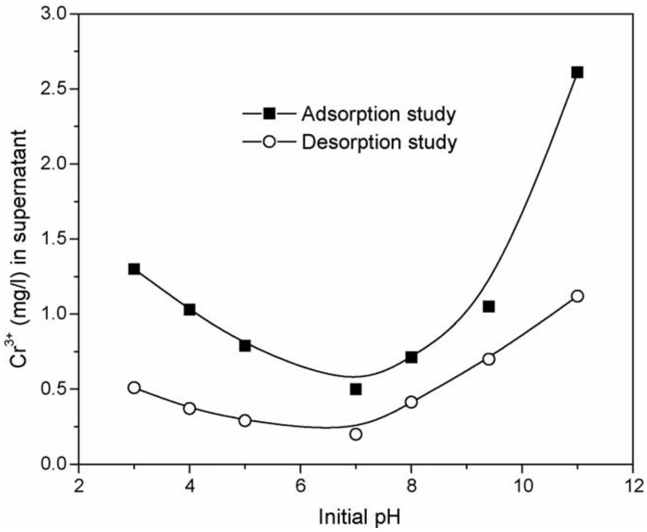


Fig. 9. Concentration of Cr^{3+} in supernatant at different pH during adsorption–desorption study.

leached Cr^{3+} concentration increases with increasing acidity and alkalinity. Minimum concentration is found to be close to neutral pH. At initial pH 7.0, about 0.2 and 0.08 mg Cr^{3+} leach out from solid EMHS to aqueous phase during adsorption and desorption studies. In the range of initial pH investigated, only beyond initial pH 10.35 the leached Cr^{3+} concentration crosses the maximum discharge concentration limit (2.0 mg/l) during adsorption study. It is therefore recommended that EMHS can be safely used for effective removal of anionic dye(s) from wastewater over a pH range of 3.0–10.

3.4. FT-IR and SEM analysis

FT-IR spectra of EMHS, CR and dye-loaded adsorbent is shown in Fig. 10. These were obtained from normalized samples in KBr pellets. The bands in 1070, 1180 and 1220 cm^{-1} are due to S=O stretching of sulfonate group (SO_3^-) of CR [43]. The band in 1070 and 1180 is reduced after adsorption and at

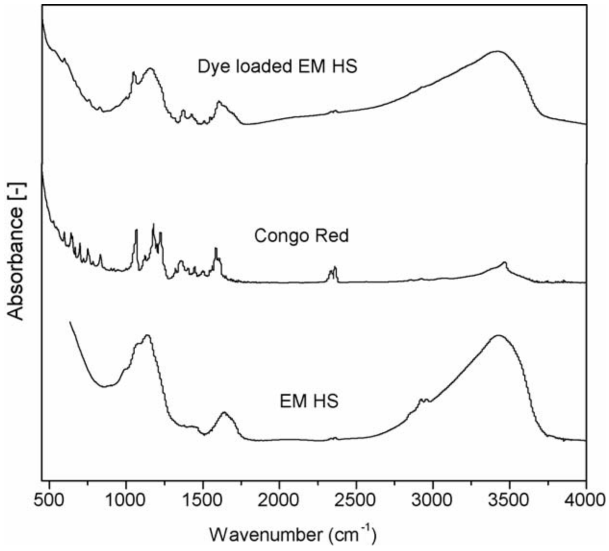
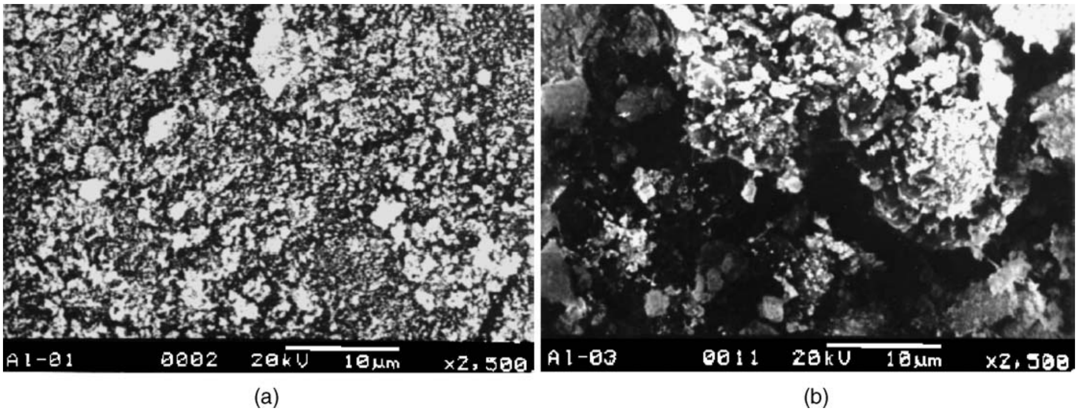


Fig. 10. FT-IR spectrum.



(a) (b)

Fig. 11. SEM morphology: (a) EMHS and (b) dye-loaded sludge.

the same time the peak in 1220 has disappeared. It also appears that the peak in 1220 is overlapped by EMHS. The broad peak in 3470 and 3410 in case of dye and EMHS is due to $-NH_2$ stretching and bonded hydroxyl groups, respectively [43]. The band due to –N=N– stretching in 1580 is slightly broadened after adsorption [43]. All this observations suggest that adsorption of CR on EMHS possibly involves chemical interaction of sulfonate group with EMHS. SEM micrograph of EMHS and dye-loaded adsorbent is presented in Fig. 11. Comparative morphology indicates larger size particles of dye-loaded sludge due to formation of organo-metallic complexes at the surface of adsorbent.

4. Conclusions

Anionic dye (Congo Red) from aqueous solution has been effectively removed by adsorption on EMHS waste containing Cr^{3+}. This adsorbent showed high adsorption capacity for CR and proved to be an effective adsorbent. Adsorption on EMHS is affected by stirrer speed, solution pH, adsorbate concentration and adsorbent dose.

- Acidic pH favors the adsorption of CR on EMHS. Under this condition adsorption of CR is the combined effect of surface complexation reaction, and electrostatic attraction.
- Close agreement of cumulative % COD reduction and cumulative % removal of color (measured spectrophotometrically) confirms effective removal of CR.
- The equilibrium data fits Langmuir isotherm equation better than the Freundlich isotherm expression. The maximum adsorption capacity (q_m) was found to be 513 mg/g at initial pH 3.0.
- In the pH range 3.0–10.0 leached out concentration of Cr^{3+} was found to be within its discharge limit (2 mg/l). This suggests that use of EMHS for CR adsorption shall not lead to secondary pollution.
- FT-IR spectrum analysis of dye-loaded sludge suggests that removal of CR on EMHS possibly involves chemical interaction of sulfonate group with EMHS.

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