Removal of total chromium from landfill leachate by electrocoagulation process using iron electrodes: effect of some major operational and chemical parameters

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The performance of electrocoagulation method for treatment of raw leachate collected from an uncontrolled active landfill site was carried out using iron electrodes in a batch reactor of 10.0-liter capacity. The leachate was slightly alkaline (pH 8.3) and contained various xenobiotic organics along with various heavy metals like chromium (Cr), lead (Pb), zinc (Zn), copper (Cu), cadmium (Cd) etc. The raw leachate collected was reddish brown in color having maximum total Cr concentration 10.54 mg L^{-1}. The effects of important parameters viz. initial pH, inter-electrode gap, charge density, current density and hydraulic retention time on total chromium removals were investigated. The minimum retention time was observed as 60 min to reach the leachate discharge standards (2.0 mg L^{-1} as per SWM Rules, 2016) of total chromium at pH 5.0 in the electrocoagulation process. The best removal efficiency was achieved at a current density of 2.07 mA cm^{-2}. Kinetic study reveals the reaction followed second order kinetics since the graph plotted between 1/(total chromium concentration) and time fitted well as a straight line with $R^2 = 0.951$. The outcomes of the current study establish that electrocoagulation using iron as a sacrificial electrode is an effective alternative to remediate total chromium from landfill leachate.

Keywords: Landfill leachate treatment, electrocoagulation, iron electrodes, chromium.

Introduction

High density of population in urban areas along with change in consumption patterns of human accelerates the rate of Municipal Solid Waste (MSW) generation day by day throughout the world. Landfilling is reckoned to be the economically feasible solution to the disposal of MSW. Presently, in many countries engineered landfilling method is used as the primary method for MSW disposal. The production of leachate is the principal difficulties in this common disposal practice[1]. Landfill leachate is defined as a liquid generated by the percolation of excess rainwater through the waste layers in a landfill and through the combination of physical, chemical, and microbial processes in the waste transfer pollutants from the waste material to the percolating water[2].The structure of leachate is very complex by nature and due to widely variable content generated within a landfill the pollutant load is also very high in leachate and the treatment of leachate is quite difficult to satisfy the discharge standards[3]. Large quantities of organic and inorganic matters which include ammoniacal nitrogen, chlorinated organic and inorganic salts are present in most of the leachate. Iron, manganese, zinc, chromium, lead, copper, mercury and cadmium are the heavy metals that commonly found in high concentration in leachate. For that reason, advanced technologies are used in various countries to treat the landfill leachate[4]. Toxicity of heavy metal is found to lower the energy levels and affect the functioning of the brain, lungs, kidney, liver, blood composition and other important organs of human beings. Long-term exposure to heavy metals can lead to gradually progressing physical, muscular, and neurological degenerative processes and in addition to that repeated long-term exposure of some metals and their compounds may even cause cancer. One of the highly toxic heavy metals present in landfill leachate is chromium (Cr), which is the seventh most abundant element on earth. Chromium occurs in several oxidation states in the environment ranging from Cr^{2+} to Cr^{6+}, with the most frequently occurring forms being trivalent Cr^{3+} and hexavalent Cr^{6+}. Chromium toxicity causes chlorosis and necrosis in plants. Cr^{6+} has been found to be much more toxic than Cr^{3+} as Cr^{6+} enters the cells more readily than does Cr^{3+} and is eventually reduced to Cr^{3+}. Due to its mu-
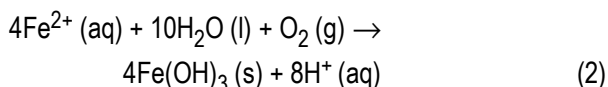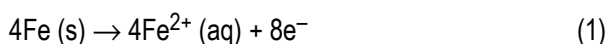
tagenic properties, Cr^{6+} is categorized as a group-1 human carcinogen by the International Agency for the Research on Cancer[5]. Consequently, landfill leachate treatment is considered as one of the most significant environmental issues. There are several methods like physico-chemical methods (viz. aeration, oxidation, coagulation-flocculation, membrane separation, adsorption etc.) and biological treatment methods to treat landfill leachate. The conventional methods are costly because of costs associated with energy, oxidants, chemicals and membranes and may become ineffective due to the variability in the quality and quantity of the generated leachate with time. Management of huge amount of sludge generated during treatment of leachate is another major drawback of conventional methods. Electrocoagulation (EC) method is relatively more cost-effective and highly efficient to tolerate the high variability of quantity and characteristics of liquid waste. As a result, EC method is being fruitfully used for the treatment of a variety of wastewaters like textile wastewater, electroplating wastewater, tannery wastewater, potato chips processing effluent, dairy wastewater, slaughterhouse wastewater, and laundry wastewater[6]. In recent times, treatment through EC process has been considered as a favorable method for treatment of leachate since it requires simple and easy to operate reactor and is capable of removal of colloidal materials present in leachate without the use of any chemicals and with a low sludge production rate at low capital and operating cost[7].

Electrocoagulation mechanism:

Electrocoagulation reactor is made up of an electrolytic cell with the standard anode and cathode arrangement. During this process the anode material undergoes oxidation and cathode will be subjected to reduction or reductive deposition of elemental metals. The chemistry of aqueous medium, especially conductivity is important for the mechanism of EC. The removal of ions by EC process can be explained by two mechanisms using iron electrodes (eqs. (1)–(8)). During electrocoagulation iron is oxidized into iron hydroxide, $Fe(OH)_n$, where n = 2 or 3.
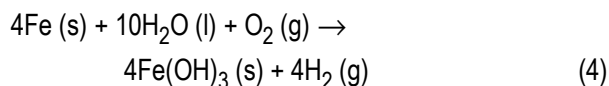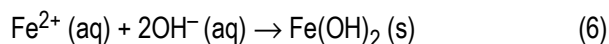
Mechanism 1:

Anode:

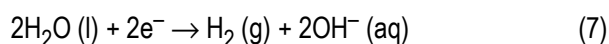$$4Fe\ (s) \rightarrow 4Fe^{2+}\ (aq) + 8e^- \tag{1}$$

$$4Fe^{2+}\ (aq) + 10H_2O\ (l) + O_2\ (g) \rightarrow$$
$$4Fe(OH)_3\ (s) + 8H^+\ (aq) \tag{2}$$

Cathode:

$$8H^+\ (aq) + 8e^- \rightarrow 4H_2\ (g) \tag{3}$$

Overall:

$$4Fe\ (s) + 10H_2O\ (l) + O_2\ (g) \rightarrow$$
$$4Fe(OH)_3\ (s) + 4H_2\ (g) \tag{4}$$

Mechanism 2:

Anode:

$$Fe\ (s) \rightarrow Fe^{2+}\ (aq) + 2e^- \tag{5}$$

$$Fe^{2+}\ (aq) + 2OH^-\ (aq) \rightarrow Fe(OH)_2\ (s) \tag{6}$$

Cathode:

$$2H_2O\ (l) + 2e^- \rightarrow H_2\ (g) + 2OH^-\ (aq) \tag{7}$$

Overall:

$$Fe\ (s) + 2H_2O\ (l) \rightarrow Fe(OH)_2\ (s) + H_2\ (g) \tag{8}$$
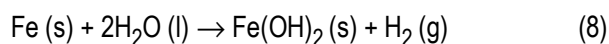
The $Fe(OH)_n$ (s) remains in the aqueous stream as a gelatinous suspension and can remove the pollutants from wastewater either by electrostatic attraction or by complexation followed by coagulation. Depending on the pH range electrogenerated ferric ions may form monomeric ions, ferric hydroxo complexes with hydroxide ions and polymeric species, namely, $Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5OH^{2+}$, $Fe(H_2O)_4(OH)_2^+$, $Fe_2(H_2O)_8(OH)_2^{4+}$, $Fe_2(H_2O)_6(OH)_4^{2+}$ and $Fe(OH)_4^{6-}$.
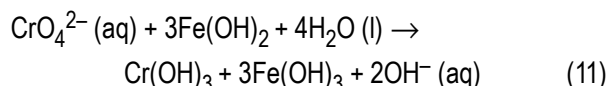
The chemical reduction of hexavalent chromium at pH range (0.9 < pH < 6.5) by iron(II) ions electrogenerated at the anode occurs according to the following reaction (eq. (9)):
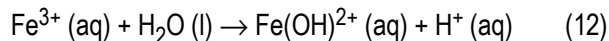
$$HCrO_4^-\ (aq) + 3Fe^{2+}\ (aq) + 7H^+\ (aq) \rightarrow$$
$$Cr^{3+}\ (aq) + 3Fe^{3+}\ (aq) + 4H_2O\ (l) \tag{9}$$
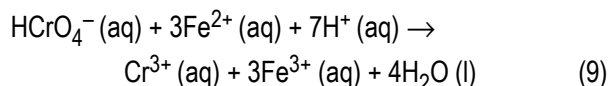
when the medium pH values are in the range of 6.5 then reaction can be written as (eq. (10)):

$$CrO_4^{2-}\ (aq) + 3Fe^{2+}\ (aq) + 4H_2O\ (l) \rightarrow$$
$$3Fe^{3+}\ (aq) + Cr^{3+}\ (aq) + 8OH^-\ (aq) \tag{10}$$
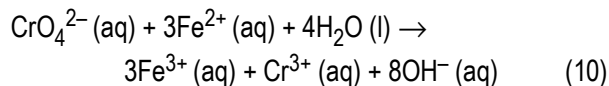
For pH values above 7.5, the reaction is (eq. (11)):

$$CrO_4^{2-}\ (aq) + 3Fe(OH)_2 + 4H_2O\ (l) \rightarrow$$
$$Cr(OH)_3 + 3Fe(OH)_3 + 2OH^-\ (aq) \tag{11}$$

However, the iron(III) ions may undergo hydrolysis depending on the pH of the solution. $Fe(OH)^{2+}$, $Fe(OH)_2^+$ and $Fe_2(OH)_2^{4+}$ species may be present under acidic conditions. The reactions involved are (eqs. (12)–(14)):

$$Fe^{3+}\ (aq) + H_2O\ (l) \rightarrow Fe(OH)^{2+}\ (aq) + H^+\ (aq) \tag{12}$$

$$Fe^{3+} (aq) + 2H_2O (l) \rightarrow Fe(OH)_2^+ (aq) + 2H^+ (aq) \quad (13)$$

$$2Fe^{3+} (aq) + 2H_2O (l) \rightarrow Fe_2(OH)_2^{4+} (aq) + H^+ (aq) \quad (14)$$
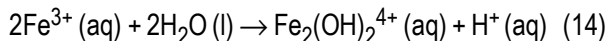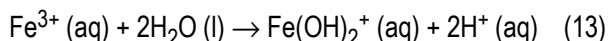
Under alkaline conditions, $Fe(OH)^{6-}$ and $Fe(OH)^{4-}$ ions may also be present.

Various parameters and conditions that control the performances of the electrocoagulation process include: electrode material, current density, electrolysis time, electrode gap, pH, conductivity, and electric power consumption[7,8]. Among the parameters, coagulant production is controlled by electrolysis time and density of current[7]. Initial pH is another important factor since it has different effects on the dissolution of iron electrodes and its speciation of hydroxides. Thus the aim of this study is to investigate the effects of parameters like initial pH, charge density and electrolysis time on removal of total chromium from raw leachate sample using iron electrode in batch mode on laboratory scale keeping inter-electrode gap and current density constant. The kinetics of the experiments were also been studied to calculate the rate of reaction.

Materials and methods

Study area:

During the experiment, leachate samples were collected from an uncontrolled landfill site located at Dhapa (22.82°N and 88.20°E), Kolkata of India in three different seasons viz. pre-monsoon, monsoon and post-monsoon. The landfill is non-engineered, unlined and open dump type and accepting non-segregated mixed wastes since 1987. There are no arrangements for leachate collection and treatment system. The location of Dhapa dumping site is presented in Fig. 1 and the aerial view of the study area is presented in Fig. 2.

Sample collection and characterization:

All the physico-chemical and biological parameters of raw leachate samples collected from active dumping ground were tested according to the Standard Methods for the Examination of Water and Wastewater[9] in triplicates. The parameters analyzed, and the methods and instruments used are presented in Table 1.

Reactor details and experimental procedure:

Electrocoagulation (EC) experiments were carried out in room temperature in an acrylic sheet batch reactor of 10 L size to examine its effectiveness in total chromium removal from raw leachate. 12 iron plates of effective length 16.8 cm and width 12.0 cm were vertically installed in series at a spacing of 2.0 cm for this purpose (Fig. 3). Effective area of plates was calculated as $12 \times 2 \times (12 \times 16.8) = 4838.4$ cm^2. The electrodes were connected with a digital power supply to regulate the applied electric current. During experiment, 7 L of raw leachate sample was filled in the reactor. Diffused air was provided in the reactor with the help of small nozzles fitted in a pipe, connected to the reactor. Aeration was provided to convert Fe^{2+} to Fe^{3+}, which has better floc forming
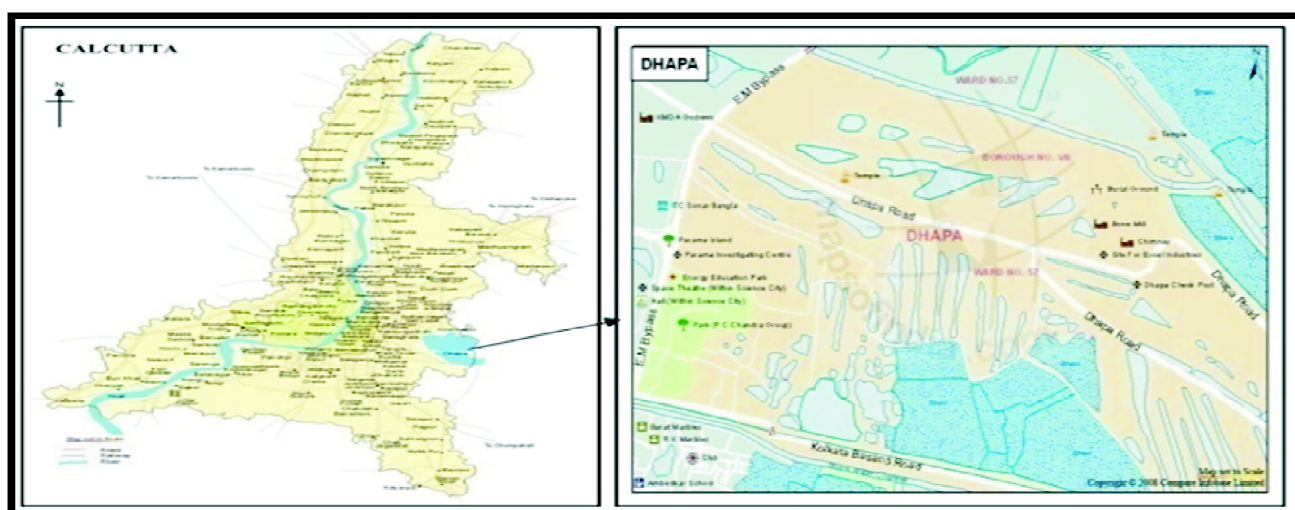

Fig. 1. Map of Kolkata (Left) indicating Map of Dhapa disposal site (Right).

Fig. 2. Aerial view of the study area (Source: Google earth).

Table 1. Details of parameters monitored, methods of analysis followed and instruments used

Parameter	Method adopted	Instrument used
pH	Electrometric method	Electronic pH meter
Total Dissolved Solid (TDS)	Gravimetric method	–
Chemical Oxygen Demand (COD)	Open reflux method	Digestion vessels
Biochemical Oxygen Demand (BOD$_5$)	Winkler's method	Air incubator
Chloride (Cl$^-$)	Argentometric method	–
Ammoniacal nitrogen (NH$_4^+$-N)	Ammonia-selective electrode method	Expandable ion analyzer, EA940 (Orion Research)
Arsenic (As), iron (Fe), cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb), zinc (Zn), copper (Cu), manganese (Mn), nickel (Ni), cobalt (Co)	Graphite furnace atomic absorption spectrometric method	Graphite furnace (HGA 900, Perkin-Elmer) Atomic absorption spectrophotometer (GAAS) (Analyst 400, Perkin-Elmer)

abilities and also to ensure uniform mixing of leachate. To study the effect of initial pH on total chromium removal the pH of raw leachate was altered by adding dilute H$_2$SO$_4$ and dilute NaOH. The experiment was conducted at constant current of 10.0 A for a predetermined fixed time 90 min. During the experiments, the supernatant were collected at each 10 min interval. The experiments were carried out thrice for three different pH (5.0, 7.0 and 9.0) values of leachates.

Removal efficiency of total Cr was calculated as:

Total chromium removal efficiency =

$$\frac{(C_0 - C_t)}{C_0} \times 100\%$$

where C_0 = initial total chromium concentration in mg L^{-1} and C_t = total chromium concentration at time t, in mg L^{-1}.

To study the rate of reaction the concentrations of total Cr obtained with different time were fitted with first and second order kinetic models.

Results and discussion

Characterization of leachate samples:

The physico-chemical and biological characteristics and level of trace metals in leachate samples were analyzed for all the three seasons. The average concentrations of each parameters along with their discharge standards in inland surface water stipulated in Solid Waste Management (SWM)
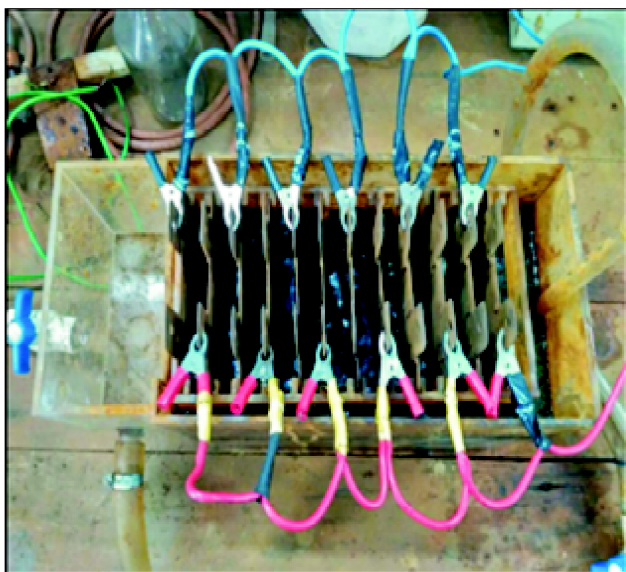
Fig. 3. Photograph of the lab-scale electrocoagulation unit.

Rules, 2016 by Ministry of Forest and Climate Change[10], India are presented in Fig. 4 and Fig. 5 respectively by 3-D column diagram. Initial pH of pre-monsoon, monsoon, and post-monsoon leachate were measured 8.4, 7.8 and 8.3 respectively where the leachate discharge standard in inland surface water is 5.5–9. The pH values of leachate samples indicate the alkaline characteristics of leachate and also indicate the methanogenic stage of landfill since during acidogenesis stage the pH is low because of the presence
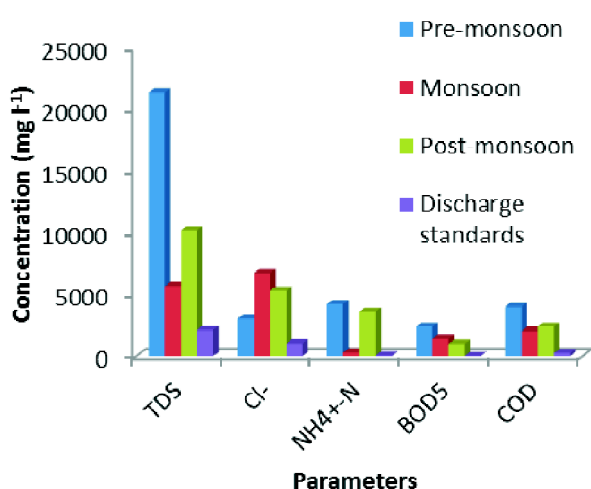

Fig. 4. 3-D Column diagram for physico-chemical and biological characteristics of leachate samples along with discharge standards.
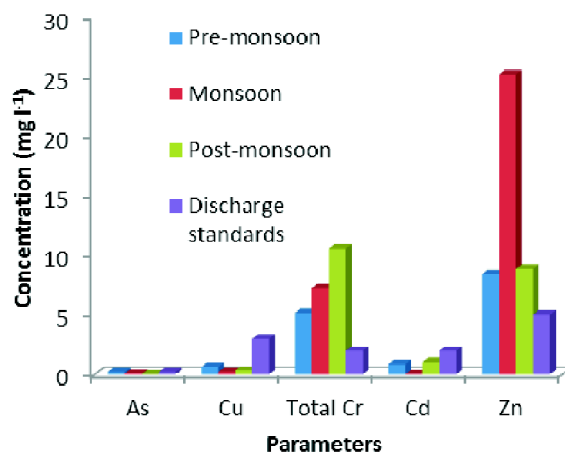

Fig. 5. 3-D Column diagram for level of trace metals in leachate samples along with discharge standards.

of volatile fatty acids. The high concentration of total dissolved solids (TDS) can be attributed to high levels of various anions and soluble salts present in landfill leachate. High concentration of chloride in leachate may be due to the animal origin like animal faeces since night soil also are disposed in Dhapa landfill site along with MSW. High range of ammoniacal nitrogen was obtained in leachate sample. This is quite common for methanogenic stage since ammonia is continuously produced due to aerobic and anaerobic decomposition of solid waste but is not consumed by microorganisms leading to high concentration in leachate. The high concentration of biochemical oxygen demand (BOD_5) in the collected leachate gives an idea about the extent of organic pollution in water environment. High concentrations of chemical oxygen demand (COD) indicate the presence of some recalcitrant organic constituents in the collected leachate samples. The concentrations of all the heavy metals analysed except total Cr and Zn were found within the permissible limit as stipulated in Solid Waste Management Rules, 2016 for discharging in inland surface water[10]. Initial total chromium concentrations of pre-monsoon, monsoon, post-monsoon leachate were 5.14, 7.25, 10.54 mg L^{-1} respectively, higher than the standard (2 mg L^{-1}) stipulated by Solid Waste Management (SWM) Rules, 2016 for discharge in inland surface water[10]. High concentrations of total Cr and Zn suggest that the wastes were mainly of municipal origin containing Cr and Zn comprising substances. The concentrations of most of the parameters viz. TDS, NH_4^+-N, BOD_5, COD, As,

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Cu, Cd in leachate decreased during the monsoon season. This may be due to the dilution of landfill leachate during monsoon by rainwater. The concentrations of Cl^- and Zn observed maximum in monsoon season which may be attributed to the presence of chloride and zinc bearing materials in solid waste dumping ground which leach with rain water and flow with leachate. The concentration of total Cr reached the maximum in post-monsoon with compare to pre-monsoon and monsoon seasons. The Cr in leachate may be attributed to the presence of Cr bearing materials along with tannery waste in dumping ground which leaches with rain water during monsoon. The Cr bearing leachate stored at the leachate collecting ditches evaporated by sunlight resulting high concentration during post monsoon season.

Electrocoagulation (EC) study – effect of pH and direct current:

The experiment was conducted using the leachate collected in post-monsoon season with maximum concentration of total chromium (10.54 mg L^{-1}) and pH of 8.3. Removal of total Cr at different pH values viz. pH 5, 7 and 9 with respect to time at 10 A direct current have been shown in Fig. 6. It appears from the afore-mentioned figure that, at a constant current total Cr removal efficiency increased with the decrease in pH till it reached the value of 5.0. Hence, pH of 5.0 can be treated as the optimum pH for the present set of experiment of electrocoagulation. 10 A current was chosen from experience of previous trial and error processes in the same experiment.
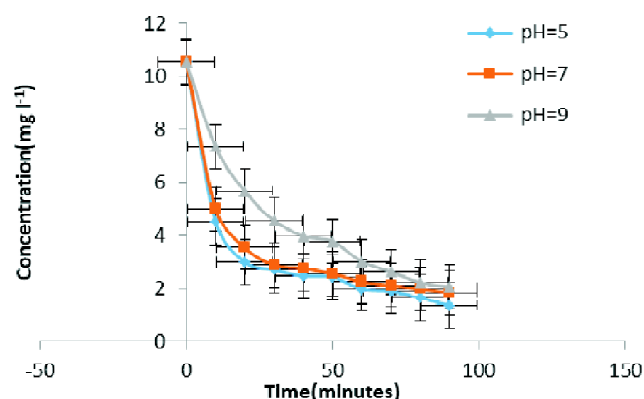
The discharge standard of total Cr (2 mg L^{-1}) was achieved by using iron as a sacrificial anode at a direct current of 10 A, pH of 5.0 and current density of 2.07 mA cm^{-2} (charge density of 7.44 C cm^{-2}) at 60 min time. At pH 7.0, the discharge standard of total Cr was achieved at current density of 2.07 mA cm^{-2} (charge density of 9.92 C cm^{-2}) at 70 min time and at pH 9.0, the discharge standard of total Cr was achieved at current density of 2.07 mA cm^{-2} (charge density of 11.16 C cm^{-2}) at 80 min time. Results clearly show that less time is required to reach the discharge standards of leachate for pH 5.0 compared to pH 7.0 and pH 9.0 for the same current density of 2.07 mA cm^{-2} reported[11] substantial decrease in initial pH of the leachate samples increased the rate of reaction. The removal efficiencies of COD, colour and turbidity were maximum at pH 5.8, when iron plates were used as sacrificial anodes[11]. The maximum applied current density yielded better results when electrocoagulation pretreatment was performed at pH 6.0[12]. Best performance in terms of Cr removal from simulated wastewater by using electrocoagulation was obtained at a pH 5.0[12]. Comparisons of the total Cr removal efficiencies with respect to time at different pH are shown in Fig. 7.

The maximum removal of total Cr was obtained at a direct current of 10 A, pH of 5.0 and current density of 2.07 mA cm^{-2} as presented in Fig. 7. In this experiment 81.21% of total Cr removal i.e. discharge standard was achieved after 60 min of reaction period.
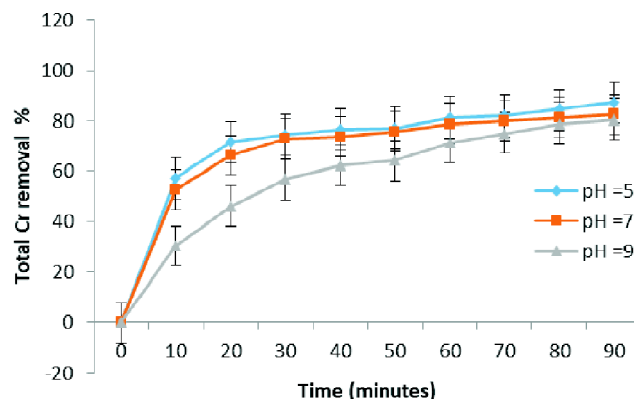

Fig. 6. Comparison of the total Cr concentration (mg L^{-1}) with respect to time at different pH at 10 A current.

Fig. 7. Comparison of the total Cr removal (%) with respect to time at different pH at 10 A.

Estimation of the rate of reaction:

The optimum conditions that had led to the maximum % of total chromium removal with initial concentration 10.54 mg L^{-1} were initial pH = 5.0, inter electrode gap = 2.0 cm, current density = 2.07 mA cm^{-2} and charge density = 7.44 C cm^{-2}. These conditions were used to determine the rate of reaction by fitting the data with first and second order kinetic models.

The plot of total Cr concentration with time for first order kinetic model, with a standard form of equation of $C_t = C_0e^{-kt}$, is presented in Fig. 8 where C_t is concentration at time t and C_0 is initial concentration (mg L^{-1}) of Cr in leachate sample.
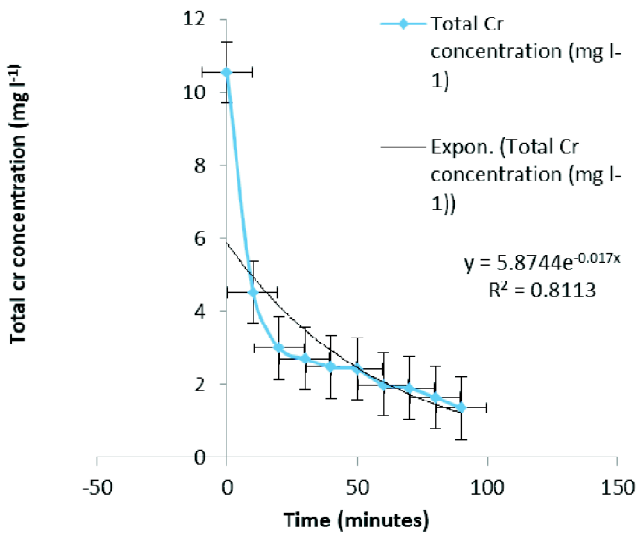

Fig. 8. Total Cr concentration (mg L^{-1}) vs time graph at optimum conditions.

The equation obtained is $y = 5.874e^{-0.01x}$, with $R^2 = 0.811$ and a rate constant of 0.01 s^{-1}.

1/(Total Cr concentration) with respect to time was plotted and presented in Fig. 9.

From Fig. 9, it can be observed that the graph fits a straight line with $R^2 = 0.951$, hence can be concluded that the kinetics of Cr removal closely follow a second order equation with a reaction rate constant of 0.006 L mg^{-1} s^{-1}.

Second order reaction rate signifies that reaction depends on concentration of Cr in leachate and it followed chemisorption.
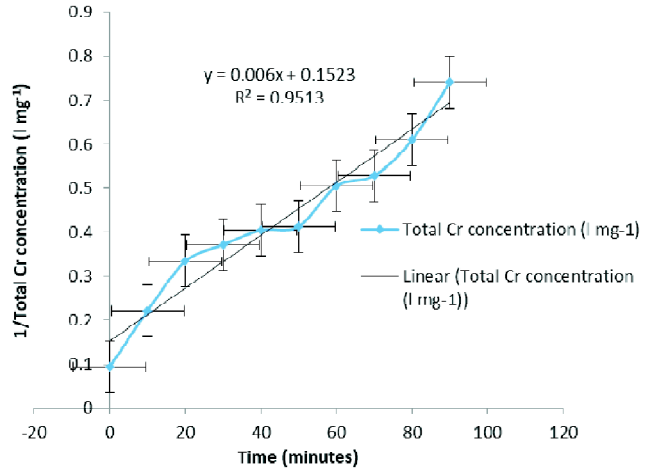

Fig. 9. 1/Total Cr concentration (L mg^{-1}) vs time graph at optimum conditions.

Energy consumption and loss of mass of electrodes:

Costs of the experiment during electrocoagulation depend on the expenditure of energy consumption and loss of mass of electrodes. The mass loss of iron electrode mFe is calculated by the Faraday's law (eq. (15)):

$$mFe = \frac{I.t.M}{z.F.V} \qquad (15)$$

where, I = current intensity (A), t = time (s), M = molecular weight of iron (g mol^{-1}), z = number of electrons transferred in the reaction Fe $\rightarrow$ Fe^{2+} + 2e$^-$.

F = Faraday's constant (96500 C mol^{-1})

V = Leachate volume

Under the given operating conditions the loss of mass of sacrificial anode of the treated leachate is 1.49 g Fe L^{-1}

Again, the electrical energy consumption E is calculated from the eq. (16):

$$E = \frac{U.I.t}{V} \qquad (16)$$

where, U = applied voltage (volts)

I = applied current (A)

t = required time (h) for EC

V = volume (L) of leachate

Here the energy consumption obtained is 4.48 kwh L^{-1} for raw leachate.

Conclusions

The important conclusions that could be drawn from the experiment can be summarized as follows:

(i) The concentrations of most of the parameters viz. TDS, Cl^-, NH_4^+-N, BOD_5, COD, total Cr and Zn in collected leachate samples were higher than the discharge standard in inland surface water stipulated by Solid Waste Management (SWM) Rules, 2016 by MoEFCC, India for leachate.

(ii) At constant current 10 A, the leachate discharge standard in inland surface water for total Cr was achieved at 60 min reaction time at initial pH 5 of leachate sample. Total chromium removal efficiency increased with the decrease in pH.

(iii) In this experiment, 81.21% total Cr removal was obtained at pH 5.0 with an initial total chromium concentration of 10.54 mg L^{-1} after 60 min time.

(iv) Total chromium removal was found to be satisfactory in electrocoagulation process in batch mode at 10 A initial current, pH 5.0, with iron electrodes connected in series. The optimum plate distance was observed as 2.0 cm.

(v) The loss of mass of sacrificial anode of the treated leachate was 1.49 g Fe L^{-1}. The energy consumption was 4.48 kwh L^{-1}.

(vi) The removal kinetics follow a second order equation (straight line with $R^2 = 0.951$) with a reaction rate constant of 0.006 L mg^{-1} s^{-1}.

(vii) Considering the outcomes of the present study, electrocoagulation process can be easily recommended as one of the most preferred technology for remediation of total chromium from raw landfill leachate.

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