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## Removal of hexavalent Chromium-Industry treated water and Wastewater: A review

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## ABSTRACT

Heavy metals present in industrial effluents enter the biological cycle through aquatic organisms. Heavy metals undergo bioconcentration and prove to be toxic even in trace quantities. Chromium is necessary for carbohydrate metabolism, but in higher concentrations, it tends to be harmful. Hexavalent chromium Cr (VI) ions are prevalent, and its toxicity causes environmental and public health concerns. Chromium (IV) based industrial effluents have become a worldwide menace. This collection of toxic metals ions from effluent streams affects both humans and the environment. The non-depleting heavy metal ions cause severe damage to the environment. Environmental pollution affects both human life and eco-system. Water pollution from municipal sources and industries are matter of concern. The solution to the fast-depleting natural water bodies and aquifers is to reuse treated effluent. Several remediation technologies are available, for reclaiming effluent after treatment for heavy metals like Cd, Cr, Cu, Hg, Ni, Pb, and Zn. This paper attempts to assimilate concise information on removing hexavalent chromium through laboratory experiments to implement cost-effective, plausible industrial treatments practically. The importance of efficient industrial effluent treatment lies in the recovery of heavy metals and usage of the treated effluent. A list of techniques is thought of for the treatment of heavy metals removal that has minimal impact on the environment in liquid / solid phases, cost of treatment, and scaling up to industrial levels. Adsorption is one of the prominent techniques used for heavy metals treatment. The adsorption kinetics and isotherms help understand the reduction of Cr (VI) from effluent streams. The wastewater treatment techniques currently employed treat hexavalent chromium-containing effluent streams with low-cost industrial byproducts. Emphasis is on novel techniques of wastewater treatment electrochemical techniques for Cr (VI), contributing to various environmental problems based on their toxicity.

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## 1. Introduction

Industrial effluents containing heavy metals pollute the aquatic environment. Chromium enters the human body through digestive organs, respiratory systems, and sensory organs. Living organisms cause disorders and diseases ingest metal ions from aqueous media. Industrial effluent is essential and challenging for both sci-

entific and economic reasons [1,2]. The toxicity of Cr (VI) effects include bleeding from the nose, infection of the respiratory system, rashes of the skin, skin irritation, and lung carcinoma [3,4]. The industries likely to contribute to heavy metals discharge are leather industries, tanning industries, and the textile industry.

## 1.1. Industrial effluents as chromium contaminating sources

Cr (VI) exists in aqueous form as a tetrahedral chromate ion ( $\text{CrO}_4^{2-}$ ). 35% of chromium used is discharged into effluents as hexavalent Cr (VI) or trivalent chromium. Cr (VI) brings in an

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oxidizing effect additionally provides free radicals to aid depletion of Cr (VI) to trivalent chromium Cr (III) [16,17]. Cr (VI) is 100 folds more virulent than Cr (III). It is hydrophilic nature, affinity to water, mobility, and readily undergoes reduction.

Cr (VI) enters cellular membranes through membrane transport proteins and has a relative speed of 500 to 1000 concerning Cr (III) [5,6]. Cr (VI) undergoes intracellular enzymatic reduction to produce reactive oxygen intermediates species (ROS) like Cr (V), Cr (IV), and Cr (III) [7,8]. Cr (VI) affects green plant life [18–21] and enters the human food chain. Chromium causes skin blisters, renal impairment, pustules, perceptual chromosomal aberration, neural cell injury, liver dysfunction, impaired cognition, hemolysis, improved generation of hydroxyl radicals, reduction of antioxidant enzymes and motor activity, and chlorosis.

The International Agency for Research on Cancer (IARC) identifies Cr (VI) as the most potent carcinogen. Cr (VI) causes irreparable deterioration to lipids, cellular proteins, and human physiological well-being [9]. Cr (IV) traces remain in effluents from dyeing units, electroplating, paints, petroleum, and tannery [1]. Cr (VI) is present in textile effluent containing synthetic dyes [10–12]. Industries other than those mentioned above and play a role in Cr (VI) pollution is listed in Fig. 1 [13,14]. Among the trivalent and hexavalent chromium plating baths used in industry, Cr (VI) is more prevalent. Chromium electroplating provides corrosive resistance, ease of cleaning, and surface hardness [15]. The World Health Organization has set a limit for Cr (VI) as 0.05 mg/L, whereas Cr (III) limit is below 2 mg/L (Fig. 2).

### 1.2. Tables techniques for wastewater treatment

Many of the industries are funding research and actively practicing chemical recovery from effluents. Industries are striving hard to decrease the effluent discharges to zero and minimize the cost of water and chemicals lost along with the wastewater stream [22]. Even though several treatment techniques are pub-

lished, an environmental engineer must carefully look at each technique's pro and cons and choose a suitable or combination of techniques. Chromium removal is accomplished by membrane separation, ion exchange, electrodialysis, electrocoagulation, chemical precipitation, and adsorption (Fathima et al. 2005).

Chemical precipitation, coagulation, Ion exchange, reverse osmosis, microfiltration, ultrafiltration, nanofiltration, membrane filtration, floatation adsorption, and advanced electrochemical process, electrodialysis, electro deionization, electrocoagulation are main methods employed for sequestration of heavy metals. The advantages and disadvantages of treatment techniques employed are listed in Table 2. Hence the effective effluent treatment for heavy metals employs a combination of techniques [22–26].

### 1.3. Chemical precipitation

Chemical precipitation is extensively in the industry due to its ease in operations and relatively low operating cost. During precipitation, the precipitating agents precipitate heavy metal ions as insoluble precipitates easily separated by filtration or sedimentation. The treated water can be reused. Usually, the chemical method involves sulfide and sodium hydroxide-based precipitation [34] (Table 3).

### 1.4. Hydroxide precipitation

For removing a heavy metal, the most desired method is Hydroxide precipitation due to its ease of usage and its low cost. As the pH changes, metal hydroxides precipitation increases, which is insoluble in the basic medium [35]. Different types of hydroxides precipitate using precipitants like sodium hydroxide, calcium hydroxide, and lime. Repeated used solutions are lime and limestone because of their easy availability and low cost.

Ramakrishnaiah and Prathima [36] tried chemical precipitation for the removal of Cr (VI) from synthetic and industrial effluents.

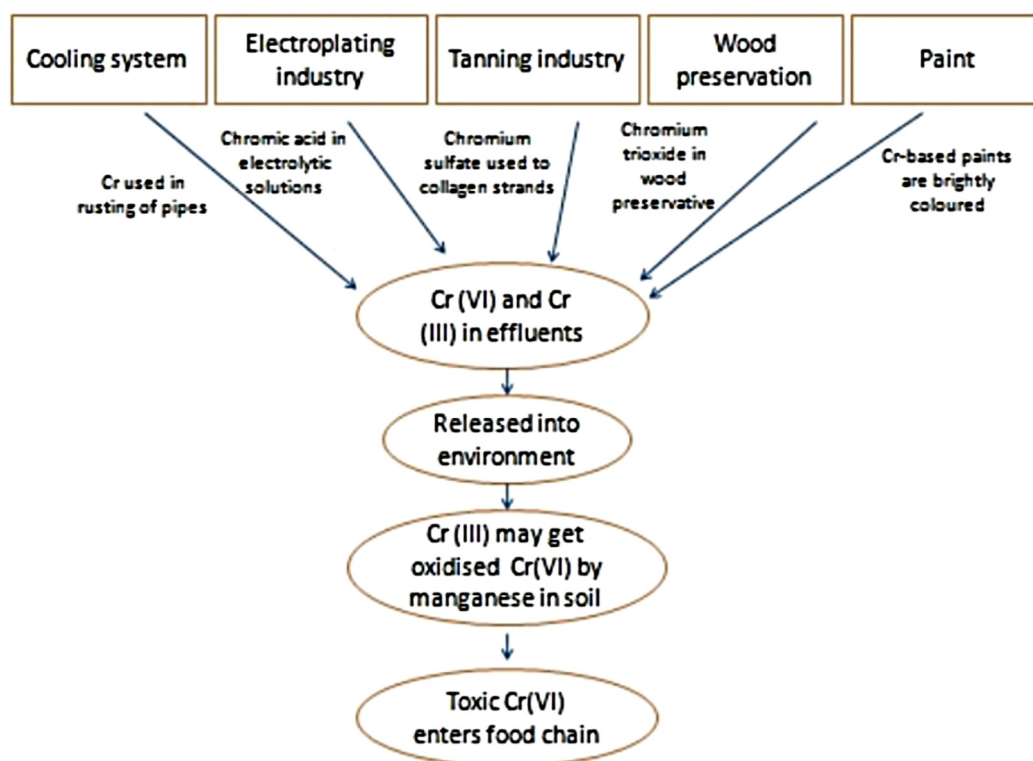


Fig. 1. Industrial effluents contributing to Cr (VI) pollution.

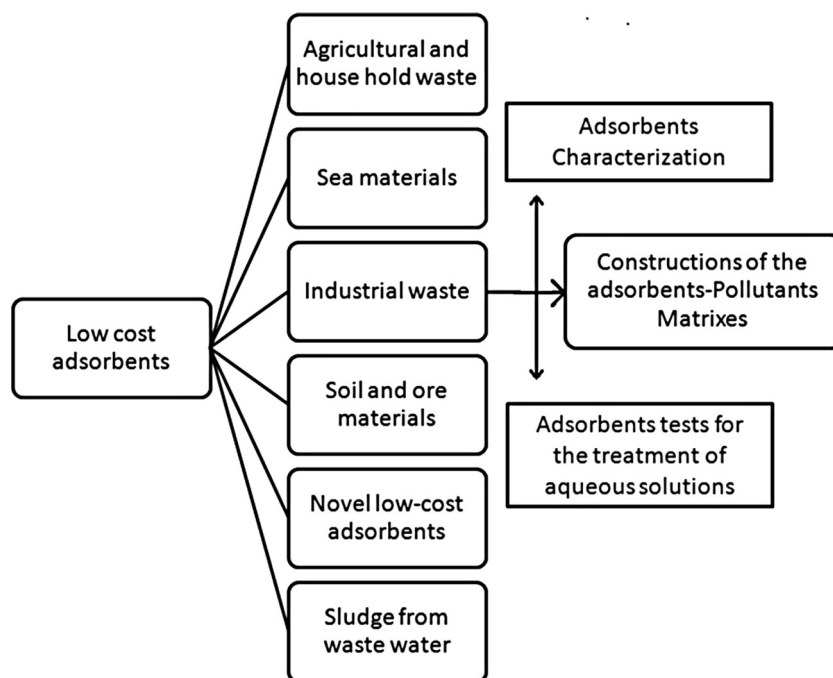


Fig. 2. Adsorbents for Cr (VI) treatment.

Table 1

Comparison of effluent treatment techniques for the heavy metal ion removal [27].

Sl. No.	Methods	Advantage	Disadvantage	Reference
1	Adsorption	Ease of operation, cost-effective	Desorption	[29]
2	Biological treatment	A promising method for the removal of heavy metals	Highly selective and unpredictable behavior	[33]
3	Coagulation	Cost-effective	High chemical cost and problems of sludge disposal	[28]
4	Electrochemical treatment	Minimal chemical usage	High fixed cost and recurring expenses on electricity	[28]
5	Electrodialysis	Segregation of metals	Fouling and frequent clogging	[30]
6	Ion exchange	Transformed components	Reduction of few metal ions, High operating cost.	[31]
7	Membrane filtration	Compact	Expensive, fouling of membranes	[28]
8	Photocatalysis	Can be employed for removal of the metal ions and other organic pollutants	Slow process	[32]

Table 2

Cr (VI) uptake capacities of adsorbents from sea origin [70].

Material	Adsorbate dosage (g/l)	Initial pollutant concentration range (ppm)	Contact time (Hour)	Temperature <sup>o</sup> C	pH	The amount adsorbed (mg/g)	References
Chitosan	13	Desorption	–	24.85	3	7.94	[75]
Oedogonium-hatell (algae)	0.1–1.0	Highly selective and unpredictable behavior	3	44.8	1.0–4.0	31.0	[74]
Peat moss	1	High chemical cost and problems of sludge disposal	2	–	–	29.0	[73]
Pumice	6	High fixed cost and recurring expenses on electricity	6	–	1	87.72	[71]
Pumice modified with MgCl <sub>2</sub>	6	Fouling and frequent clogging	6	–	1	105.26	[71]
ZVI mod. Pumice	1.1	Slow process	1	25	3	107.00	[72]

Laboratory studies for sample sizes range from 100 to 400 mg/L with calcium hydroxide, sodium hydroxide, and FeCl<sub>3</sub> as precipitants. 99.7% removal efficiency of Cr (VI) was observed with a sludge generation of about 7 ml/L. The authors conclude the suitability of calcium hydroxide and sodium hydroxide as suitable precipitant for chromium removal.

### 1.5. Sulfide precipitation

Sulfide precipitation is a precipitation method used for treating effluent with heavy metal ions. Sulfide precipitation solubility of sulfide precipitate is lower than that of the hydroxide precipitate. Sulfide precipitants are in the form of solid or gaseous sulfide

**Table 3**

Uptake capacities of industrial solid wastes for the reduction of Cr [70].

Adsorbents	Contaminants to be removed	Adsorbent dosage g/l	Initial contaminant concentration range mg/l	Contact time (minutes)	Temperature <sup>o</sup> C	pH	Amount adsorbed (q <sub>e</sub> ) mg//g	References
Blast Furnace sludge	Cr (III)	50	1600	300	20	–	9.55–16.05	[76]
Iron mixed leather industry waste	Cr (VI)	5	400	180	–	4	51	[77]
Red mud	Cr (VI)	10	9.60 x10 <sup>-4</sup> –9.60 x10 <sup>-3</sup>	1440	30	2	35.66	[78]
Solid waste from the tannery	Cr (VI)	–	40 to 60	1440	25	1	26.4	[79]

sources (H<sub>2</sub>S) [37,38]. Few authors have also reported that the blended cultures of bacteria for removing metals from bioleaching solution by the sulfide precipitation method. This process occurs in two stages: the sulfur-reducing bacteria generation of hydrogen Sulfide in the first stage and precipitation of heavy metals in the second stage. The authors state the advantages of chemical precipitation using hydrogen sulfide and fast metal recovery [39].

### 1.6. Coagulation/flocculation

Coagulation and flocculation techniques are used to remove suspended solids from the effluents. The separation efficiency of suspended particles depends on particle size, shape, and density. Suspended solids with similar surface charge repel each other and remain suspended in water. Coagulation and flocculation enhance particle collision, neutralize surface charges, and grow floc by sedimentation. Coagulants neutralize the negative surface charges present on non-settleable solids and create micro flocs of small suspended particles.

Agitation disperses coagulant and promotes particle collisions and adequate coagulation. Contact time in the rapid-mix chamber is typically 1 to 3 min. Flocculation increases the particle size from micro flocs produce larger flocs called pin flocs. Flocculation contact times range from 15 or 20 min. The mixing velocity is gradually decreased to prevent flocs from being torn apart. Coagulation techniques precipitate low soluble compounds like hydroxides, sulfides, and carbonates [40]. A colloid is a suspension of atoms or molecules whose density is equal to water density. These particles are unable to settle down because of low density [41]. The coagulation treatment method increases the density and removes these colloidal particles. Coagulation efficiency depends on the type of coagulant, coagulant dosage, pH, temperature, alkalinity, and mixing conditions. In this method, chemical reagents or inorganic flocculants like Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, and FeCl<sub>3</sub> [42] and derivatives of these materials such as poly aluminum chloride and poly ferric chloride are flocculants used in the wastewater treatment process.

Ferric ammonium sulfate (FAS) produces large amount of sludge which precipitates during sedimentation stage of the coagulation process. The coagulation process is known to treat cadmium, chromium, nickel, and zinc [43]. The sludge may be recovered, recycled, and used again [44]. Coagulation/flocculation is efficient for eliminating heavy metals from wastewater. Coagulation produces secondary solid contaminant in the form of flocs and sludge. The added chemical solvents are low reusable that is harmful to both the human and the environment.

### 1.7. Ion-exchange

Ion Exchange resins are ketonic granular particles with molecular structure promoting the exchange of acidic or basic radicals. The positive or negative ions present on these radicals surface is replaced by ions of the same signs present in the solution in contact with them. Sludge production is relatively slow in the ion exchange process [45]. Ion exchange system, have cation and anion

exchange resins. Anionic resins are suitable for the low concentration effluents. Kononova et al. used ion exchange for the treatment of Cr (VI) and Mn (II) [46]. Regeneration of ion exchange resin with chemical reagents, large backwashing water generated, and high operational cost are disadvantages of the ion exchange process, limiting the use of ion exchange for industrial effluent treatments [45].

### 1.8. Reverse osmosis

Reverse osmosis (RO) uses a selectively permeable or semi-permeable membrane of 0.1 to 1.0 nm thickness and selectively removes dissolved impurities based on the principle of charge exclusion and size exclusion. RO is widely used in desalination plants and permits passage of only water molecules [47]. RO applications are on the rise in wastewater treatment for the removal of heavy metals. Petrini et al. studied effluent treatment of the metal finishing industry combined with ultrafiltration to remove heavy metals ions and suspended solids from industrial effluents [48].

### 1.9. Microfiltration

The microfiltration (MF) is a pretreatment for industrial effluents and aids in removing suspended solids in size range from 100 to 1000 nm. The microfiltration process advantages are the high wet strength of the membrane and large filtrate handling capacities. Clogging and blinding in the microfiltration membrane is a primary matter of concern. MF can be operated either in inert-end mode or in cross-flow mode. Molgora et al. used a combination of coagulation and microfiltration techniques for arsenic removal with a removal efficiency of 97% [49].

### 1.10. Ultrafiltration

Ultrafiltration treats effluents are suitable for hydrophobic metal ions in a size range of 10–100 nm from aqueous solutions based on electrostatic interactions. Ultrafiltration is a clarification technique and deep bed filtration. The film pore size is greater than the size of metal ions. An ultrafiltration membrane permits passage of the metal ions. It hence should be used with caution and as a combination treatment with other techniques. Ultrafiltration and polymeric agents are classified as enhanced micellar ultrafiltration and polymer enhanced ultrafiltration [50]. Landaburu-Aguirre et al. have used enhanced micellar ultrafiltration to treat heavy metals from phosphorus-rich effluent of a fertilizer manufacturing unit [51].

### 1.11. Nanofiltration

Membrane separation techniques for effluent treatment are becoming popular due to strict implementation of effluent discharge standards. Nanofiltration (NF) is a widely used membrane process for water, effluent treatment, and desalination. NF has changed RO membranes in many applications because of its higher flux and lower energy consumption rates [52–54].

Nano-filtration (NF) is the intermediate process between reverse osmosis and ultrafiltration, suitable for the elimination of metal ions such as nickel, chromium, copper, and arsenic from industrial effluent. The influence of the feed solution concentration, feed solution pH, and pressure applied, on the NF membrane ability to remove ions are well established. [55–57].

### 1.12. Membrane filtration

The membrane filtration process uses a pressure gradient as a driving force in wastewater treatment. Membrane filtration treats effluents with heavy metal and disinfects the sample [58]. The separation depends on particle size, pore size, solution concentration, pH, and pressure gradient [59]. Membranes are made from porous ceramic and polymers. The separation occurs inside the pores due to the high intermolecular forces between the membrane and the heavy metal ion and not necessarily the size of the particles [60].

Polymeric membranes are versatile due to its hydrophobic nature and resistance to chemicals. Ceramic materials have relatively weak wet strength and expensive. Membranes of polypropylene, polyvinylidene fluoride, polyethylene are commercially available and used for industrial effluent treatment [61]. The membrane separators are easy to operate, require less space requirement but need frequent cleaning due to their hydrophobic nature [62].

### 1.13. Froath flotation

The Froath flotation is a solid–liquid partition technique. The frothing agents are added to the wastewater, subjected to intense agitation and aeration. The air bubbles concentrate the hydrophobic particles. It has excellent potential for wastewater management because of low sludge formation and high partition efficiency. Flotation is suitable for a mixture of hydrophilic and hydrophobic compounds [63]. Parameters affecting the flotation process are air bubble size and bubble formation frequency. The efficiency and selectivity of flotation can be enhanced by using flotation reagents [60].

### 1.14. Adsorption

#### 1.14.1. Adsorbent substance

Adsorbents from industrial wastes possess high porosity, rich adsorption sites, and porous prominence [64–65]. The porous structure of adsorbents includes a high surface area leading to a reduction in time to achieve adsorption equilibrium. To summarize the novel, adsorbents with large specific surface areas and rapid reaction kinetics to eliminate pollutants are desirable. Promising adsorbents for Cr (VI) removal are presented below.

**Table 4**  
Uptake capacities of industrial solid wastes for the reduction of Cr [70].

Adsorbents	Cr (VI), mg/g	Isotherms observed	Kinetics observed	References
Bagasse fly ash	260	**LF	–	[83]
Blast heater slag	7.5	**LF	1st order	[81]
Chestnut tannins	42	*L	2nd order kinetics	[86]
Clarified sludge	26.31	**LF	2nd order kinetics I-P-Diffusion model	[88]
Iron (III) hydroxide	0.47	**LF	–	[80]
Mimosa tannis	38	*L	2nd order kinetics	[86]
Oak bark char & Oakwood &	7.51 & 4.93	**LF, Radke Form, R-P-Form, Sips Form, Toth Form,	2nd order kinetics	[87]
Tannery waste	177–217	*L	2nd order kinetics	[85]
Tea factory waste	54.65	**LF	1st order kinetics,	[84]
Treated red mud	1.6	**LF	I-P-Model	[82]

\*\*LF(Langmuir, Freundlich), \*L(Langmuir).

### 1.15. Adsorption method

Adsorption is a mass transfer operation, exothermic. It separates selectively one of the fluid phases by amassing it on the adsorbent surface. Physical adsorption and chemisorption's are classified as forms of adsorption. Physical adsorption leads to reduced system entropy and free energy [66]. The uptake of adsorbate depends on the temperature and concentration of adsorbate. At a constant temperature, adsorption is expressed by the equation [67].

$$qt = \{V(C_0 - C_t)\}/m \quad (1)$$

$C_0$  and  $C_t$  are the initial concentrations of adsorbate at time  $t$ ,  $V$  is the solution volume,  $q_t$  is the specific adsorption or adsorbate collected per unit of adsorbent  $t$ , and  $m$  is the mass of adsorbent [66].

### 1.16. Adsorbent materials

Activated carbon is a potent adsorbent that can be employed for treating sewage and industrial effluents. Industrial effluents contain various contaminants. In a multistage operation, activated carbon finds application to remove specific contaminants and treat the total flow. Activated carbon prepared from various sources exhibits different characteristic properties [68]. The qualities of adsorbent improve by chemical or thermal activation.

### 1.17. Industrial wastes as adsorbents

Industries aspire to become a zero-pollution industry, attempts to minimize waste, or convert waste into byproducts. Solid waste is causing disposal problems that mandate utilization and hence become a potential carbonaceous source for adsorption. Industrial solid wastes or by-products, namely fly ash from thermal power stations, red mud from alumina plants, blast furnace slag from iron and steel plants, and talc from the paper industry, are also tried as adsorbents [69]. Sea products are naturally available sources and find applications in water treatment. Metal uptake capacities of many of the sea products used for heavy metal reduction are presented in Table 1 and Table 2, [70].

Industrial activities produce several solid wastes in different proportions. A few of these solid wastes can be potential byproducts. The solid wastes currently find no proper utilization and are being discarded. Solid wastes need treatment, and if used as a low-cost adsorbent, and enable economic wastewater treatment. Attempts to use industrial waste as adsorbents with or without treatment are gaining prominence. If used as an adsorbent, industrial solid wastes help reduce the solid waste treatment menace as treat effluents. Industrial solid wastes like blast furnace slag and fly ash possessing a potential for metal uptake are presented in Table 4.

## 2. Modeling of adsorption

Adsorption kinetics reflects the physical and chemical character of the adsorbent. Kinetic and equilibrium models are developed based on adsorption data can be performed using. Chemical kinetics, kinetic models provide information about reaction pathways, time requirements, and adsorption dynamics. The correlation coefficient indicates the correctness of the devised equation through modeling and experimental data. The coefficient of determination coefficient coefficients R-squared values indicates the model accuracy and precision for the same data.

### 2.1. Lagergen kinetic model

The Lagergen kinetic model is a pseudo first order isotherm and estimates solid or fluid sorption based on solid ability/capability [89,90].

The Lagergen kinetic model is expressed as:

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (2)$$

Here  $q_t$  and  $q_e$  are the adsorption capacity at time  $t$  and equilibrium respectively (mg/g), and  $k_1$  is the rate constant ( $\text{min}^{-1}$ ). Eq. (2) is rearranged to acquire a more suitable form

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.300}t \quad (3)$$

$\log(q_e - q_t)$  varies linearly with time with a gradient of  $k_1$ . The intercept of the plot of  $\log(q_e - q_t)$  vs.  $t$ , in a first-order  $\log q_e$  is equal to the intercept. The terms  $k_1$ ,  $(q_e - q_t)$  is not directly related to existing sites.

### 2.2. Pseudo-second-order kinetic model

The kinetic adsorption rate for pseudo-second-order kinetic order is expressed as:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

The pseudo-second-order adsorption ( $\text{g}^{-1} \text{min}^{-1}$ ) being the rate constant  $k_2$ . Simplification of Eq. No. 4 obtains a more useful form as-

$$\left(\frac{1}{q_e - q_t}\right) = \frac{1}{q_e} + k_2t \quad (5)$$

The linear form is

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e} \quad (6)$$

The graph of  $t/q_t$  vs.  $t$  gives the value of  $k_2$ . This model best explains the hexavalent chromium Cr (VI) removal from removal by many agents.

### 2.3. Intra-particle diffusion model

The hexavalent chromium adsorption occurs in four stages. The first stage is distribution throughout the bulk of the solution, diffusion in film in the near vicinity of the adsorbent particles, the intra-particle diffusion, and, finally, the adsorption into the particle pores [91].

Weber et al. [92] state that intra-particle diffusion critical parameter is the rate-restricting constraint  $k_2$ . The amount of adsorption is a linear relationship and directly related to a power function of contact time  $t$ , expressed in eq. (7).

$$q_t = k_{id}t^{0.5} \quad (7)$$

In eq. (7)  $q_t$  is the amount of Cr (VI) adsorbed.  $t$  is the contact time.  $k_{id}$  is the intra-particle diffusion coefficient

$$\log q_t = \log k_{id} + 0.5 \log t \quad (8)$$

A log-log plot of  $q_t$  against  $t$  gives a straight line. The positive intercept indicates that interparticle diffusion is the controlling factor in adsorption.  $k_{id}$  is the constant term of the linear equation. High indicates amplification in adsorption rate. Many researchers have attempted to understand the relation between the intraparticle diffusion coefficient and adsorption.

### 2.4. Elovich kinetic equation

The Elovich equation, as proposed by Roginsky and Zeldovich, is generally known as the Elovich eq. (9) and is being expansively applied to chemical adsorption data.

$$\frac{dq}{dt} = \alpha e^{-\beta q_t} \quad (9)$$

$\beta$  is the desorption constant expressed in g/mg, and  $\alpha$  is the initial adsorption rate (mg/g min).  $q_t$  is the amount of gas chemisorbed at time  $t$ .  $\alpha$  and  $\beta$  depend on the extent of the surface covered. On the application of boundary condition of adsorption capacity being 0 at the onset of adsorption that is  $t = 0$ , adsorption capacity being  $q_t$  at time  $t$  and both  $\alpha$ ,  $\beta$  greater than 1 [93].

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (10)$$

Elovich model is exhibited in the graph of  $q_t$  vs.  $t$ . A linear equation is obtained with an intercept of the product of  $(1/\beta)$  and  $\ln(\alpha\beta)$ . The slope of the straight line being  $1/\beta$ .

### 2.5. Equilibrium model

An adsorption isotherm distinguishes metal ions from the adsorbents. Whenever two phases are at equilibrium, an adsorption isotherm provides a relation between the concentration of metal ions in the solution to metal ions adsorbed.

### 2.6. Langmuir model

The Langmuir isotherm [94] explains gas adsorption activity on the activated adsorbent surface. The assumptions of Langmuir isotherm are: minimal transmigration of the adsorbate and uniform distribution of energy on the adsorbent surface. The Langmuir model estimates monolayer adsorption occurring on a homogeneous surface by sorption between noninteracting adsorbed molecules. The Langmuir adsorption isotherm is represented as Eq. (11).

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (11)$$

Here  $q_e$  is the adsorbed metal ion concentration on adsorbent;  $C_e$  is the residual metal concentration.  $q_{\max}$  is the maximum uptake at saturation, and  $b$  is the ratio of adsorption/desorption rates. Langmuir isotherm is expressed in Eq. (12) and Eq. (13).

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \quad (12)$$

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} b C_e} \quad (13)$$

### 2.7. Freundlich model

The Freundlich isotherm, proposed in 1906, is one of the earliest known relationships for multilayer adsorption between adsorbed

molecules explains adsorption being reversible [95]. Freundlich isotherm model restricts to adsorption on heterogeneous surfaces with uniform energy distribution. Freundlich equation interprets an exponential decrease of adsorption energy at adsorption centers on saturation or completing an adsorbent activity. For adsorption from solutions, Freundlich isotherm is represented by Eq. (14)

$$q_e = K_f C_e^{1/n} \quad (14)$$

Here  $C_e$  is the residual concentration of Cr (VI) in solution,  $K_f$  is the Freundlich constant (Freundlich capacity),  $q_e$  is the amount of chromium adsorbed at equilibrium, and  $n$  stands for adsorption intensity. The Freundlich equation is expressed as a linear relationship in Eq (15).

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (15)$$

The values of  $K_f$  and  $n$  are determined from the slope and intercept of a plot of  $\log q_e$  versus  $\log C_e$ . The constant  $K_f$  and  $n$  positively affect the adsorption isotherm.

## 2.8. Langmuir-Freundlich model

Langmuir-Freundlich model explains the adsorption process as a supportive method for the interactions between the fluid adsorbate and solid adsorbent when the adsorbent surface is identical [96]. The Langmuir-Freundlich form is written as Eq (16).

$$\log q_e = \log K_f + \frac{q_{\max} b C_e^{1/n}}{1 + b C_e^{1/n}} \quad (16)$$

## 2.9. Tempkin model

Tempkin determined experimentally the decrease in heat of adsorption with increasing treatment. The Tempkin model measures indirect effects of adsorbate/adsorbate on adsorption isotherms [97]. Tempkin equation in nonlinear and linear forms are expressed in Eq. (17) and Eq. (18) respectively.

$$q_e = \frac{R_T}{b_T} \ln (A_T C_e) \quad (17)$$

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (18)$$

Here  $B_T = (R_T/b_T)$ .  $A_T$  is the equilibrium binding constant (a function of highest binding energy),  $b_T$  is the proportionality constant (a function of the heat of adsorption).  $T$  is the absolute temperature.  $R$  is the universal gas constant. At constant temperature graph of  $q_e$  vs  $\log (C_e)$  will give  $A_T$ , and  $b_T$  (Tempkin isotherm constants).

## 2.10. Redlich-Peterson model

The Redlich-Peterson isotherm has three variables and is used to characterize adsorption equilibrium in a wide range of concentrations. Owing to its flexibility, this model is useful in both heterogeneous and homogeneous systems [98,99]. Eq. (19) explains the Redlich-Peterson model

$$q_e = \frac{K_R C_e}{1 + \alpha C_e^{b_R}} \quad (19)$$

The linearized form of Eq. (19) is

$$q_e = \ln \frac{K_R C_e}{1 + \alpha C_e^{b_R}} = b_R \ln (C_e) + \ln (\alpha_R) \quad (20)$$

Redlich-Peterson model a limitation that the three isotherm constants  $K_R$ ,  $\alpha_R$ , and  $b_R$  of this isotherm cannot be determined using a graph [98,99].

## 2.11. BET model

Stephen Brunauer, Paul H. Emmett, and Edward Teller isotherm model enables deviating ideal to actual analysis based on pore size distribution, voidage fraction and surface area. The basic assumptions being that there are no interactions in lateral direction between molecules, the adsorption on the adsorbent occurs in infinite layers, the top layer is in equilibrium with the vapour phase, and all surface sites have the same adsorption energy for adsorbate. BET isotherm is mathematically represented by Eq. (21).

$$q_e = \frac{q_{\max} B C_s}{C_s - C_e} [1 + (B - 1) \frac{C_s}{C_e}] \quad (21)$$

$C_s$  is solute saturation concentration, and  $B$  is a variable relating to the interface energy of the interface with the surface.

## 3. Electrochemical studies

Chemicals used in electro finishing, leather tanning, paints, pigments, printing inks, textile industry, and wood preservatives contain chromium compounds [101,102]. Potassium and sodium dichromate used in the tanning industry is responsible for large release amounts of chromium to water bodies [103]. Cr (VI) causes bone cancer and leukemia [103–105]. The fundamental difference between metals and organic pollutants in their accumulation in existing tissues coupled with non-biodegradability. Metal ions serve as micronutrients and occur as trace elements in plants and animals. High metal doses cause harmful health issues in living beings [106,107].

Diverse methods are available to treat chromium-based pollutants; the most common are electrochemical oxidation, ion-exchange resins [108], and nanofiltration to remove divalent ions [109]. Bio-adsorption and bioaccumulation studies anticipate Cr (VI) anti-bacteria [110]. The precipitation and reduction by chemical techniques treat Chromium (VI) by changing the initial oxidation state from Cr (VI) to Cr (III). Removal of chromium from wastewater using carbon or graphite wafers or felt as cathode construction materials in the electrochemical technique are widely known [111–114]. The electroplating industry treatment process reduces chromium from the effluents by using iron electrodes in the bipolar form to electrochemical precipitate Cr (VI) [115].

The kinetic studies reveal that electro reduction is relatively more energy-intensive than electrochemical reduction [116–118]. The recovery and reuse of water and chromium are not possible due to the sludge iron contamination. During the initial stages, absorption of Cr (VI) in the feedwater reduces, and Fe (II) absorption is higher than the stoichiometric quantity observed. Cr (VI) removal from groundwater is achieved by electrochemical precipitation method [119]. The electricity is produced in a galvanic cell using scrap iron, where Cr (VI) undergoes a reduction [120].

This process reduces power utilization in the storage; electrolysis uses the direct current energy produced and reduces Cr (VI) in the process. Measurement of energy, temperature, and initial concentration leads to the inference that a rise in temperature and initial concentration leads to an increase in Cr (VI) reduction. The cell voltage and cell current indicate increased solution temperature, increasing initial Cr(VI) concentration. Martinez and co-workers [121–123] studied Cr (VI) removal from the electroplating industry in batch and continuous electrochemical reactors. Modeling studies of kinetics in a constant stirred electrochemical reactor for treating synthetic wastewater and industrial effluents infer Cr (VI) removal [124,125].

This kinetics of modeling performed under acidic conditions show dissolving of Fe(II), and because of cathodic reduction of Ferric (III) to Ferrous (II) corrosion. The results of this reaction indicate

zero-order kinetics at higher concentrations of Cr (VI). First-order kinetics is observed at lower concentrations. A dynamic model with consideration to results from the dispersion of electrochemical Cr (VI) removal and pH has been developed. In a tubular reactor, at low pH an increase in the residence time raises in the influent Cr (VI) [126]. In the continuous stirring process, the effect of Reynolds number, kinetic rate equation is studied for a short action time, and low energy agitation requirement is obtained with the expansion of current density [127–131].

A model is developed for electrochemical reduction of Cr (VI) in a continuous tubular reactor using a spiral-shaped anode emphasizing current density, dispersion results, and pH [132].

Cr(VI) exists in aqueous effluent, and the conditions depend on factors such as the concentration of Cr (VI), pH and the redox potential [133]. Precipitation of Cr (VI) is not possible. Changing the oxidation state may ease the separation of Cr (VI) from aqueous solutions. The form of Cr (VI) depends on the theoretical allotment of Cr (VI). pH may not change insoluble Cr (VI) arrangement and is reflected in the high proportion, pourbaix region. The mobility of metal at this oxidation state is high in soil and water. The pH range determines the settling of insoluble trivalent Cr (VI). This paper reviews basic electrochemical methods for the detection of Cr (VI), namely electrodialysis, electrocoagulation and electro deionization approaches.

### 3.1. Electrodialysis

Electrodialysis is a promising technique for treating wastewater. Many researchers emphasize using Cr (III) and Cr (VI) ions by electrodialysis using ion-exchange membranes. Ion-exchange membranes with removable cells can help remove both Cr (III) and Cr (VI) [134]. The electrodialysis setup for electrolysis comprises a one-step electro-electrodialysis unit with a provision for water cleansing, metallic impurities removal, and chromic acid recovery [135]. The cation-exchange membrane modified by electrodeposition of polyethyleneimine was utilization for the recovery of Cr (III) [136]. A pilot plant was set up for potable water by removing Cr (VI) [137].

A two-stage electrodialysis setup for chromate recovery to treat electroplating industry wastewater has been suggested [138]. Ion exchange and electrodialysis for effective removal of chromate ion at different concentrations from chromium electroplating waste rinse water were reported [139,140]. Chromium removal from electroplating, metal finishing, and leather processing industrial effluents exhibited enhancement in the effect of treatment on the utilization of synthetic membranes, and electrodialysis was reported [141,142]. The first step involves the concentration of chromic acid and separation of the monovalent inorganic anion of hydrogen chromate. The second step of attention is focused on monovalent/divalent anions at differing pH values.

### 3.2. Electro deionization

In 1950's continuous electro deionization (CEDI), electrodialysis systems or Electrodeionization (EDI) were developed and used to reduce the occurrence of concentration polarization [143]. During the electroplating and mining processes, Cr (VI) gets discharged along with industrial wastewaters. EDI can be used to calculate the elimination of different ions. EDI helps in maintaining the ecological balance by removal of Cr (VI) to the extent of 98% along with electrodialysis and ion exchange [144–146].

Bergmann and co-workers et al. [147] have recommended different resins and varied operating parameters to remove  $\text{CrO}_4^{2-}$ . An ion-exchange bed is used to transfer ion conductivity. Dzyazko et al. [148] have screened the ion-exchange materials used in electro deionization measurement based on dispersion coefficients. A

comprehensive study of ED, EDI, and IX showed that 99.8% Cr (VI) removal by EDI [149]. Xing et al. [150,151] report the removal of Cr (VI) by CEDI's in the concentration range of 0.09 to 0.49 ppm, with an operation cycle of more than 50 h. The observations indicate for 40 ppm and 100 ppm Cr (VI) solutions, with an energy consumption of 4.1–7.3 kWh/mol of Cr (VI) [150,151]. Alvarado and co-workers [152] devised a theory for electro deionization amalgamated with ion exchange. The continuous column studies indicate the satisfactory treatment of effluents containing hexavalent chromium.

### 3.3. Electrocoagulation

In the Electrocoagulation (EC) process, the metal ions are electrochemically produced and later used as destabilizing agents and Cr (VI) scavengers. In this method, the oppositely charged particles attract each other, using electric charge neutralization to eliminate ionic pollutants. The ease of process with no sludge and minimal use of reagents makes this process useful for the reduction of Cr (VI) from effluent. During the early 20th century, EC was practiced for wastewater management, but the results were not promising. In the last decade, EC's popularity as a technique for treating effluents increases Europe and South America [153]. Electrocoagulation is being adopted in pulp and paper mills [154,155] in the mining and metal development industry [156]. EC is being implemented to treat petroleum refining, oil shale, nitrate solutions, tar sand, arsenic-containing smelter wastewater, domestic and commercial wastewater [157,158]. EC is used as a stage in conventional effluent treatment units to enhance the effectiveness of treatment. Studies were undertaken to optimize electrical power consumption and effluent throughput rate

## 4. Conclusions

Industrialists need convincing that the effluent treatment units are profit centers and not cost centers in the existing industrial scenario. In the long run, an effective treatment technique leads to a greener and sustainable environment at the same time, improving the economics of the industries concerned. The strict implementation of environmental regulations along with growing concern for the environment has led to search of various methods like coagulation/flocculation, ion exchange, flotation, membrane filtration, chemical precipitation, electrochemical treatment, and adsorption for the elimination of heavy metals. Comparison, interpretation and deciding suitability of techniques is not easy. The Cr(VI) in industrial wastewater, is highly toxic and presents a severe threat to human health and the environment. The adsorption mechanism described in the paper intends usage of locally available industrial byproducts as adsorbent and treat effluents. Adsorption is a reasonably well-known treatment process in industrial sectors and provides a solution to many existing effluent problems. The adsorption mechanism will be beneficial if locally available industrial byproducts are used as adsorbent to treat effluents. Chemical precipitation is a low cost, high efficiency operation and generates sludge a secondary pollutant which needs proper disposal. The electrochemical treatment uses electrical energy, low-cost highly selective and the treated water can be reused. Ion exchange is selective and not available for all heavy metals and has major problem of disposal of backwash waters. Membrane filtration is employed to treat inorganic effluent with a high Cr(VI) concentration. Flotation, flocculation and coagulation are established methods for wastewater treatment. In the membrane separation process, the space requirement is lower than the conventional treatment for separating many kinds of heavy metals. It is implied that by combining treatment techniques such as adsorption, elec-

trocoagulation, electro deionization, and electrodialysis is useful for treating effluents containing Cr (VI).

Effluent treatment should not restrict to laboratory studies and synthetic samples alone. The available treatment technologies discussed in this paper but the choice of appropriate treatment technique depends on the initial heavy metal concentration, operational cost, and wastewater characteristics. It is essential to choose the most applicable method based on heavy metal concentration, operational cost and wastewater characteristics.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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