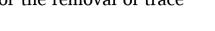
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Integrated electrochemical-adsorption process for the removal of trace heavy metals from wastewater



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ABSTRACT

In the light of the spread of treated wastewater use for irrigation, trace heavy metals pose a great risk to humans and aquatic life. An integrated electrochemical-adsorption (i.e. EC-AD) hybrid system was investigated for the removal of iron (Fe), zinc (Zn), and copper (Cu) traces from synthetic wastewater mimicking industrial wastewater. Slag, a by-product produced in steel industries, was utilized as the adsorbent. The performance of the EC-AD hybrid system was evaluated at mass to wastewater volume ratio (i.e. M/V) ranging from 0.01 to 0.07 g/mL, current density (CD) ranging between 5 and 15 A/m² and treatment time ranging between 60 and 120 minutes. Furthermore, process kinetics (pseudo-first-order, pseudo-second-order, Elovich, adsorption kinetic models, and Weber-Morris intraparticle diffusion), and adsorption isotherms (Langmuir and Freundlich) were investigated to provide adsorption mechanisms that reflect the interaction between EC and AD processes in the hybrid system. The results indicated that Freundlich isotherm was able to fit the linearized data points compared to Langmuir with Fe and Zn. In addition, kinetic models suggested chemisorption as the predominant removal mechanism of Fe, Zn, and Cu using slag for the EC-AD system. Results showed that the use of EC-AD significantly enhanced the removal efficiency of heavy metal traces from wastewater, reaching 99%.

1. Introduction

Water scarcity is a critical problem arising as a result of increasing water demand globally. The increasing demand for irrigation water specifically has led many regions around the world to find alternative water resources for acceptable water quality. Thus, many developing regions around the world have adopted treated wastewater for irrigation purposes [1,2]. Conventional water treatment methods leave behind a large range of trace chemicals, such as inorganic compounds, heavy metals, and persistent organic pollutants [2]. Heavy metals are characterized by high density and are well-known as toxic and carcinogenic agents when discharged, which poses serious health problems and threats the fauna and flora in the water bodies [3]. Iron (Fe) can lead to serious health issues, as it may cause conjunctivitis, choroiditis, and retinitis. Zinc (Zn) can also cause imminent health problems, such as skin irritations, vomiting, stomach nausea, cramps, and anemia. Moreover, copper (Cu) could cause serious problems, such as increasing blood pressure, damaged kidney, allergies, vomiting, and even death [4].

Hence, the removal of trace heavy metals from wastewater is crucial before releasing them into the environment. A major waste by-product in the steel industry is slag through which 200-420 kg/tonne.steel is produced [5]. If not utilized properly, toxic chemicals can leach out of the waste slag, causing soil or water pollution [6]. Waste slag is produced in very large quantities, making its volume another major challenge [7]. Its physical, chemical and mineralogical properties can make it a suitable substitute in many applications [5,7].

Physical, chemical and biological treatment methods can be used for heavy metal removal. Different conventional processes are implemented to remove heavy metals from wastewater, such as chemical precipitation, flotation, adsorption, ion exchange, and electrochemical deposition [8]. Adsorption is an example of a physio-chemical method that is commonly implemented for heavy metal removal from wastewater. It is mainly based on mass transfer between the liquid phase and the solid phase 'adsorbent' [9]. Adsorption has flexible design and operation, but its cost and removal efficiency can be limited by the choice of adsorbent [10]. Similarly, electrochemical (EC) treatment is a clean, flexible, and

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powerful method for wastewater treatment [10]. This process utilizes electricity to pass an electric current through a metal-bearing solution containing a cathode plate and an anode. Examples of EC include electro-deposition, electro-coagulation, electro-flotation and electro-oxidation [11]. The main characteristics of the EC treatment include simple equipment, ease of operation, and short retention time (5–120 mins) [8,11].

The combined electrochemical-adsorption (i.e. EC-AD thereafter) system is a modified EC system. This was introduced by Linares Hernandez et al. (2007), aiming at utilizing adsorption to further enhance pollutant removal. The authors reported significant removal of chemical oxygen demand (COD), color, and turbidity [12]. Later on, other studies focused on chromium (Cr), dye, and manganese (Mn) removal using mainly activated carbon (AC) as an adsorbent (Table S1). The studies on EC-AD hybridization ranged from using separate vessels to using the combined system in the same vessel. A wide range of adsorbents, such as AC, carbon nanotubes (CNTs), bio-sorbents and low-cost adsorbents, such as agricultural wastes, industrial by-products, sands and clays can be utilized [13]. A notable by-product of the steel industry presented herein is slag, of which its use can form a worthy route to a circular economy. Herein, adsorption and EC hybrid processes have been exploited for trace heavy metal removal using slag as an adsorbent. The optimal adsorbent dose was selected and integrated into an EC-AD system for the removal of trace heavy metals from synthetic wastewater. The objective of this study was to first investigate the use of adsorption for the removal of trace heavy metals from wastewater, using waste slag as an adsorbent, and subsequently use a hybrid EC-AD system for the removal of trace Fe, Zn, and Cu from wastewater. The effect of treatment time and current density (CD) on the removal efficiency was reported. The adsorption mechanism and kinetics were identified upon comparing different isotherms and kinetic models.

2. Materials and methods

2.1. Materials and wastewater preparation

Slag was investigated as a potential adsorbent for this study. Slag was obtained from the Emirates Steel Industry (ESI) in Abu Dhabi (UAE) and crushed finely (Fig. S1). Anhydrous ferric chloride (FeCl₃) with 99% purity, zinc chloride (ZnCl₂) with 95% purity, and copper nitrate (Cu (NO₃)₂·H₂O) with 99.5% purity were purchased from Sigma-Aldrich and were used for the preparation of synthetic wastewater mimicking industrial wastewater. Initial concentrations of 0.5 mg/L Fe, 0.85 mg/L Zn and 0.43 mg/L Cu [14] were obtained and used throughout all experimental investigations.

2.2. Experimental procedure

2.2.1. Adsorption (AD)

Batch AD experiments were conducted using the synthetic wastewater. Different adsorbent mass to wastewater volume ratios (i.e. M/V) ranging from 0.01, 0.03, 0.05, and 0.07 g/mL were tested. The prepared samples were placed at the rotary shaker (Daihan Labtech) at 120 rpm for 24 h. Each experiment was repeated in triplicates to minimize error. Subsequently, the samples were collected and filtered through 4 cm diameter glass fiber filter papers via vacuum filtration using Welch vacuum pump (Model No. 2545C-02 A) at a gauge pressure of -0.7 bar. Filtrates were analyzed for Fe, Zn, and Cu, using Hach DR 3900 spectrophotometer, and compared to the initial concentrations. The removal efficiency of heavy metals was calculated using Eq. (1):

Removal efficiency (%) =
$$\frac{(C_i - C_f)}{C_i} *100\%$$
 (1)

where C_i and C_f are the initial and final concentrations of the metal ions; respectively. The pH of the wastewater solution and treated water was

measured using pH/ION 7320 meter.

2.2.2. Electrochemical-adsorption (EC-AD)

This part of the study investigated the removal of Fe, Zn, and Cu using a hybrid EC-AD system, based on the results of the batch AD experiments. A total of four reactors were used through which three reactors were provided with aluminum plate anodes and stainless-steel plate cathodes as shown in Fig. 1. All reactors were operated at least three times to minimize error. The electrodes were fixed in the reactors and spaced apart 5 cm. An electric field was applied to the wastewater via a low voltage DC power supply. An effective surface area (A_s) of 95.2 cm² was used for the electrodes. The current (I) of each power supply was adjusted by controlling the voltage knob to maintain a constant current density (CD) of 5, 10 and 15 A/m² in the hybrid reactors, where CD was calculated using Eq. (2):

$$CD = I/A_s$$
 (2)

An adsorption reactor having no electrodes was used as a control to study the impact of incorporating electrokinetic treatment in the hybrid EC-AD systems. The adsorbent M/V ratio, which was optimized from the AD experiments, was used in the four reactors. Aquarium air pumps were used to provide sufficient mixing in the reactors, allowing for a higher surface interaction between the heavy metals and adsorbents. Water quality analysis was done using Hach DR 3900 spectrophotometer. The effect of removal time (60–120 minutes) was studied using the 5 A/m² reactor, after which the optimal removal time was applied to all other reactors.

2.3. Characterization of the adsorbents

After the completion of each experiment, adsorbent precipitates were collected from the reactors and dried in the oven at 105 $^\circ\text{C}$ for 24 h. The anodes were left to dry and the deposits were collected. Scanning electron microscope (SEM), X-ray fluorescence (XRF), Fourier-transform infrared spectroscopy (FTIR), and particle size analysis (PSA) were carried out on the samples to provide adequate interpretation to the research findings and removal mechanisms. Quanta 250 SEM was used to examine the surface morphology, the aggregate particles, and the surface characteristics of different materials, and thereby interpret the removal mechanism of heavy metal ions in this study. To clarify, the SEM image of the non-conductive samples, gold-palladium coating was applied to enhance conductivity and eliminate the effect of charging. XRF analysis was conducted by NITONXL3t 600 XRF analyzer to determine the elemental composition of the adsorbent precipitates. FTIR analysis was used to characterize the functional groups present on the adsorbent precipitate surfaces and the anode deposits. PSA was mainly used to investigate the characteristics of the size distribution of particles

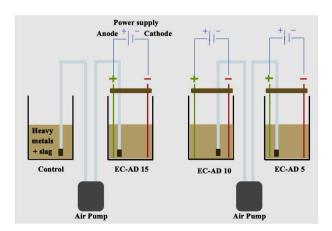


Fig. 1. Experimental set-up of hybrid EC-AD systems.

in the hybrid EC-AD system. The particle size of adsorbent precipitates was measured using the Horiba laser scattering particle size distribution analyzer (LA-950).

2.4. Isotherms and kinetics

Langmuir and Freundlich adsorption isotherms (Table 1) were used in this study to analyze the removal mechanisms of the proposed process. Different kinetic studies (Table 2) were also modelled to study the contact time between the metal ions and adsorbent. See Table S2 and Table S3 for a more in-depth methodology.

3. Results and discussion

3.1. Optimal adsorbent dose

Fig. 2 presents the removal efficiency of Fe, Zn and Cu from wastewater as a result of adsorption onto slag. Around 72% and 75% removal efficiency of Fe and Cu, respectively were reported at all M/V ratios. 78% removal of Zn was reported at M/V ratio of 0.03 g/mL using slag. Slag was considered an effective adsorbent of all heavy metals with an optimal M/V ratio of 0.03 g/mL. The efficiency of the AD process can be controlled by the M/V ratio of the adsorbent. It is commonly seen that a high adsorbent dose results in higher removal efficiency [15]. This phenomenon is associated with the fact that increasing the adsorbent dose resulted in an increase in the surface area, which in turn increases the removal efficiency. In the present study, when the slag M/V ratio increased from 0.01 to 0.03 g/mL, an almost 60% increase in the removal efficiency of Zn was observed (Fig. 2b).

Adsorbent regeneration is crucial for considering the practical reuse aspect of the adsorbent, as well as the economical aspect. The feasibility of regenerating the consumed slag was evaluated using physical and chemical techniques, according to Marshall and Johns (1996) [16], using Zn as a representative for heavy metals due to its high concentration compared to other heavy metals in this study. In the physical technique, the consumed slag was placed in 50 mL of deionized water (DI) (resistivity = 15 M Ω ·cm at 25 °C) whereas 50 mL of 0.1 M HCl was used for the chemical wash. Both reactors were shaken for 2 h at 120 rpm. The results indicated up to 98.6% and 11% recovery of slag adsorbent using 0.1 M HCl and DI, respectively. This indicates that a high adsorbent regeneration is feasible chemically, which shows that slag is a suitable adsorbent. Although slag resulted in a high adsorbent regeneration, there is still place for improvement in the removal efficiency of heavy metals at 78%, 72%, 75% for Zn, Fe, and Cu respectively. Therefore, EC-AD is suggested to maximize the removal rate of heavy metals using slag as an adsorbent. The applied electric field is expected to increase the removal efficiency by combining other processes such as electro-coagulation, electro-floatation, among others, which aid in the removal of a variety of contaminants [17-19].

Equations of adsorption isotherms.

Isotherm	Equation	Linearized form
Langmuir Freundlich	$\begin{array}{l} q_e = \frac{q_m \ K_L C_e}{1 + K_L C_e} \\ q_e = K_F \ C_e^{\overline{n}} \end{array}$	$\label{eq:cell} \begin{split} \frac{C_e}{q_e} &= \frac{1}{q_m K_L} + \frac{C_e}{q_m} \\ lnq_e &= lnK_F \ + \frac{1}{n} lnC_e \end{split}$

where q_e and q_m (mg/g) are the amount of the adsorbed ions per unit mass of adsorbent, and the maximum number of ions per unit mass of adsorbent to form a complete monolayer on the surface, respectively. C_e is the concentration of adsorbate at equilibrium (mg/L). K_L represents the Langmuir equilibrium constant (L/mg), n and K_F are Freundlich constants of the system, indicating the extent of the adsorption and the degree of non-linearity between metal solution concentrates and adsorption, respectively.

Table 2

Model	Equation	Linearized form
Pseudo-first-order model	$\begin{array}{ll} \displaystyle \frac{q_e}{q_t} = & k_1(q_e \ - \\ & q_t) \end{array}$	$\begin{array}{l} log(q_e \ - \ q_t) = \\ logq_e \ - \frac{k_1 t}{2.303} \end{array}$
Pseudo-second-order model	$q_{e} = \frac{k_2 q_e^2 t}{k_2 q_e^2 t}$	$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$
Elovich model	$\begin{array}{l} q_t \ = \displaystyle \frac{k_2 q_e^2 \ t}{1 + \ q_e k_2 t} \\ q_t \ = \displaystyle \frac{1}{\beta} \ lnt + \end{array}$	$q_t K_2 q_e^2 q_e$
	$\begin{array}{rcl} \displaystyle \frac{1}{\beta} & ln(\alpha\beta) \\ \displaystyle q_t & = & k_{id}t^{1/2} + c \end{array}$	
Weber-Morris Intraparticle diffusion model	$\begin{array}{lll} \rho \\ q_t & = & k_{id}t^{1/2} + c \end{array}$	

where q_e and q_t (mg/g) are the capacities of heavy metal adsorbed at equilibrium and time t (min), respectively. k_1 is the pseudo-first-order rate constant (1/min) and k_2 is the pseudo-second-order rate constant (g/mg.min). α and β are the Elovich coefficients, where α represents the initial sorption rate (mg/g.m) and β represents the desorption constant (g/mg). k_{id} is the intraparticle diffusion rate constant (g/mg. min^{1/2}) and c is the intercept in the plot of q_t vs. $t_{1/2}$.

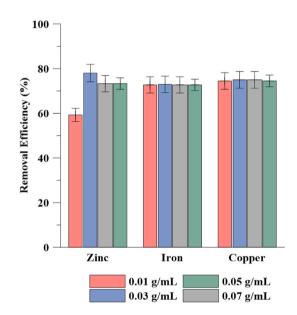


Fig. 2. (a) Removal efficiency of heavy metals from synthetic industrial wastewater using different adsorbents at different M/V ratios.

3.2. Electrochemical-adsorption (EC-AD) hybrid system

The EC-AD system was applied for the removal of Zn, Fe, and Cu from wastewater at different treatment times (60-120 minutes) and CDs $(5-15 \text{ A/m}^2)$. Fig. 3a shows that there is a variation in the removal efficiency values with time for Fe, Zn, and Cu at 5 A/m^2 . For example, the removal efficiency (96-97%) of Fe did not change over 120 minutes. However, increasing the removal time resulted in an increase in the removal efficiency for both Zn and Cu, achieving the highest removal efficiency at 90 minutes. Higher treatment time increased the generation of metal hydroxide, resulting in a higher removal efficiency at a constant CD in electrocoagulation [8]. Furthermore, the adsorbent surface contains voids that contribute to the rapid and high adsorption rate, so by increasing the exposure time, these pores were gradually filled in with adsorbents that increase the removal efficiency. Due to the stated reasons, the increase of the treatment time from 60 to 120 minutes at 5 A/m² resulted in an approximately 35% and 10% higher removal efficiency of Zn and Cu, respectively.

The different processes that occur in the proposed EC-AD system are highlighted in Fig. 4. Electrophoresis describes the process of separating ions based on their movement through a fluid under the influence of the

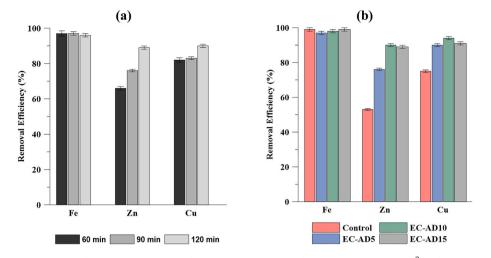


Fig. 3. (a) The effect of time on the removal efficiency of Fe, Zn, and Cu from wastewater for the EC-AD system at 5 A/m^2 , and (b) removal of heavy metals by the hybrid EC-AD system from wastewater at different CDs at 90 minutes treatment time.

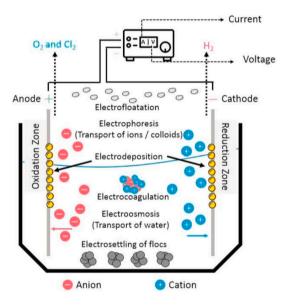


Fig. 4. Schematic of electrokinetic phenomena occurring in the EC-AD system.

electric field. Following electrophoresis, electroflotation, electrocoagulation, electrodeposition and electrocoagulation occur simultaneously. In electrocoagulation, Al(OH)₃ coagulants are generated through this process in situ by aluminum dissolving from the aluminum electrode [8]. The equations associated with this process are highlighted below:

The oxidation reaction at the anode:

$$AI \to AI^{+3} + 3e^{-} \tag{3}$$

$$2H_2O_{(l)} \rightarrow 4H^+ + O_2 + 4e^-$$
 (4)

The reduction reaction at the cathode:

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-$$
(5)

The hydrolysis reaction:

$$Al^{+3} + 3H_2O \rightarrow Al(OH)_{3(s)} + 3H^+$$
 (6)

From these reactions, Al^{3+} and OH^{-} ions generated and form various monomeric species, such as $Al(OH)_{2}^{+}$ and $Al(OH)_{2}^{2+}$ and polymeric species such as $Al_{6}(OH)_{15}^{3+}$, $Al_{7}(OH)_{17}^{4+}$ and $Al_{13}(OH)_{34}^{5+}$, which is

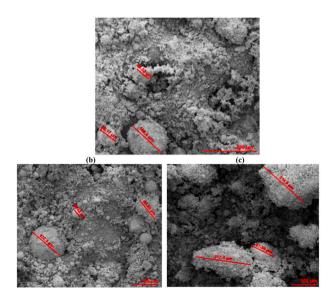
transformed finally into Al(OH)3 according to complex precipitation kinetics [8]. Consequently, monomeric and polymeric species leads to the formation of the amorphous Al(OH)3 "sweep flocs", which have large surface areas that is valuable for a rapid AD of soluble organic compounds and trapping of colloidal particles [8,15]. The main processes in the electrocoagulation process are: anode dissolution, OH- and H₂ generation at the cathode, electrolytic reactions at electrode surfaces, coagulant AD on colloidal pollutants, and removal of colloids by sedimentation or flotation [9]. Aggregated flocs form and finally fall to the surface as sediments. Coagulation forms as a result of the adsorption of the heavy metal ions onto the surface of the slag, which acts as an adsorbent. Flocs can either settle at the bottom of the tank as sediments or float to the surface. Electro-flotation results from the hydrogen gas bubbles trapping the formed flocs, which float onto the surface to form a froth that is skimmed off. Finally, in electrodeposition, the positively charged metal deposits are formed on the surface of the negative cathode as the heavy metal ions are attracted. Al(OH)₃ is also adsorbed into the high surface area slag. Hence, adsorbent and the generated metal hydroxide come together and simultaneously contribute to the adsorption of heavy metals.

It was shown that among the factors that can contribute to the EC-AD is the treatment, which translates to the contact time between the metal ion and adsorbent, in addition to the insitu coagulant generation. The adsorbent capacity, particle size diameter and specific area of the adsorbent are additional factors. An additional factor that could contribute to the efficiency of the EC-AD process is the current density. Hence, the effect of CD on Fe, Zn, and Cu removal was investigated at 5, 10 and 15 A/m^2 with a distance of 5 cm between the electrodes at 90 minutes treatment time (Fig. 3b). The application of the electric field in the treatment enhanced the removal of Zn and Cu compared to the treatment by sole adsorption. This could be attributed to a higher coagulant production rate, bubble production rate, size and growth of the flocs [8]. The anode dissolution rate increased with increasing CD, thus more metal ions moved the metal lattice into the solution to form complex or hydrated ions, which aid in coagulation, thus enhancing the removal efficiency. However, Fig. 3b shows that increasing the CD beyond 10 A/m^2 resulted in a slight drop in the removal efficiency. This is because by increasing the CD above the threshold, sufficient numbers of metal hydroxide, which acts as adsorbents, would be available for metal adsorption. A further increase in CD would not result in additional floc formation but might result in floc destabilization, hence a slight drop was observed. Fig. 3b shows that the efficiency of the removal of the ions from wastewater at 5 A/m^2 was 97%, 90%, and 76% in the following order: Fe > Cu > Zn. The difference in the removal efficiency could be attributed to the differences in the radius of ions,

electronegativity, and solubility. The radius of the ions affects their adsorption strength; therefore, the smaller radius ions could be adsorbed stronger than the larger radius ions. Zn, Cu, and Fe have atomic radii of 137, 128, and 126 p.m.; respectively, which explains why Fe resulted in the highest removal. Furthermore, the metal ions of higher electronegativity can be adsorbed more easily [20]. For example, Cu and Fe have higher electronegativities (1.9 and 1.83 respectively) compared to Zn (1.65). Substances that have low solubility prefer accumulating on the surface of the adsorbents rather than dissolving in water, and hence would more easily be removed from wastewater compared to ions with high solubility. Besides the higher efficiency, electrocoagulation could be more economical compared to chemical coagulation. For instance, the energy consumption due to the addition of an electric field in this study was found to be 0.89 kWh/m³ according to Ohm's law (see Section S2). Furthermore, it has been reported that the operating cost of chemical coagulation is 3.2 times higher than EC for wastewater treatment [21]. Hence, electrocoagulation was found to not only result in higher removal efficiency but also can be more cost-effective compared to its conventional counterpart.

3.3. Characterization of slag precipitates and anode deposits

The surface morphology of the slag adsorbent was examined using SEM (Fig. 5). The SEM image detected the structure of the slag surface to be porous, which indicates the amorphous nature of the slag. The surface of slag was analyzed by SEM before (Fig. 5a) and after adsorption (Fig. 5b), and after the EC-AD hybrid system (Fig. 5c) at a CD of 5 A/m^2 . The images showed the presence of pores in the surface of slag, confirming its high surface area and hence adsorption capacity. The main factors affecting the adsorption capacity of the adsorbent are the particle size, pore diameter and specific surface area [15]. Fig. 5 shows how the particle size diameter of the slag changed from 108.4 μm (before treatment) to 132.1 µm (adsorption only) to 217.5 µm (EC-AD). The large particle size diameter in the EC-AD hybrid system, due to the application of electric field, implies that more heavy metals were accumulated on the slag deposits, hence resulting in a higher removal efficiency. The density of particles can also be observed to increase in the raw slag compared to adsorption and EC-AD treatment, indicating increased heavy metal adsorption by the slag adsorbent. The FTIR spectra of the slag precipitates and anode deposits were carried out to determine the main functional groups present in the adsorbent before treatment, after adsorption and after EC-AD processes. The peaks



indicated the presence of Cu and Zn salts, as well as strong interactions between Fe ions and slag. Details of spectral analysis are discussed in Section S3 (Fig. S2(a) and Figs. S3(a,b,c)). XRF analysis was also carried out on the slag precipitates taken from the EC-AD hybrid systems. The results in Fig. S2(b) confirmed the effective adsorption of Fe, Zn, and Cu.

Particle size analysis was conducted on samples of the slag precipitates taken from the reactors following the experiments. Table 3 shows that mean particle size changed significantly by varying the current density. The diameter of the slag from the adsorption only reactor increased by 6.7 μ m, as the CD increased to 10 A/m², and further increased by 32.1 μ m at 15 A/m². The particle size analysis confirms the SEM results, which indicate that floc formation occurred due to the application of an electric field. This confirms the occurrence of the electrocoagulation process in the EC-AD hybrid system.

3.4. Adsorption isotherms

Adsorption isotherms were obtained by varying the initial concentration of adsorbent, which in this case is slag from 0.5 g to 1.5 g in 1 L of synthetic wastewater. Results have used Freundlich and Langmuir models to fit the experimental data so that mechanisms of the process can be obtained. The obtained plots are shown in Fig. S4. It was shown that Freundlich isotherm fitted better with the linearized data points than Langmuir with Fe and Zn. However, any isotherm was successful with Cu. The Freundlich isotherm indicates that all sites on the adsorbent have equal affinity for the adsorbates. The adsorption of Fe and Zn using slag obeyed the Freundlich isotherm with R^2 values equal to 0.99 and 0.96 (Table S2); respectively implying the adsorption of Fe and Zn occurred due to the chemical bonding for the control reactor (i.e. adsorption only). The Freundlich isotherm was also the best model to fit the Zn experimental data in the EC-AD hybrid system with an R^2 of 0.98.

3.5. Adsorption kinetics

To study the kinetics of the removal using slag, pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion kinetic equations were used to fit the experimental data. The kinetics were examined for both adsorption only and EC-AD hybrid systems inside two reactors 1 L each, containing 33 g adsorbent (i.e. M/V ratio of 0.03 g/mL) at CD of 5 A/m^2 for EC-AD hybrid system. The contact time was ranging from 15 to 90 minutes. The results are shown in Fig. S5. Physical, chemical and exchange adsorption are the main types of adsorption processes. In the physical adsorption, adsorbed molecules are not affixed to a specific site on the solid surface, but are free to move about over the surface. In addition, the adsorbed solid may condense and form several superimposed layers on the surface of the adsorbent. In the chemical adsorption (i.e. chemisorption), the adsorbed material accumulates on the surface of the adsorbent and form a layer of one molecule thick, and these molecules are not considered free to move from one surface site to another. Exchange adsorption involves ion exchange, which is characterized by the attraction of electricity between the adsorbate and the surface [22]. The kinetic models suggested that chemisorption is the predominant removal mechanism of Zn, using slag as an adsorbent for both adsorption and the EC-AD hybrid system. The pseudo-second-order model was found to best fit the results. Table S3 shows the calculated kinetic parameters for the adsorption and EC-AD processes.

Table 3Mean particle size diameter of the slag precipitates.

Reactor	Mean particle size diameter (µm)	Standard deviation (µm)
AD	13.8	0.1
EC-AD 5	15.8	0.1
EC-AD 10	20.5	0.1
EC-AD 15	52.6	0.3
EC-AD 5 EC-AD 10	15.8 20.5	0.1 0.1

4. Conclusions

An integrated EC-AD hybrid system was developed for the removal of trace heavy metals from industrial wastewater. Indigenous waste slag at 0.03 g/mL coagulant dose was found to be optimal for heavy metal removal from wastewater. Maximum removal efficiency of up to 99%, 91%, 99% were achieved for Fe, Zn, and Cu; respectively, using EC-AD, which was associated with the dual impacts of electrokinetic treatment and adsorption. The impact of EC was evident in improving the removal efficiency, as indicated by the XRF, SEM, FTIR and PSA analyses. The results followed a Freundlich isotherm with Fe and Zn. However, any isotherm was successful for Cu. The kinetic models suggested that chemisorption was the predominant removal mechanism of Fe, Zn, and Cu, using slag as an adsorbent for both adsorption and the EC-AD hybrid system. Consequently, the proposed integrated EC-AD hybrid system using slag could have a great potential as an alternative, one-step, and low-cost treatment system for the removal of trace heavy metals from wastewaters within a circular economy approach.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cscee.2021.100147.

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