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Electrochemical Removal of Cobalt From Aqueous Solutions Using A Flow-by Fixed Bed Bio-Electrochemical Reactor - A Kinetic Study

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Abstract

The present work was conducted to investigate the kinetics of cobalt removal from aqueous solutions using a Flow-by fixed bed bio-electrochemical reactor. Effects of process parameters namely applied voltage, Initial cobalt concentration, and pH on the reaction rate constant (k) were investigated. The results shows that the cathodic deposition was occurred under mass transfer control for all values of the applied voltage used in this research. Accordingly, the relation between concentration and time can be represented by a first order equation. The rate constant was found to be dependent on the applied voltage, initial cobalt concentration and pH. It was increased as the applied voltage increased and decreased as the initial concentration increased. The dependency of rate constant on the applied voltage was found to an exponential form similar to Arrhenius form. pH has two dissimilar effects on the rate constant, its increasing from 3-7 leads to an increase in the rate constant while at alkaline condition , the rate constant was found to be decreased..

Keywords: Cobalt, Fixed bed electrode, Microbial electrolysis cell, Kinetics.

1. Introduction

Nowadays, the most important environmental issue is the pollution resulted from heavy metals because these metals are toxic and, non-biodegradable and could be bio-accumulated in environment [1]. Cobalt considers as one of heavy metals which is toxic and poses several health and environmental threats [2]. Several methods have been utilized for cobalt removal such as physiochemical methods (adsorption, coagulation, chemical precipitation, and oxidation), and membrane methods (reverse osmosis, ion exchange membrane) [3]. Most of these methods are not efficient especially at low concentrations of heavy metals, in addition to their high operational costs [4]. On the other hand, cobalt can be removed by cathodic deposition via an electrochemical process which has been verified as an efficient approach in comparison with traditional methods due to the utilizing of electrons as clean reducing agent [5]. Application of cathodic deposition has been increased recently due to the utilization of three-dimensional electrodes which have high specific surface area leading to high mass transfer rate , in this context, different designs of these fixed bed electrodes have been used such as packed bed of screens, metal-plated foams, reticulated vitreous carbon, and felts [6,7]. Cobalt removal by cathodic deposition, in spite of its excellent performance in comparison with traditional methods, it needs high energy to reduce cobalt at the required potential [8]. This drawback has been overcome by using microbial electrolysis cells (MECs), which have proved efficiently in removal heavy metals at considerably low cost [9]. Recently, cobalt had been removed with high removal efficiency and lower cost by using bioelectrochemeical cell with a fixed bed cathode combined with soil as a source of bacteria at the anode in our laboratory and significant results were obtained [10].

In any electrochemical process carried out under galvanostatic condition, two distinct cases could be identified in the cathodic deposition process: the first case is electron transport control while the second case is mass-transport control. In the first case, metal percent removal increases linearly with time while in the second case, an exponential decay of the concentration with time is occurred combined with decreasing of current efficiency with time [11]. Therefore, studying the kinetics of cathodic deposition is an essential process by which information about the process dynamics such as reaction rate, order of reaction, and mass transfer properties can be obtained [12].

Rios-Reyes et al.[13] studied the kinetics of cobalt electrodeposition onto cathode made from glassy carbon in a synthetic solution composed of (0.01M) cobalt sulfate dissolved in (1M) ammonium sulfate at pH 4.5 using potentiostatic method. No reaction rate correlation has been reported in their work. Chu et al.[14] investigated the kinetics of copper removal from aqueous solution using backed bed cathode. They found that removal rate of copper is under mass transfer and the concentration of copper declined exponentially according to the following equation:

$$C_{(t)} = C_o \exp\left[-\frac{aut}{V}\left(1 - exp\left(-\frac{L}{\lambda}\right)\right)\right] \qquad (1)$$

where C(t) refers to copper concentration at any time t, second, C_0 is copper initial concentration, mg/l, V is electrolyte volume, cm^3, (u) is the superficial velocity , cm/s, (a) refers to cathodic cross-sectional area, cm^2, , L represents the bed height, cm, (λ) is the characteristic length and its value depends on the configuration of cathode.

In a relevant research achieved by Ruotolo and Gubulin[15], the kinetic behavior of copper deposition on a fixed-bed electrochemical reactor was studied. They found that the decline of copper concentration is linear for the initial period of electrolysis then changed to exponential for the rest. However, no rate expression has been reported.

Khattab et al. [12] investigated the kinetics of copper removal using backed bed cathode. They found that the concentration profile of Cu(II) with time can be represented by the following rate equation:

$$C_{(t)} = C_o \exp[-kt] \qquad (2)$$

To our knowledge, no study has been conducted to investigate the kinetics of cobalt removal using packed bed bio-electrochemical reactor, nor correlation of rate constant were reported based on this design of electrochemical system. Therefore the novelty of present work is based on getting new results that are essential in scale up bioelectrochemical system based on the kinetic rate equation.

In our previous study [10], we found that the cobalt removal in a flow-by fixed bed bio-electrochemical reactor is related to three main parameters namely the applied voltage, Co initial concentration, and pH at constant flow rate of 250ml/min. Therefore, the aim of the present research is to investigate the kinetics of the cathodic deposition of cobalt in such system and determine the correlations between the reaction rate constant with the above mentioned variables.

2. Material and Apparatus

Cobalt removal was achieved by bio-electrochemical system composed of a fixed bed electrochemical cell (shown in Figure 1)with two conical Pyrex flasks with capacity (1L for each) serving as reservoirs for anolyte and catholyte solutions, two flow meters with a flow range from 0 to 0.25 l/min, and two dosing pumps (IML, HC-100, Italy) with flow rate range (5-8 l/hr). The scheme drawing of this system is presented in

Figure 2. . The packed bed electrochemical cell used in the present work was composed from two Perspex blocks separated by cationic membrane (IONIC-64LMR). The first is the anodic compartment with dimensions 14 cm length $\times$ 10 cm width $\times$ 2.5 cm thickness, while the second is the cathodic compartment having external dimensions 14 cm length $\times$ 10 cm width $\times$ 2 cm thickness. Stainless steel screen (316-AISI)with mesh number 30 in^{-1} having a specific area of 38.06 cm^{-1}was used as cathode materials while porous graphite having BET surface are of 22.7509m²/g was used as anode and inoculated with 2 g of soil, more details of cell design and experimental set up can be found in [10].
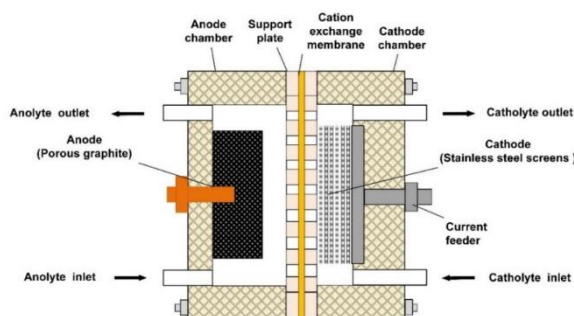

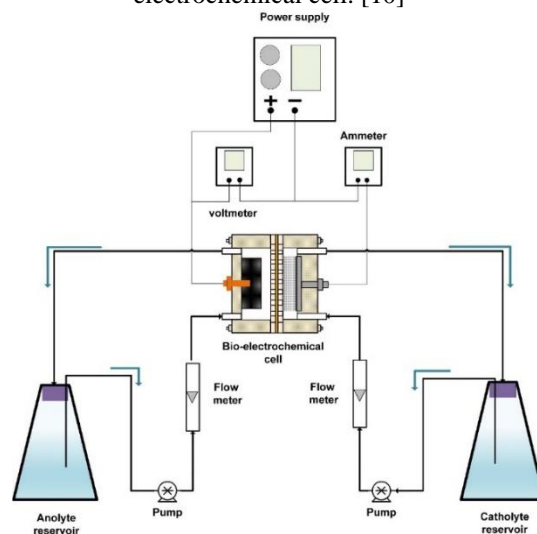**FIGURE 1** Schematic diagram of the bio-electrochemical cell. [10]

FIGURE 2 Schematic diagram of the bio-electrochemical system. [10]

Soil was used as a source of bacteria. Samples were taken at a depth of 0.1 m from the surface of soil located at al-Ghwarizm College, University of Baghdad, Al-Jadriya, Iraq. They were screened by using sieve with 0.2 cm opening diameter then kept at 4ºC. Details of soil physiochemical properties are mentioned elsewhere [10]. Examination the kinds of bacteria in the soil was accomplished by VITEK 2 compact system (bioMérieux, France) and it was found that they were mostly *Pseudomonas aeruginosa*

and *Klebsiella pneumonia* as exoelectrogenic bacteria, more details found in [10].

The anolyte for the bio-electrochemical cell was composed of (per litre): 1 g CH_3COONa, 4.58 g Na_2HPO_4, 2.45 g $NaH_2PO_4 \cdot H_2O$, 0.31 g NH_4Cl, 0.13 g KCl, adjusted to pH = 7 while $CoCl_2$ solution was used as catholyte [10]. In the present work, we used $CoCl_2$ as a source of Co^{+2}, beside the two compartment(anodic and cathodic) are separated by a cation exchange membrane, therefore no generation of Co^{+3} or Co^{+6} ions could be happened via oxidation on anode and cobalt exists only as Co^{+2}. Atomic absorption spectroscopy (Varian SpectrAA 200 spectrometer) was used to identify cobalt concentration.

3. Results and Discussion

3.1 Effect of applied voltage

For identifying the order of cobalt deposition on the flow-by fixed bed cathode, plots of ln(C/Co) against the time at different applied voltages were constructed. Figure 3 displays the plots of ln(C/Co) against time at applied voltage of 0.6V, 0.9V, 1.2V, 1.5V, and 1.8V. The effect has been investigated at constant concentration of cobalt 25ppm and pH=7. It was observed from the set of plots that the relation is almost linear with correlation coefficient (R^2) greater than 0.99 confirming that cathodic deposition of cobalt obeys a first order reaction kinetics. Table 1 displays rate constant (k) values at several applied voltage which also plotted in Figure 4. It was cleared that any increase in the applied voltage results in increase the rate constant and Figure 4 shows that the relation between rate constant and applied voltage is almost fitted to an exponential form. Therefore, the correlation between rate constant and applied voltage could be designated by equation (3):

$$k = k_o e^{-\beta(E)} \qquad (3)$$

Where k refers to rate constant in min^{-1}, k_o refers to the rate constant at no current supplied, β refers to the slop of above relation when plotted in term of neutral logarithm and E refers to the applied voltage in Volt.

Equation 3 shows the dependency of rate constant on the applied voltage which is similar to Arrhenius form. Values of k_o and β can be determined from the plot of ln(k) verses applied voltage as shown in Figure 5. From Figure 5,–β=1.130869 and value of k_o is equal to 1.5827×10^{-3} min^{-1}. Similar correlation was obtained by Khattab et al.[12] in their studying the kinetics of copper removal on packed bed cathode but the relation was between rate constant and current density instead of applied voltage used in present research. For a comparison of rate constant with similar work, Khattab et al[12] found that the rate constant was in the range of (0.0066 to 0.1272 min^{-1}) as the current density increased from 100 to 500 A/m^2 while in the present work the rate constant was not exceeded 0.013798 min^{-1} as voltage approach to 1.8 volt. This is

expected since present work operated at low voltage that is given high current efficiency approach to 62.73% after 6hr operation time [10], while it not exceeded 50% at 500A/m^2 after 10 min in Khattab et al work[12] hence the present system is more efficient than traditional electrochemical removal of heavy metals in term of low voltage and high current efficiency .

TABLE 1 Rate constant at different applied voltage, $[Co^{+2}]$=25ppm,pH=7

E(Volt)	K(min^{-1})
0.6	0.003395
0.9	0.004415
1.2	0.005344
1.5	0.007950
1.8	0.013798

3.2. Effect of the initial concentration of cobalt

The impact of initial concentration of cobalt on the rate constant was also considered. Figure 6 shows the plots of ln(C/Co) against time at cobalt initial concentration of 25, 50, 75, 100, and 125ppm. The effect has been investigated at constant applied voltage of 1.8V and pH=7. From this set of plots, It can be seen that the relation is almost linear with correlation coefficient (R^2) greater than 0.95. Rate constant (k) values at several cobalt initial concentration are tabulated in Table 2 and plotted as shown in Figure 7. It was observed that rate constant decreased as the initial concentration increased and Figure 7 shows that the relation between rate constant and initial concentration is almost fitted to an exponential form with correlation coefficient (R^2) greater than 0.97. Similar trend was observed by Khattab et al.[12] in their studying kinetics of copper removal on a packed bed cathode. At higher concentration, the system may be became under mixed control and with more increasing concentration, the system became solely under electron transfer control. However, no such phenomena was observed as confirmed by high value of R^2. Mixed control operation was happened in previous studies [14, 15].

TABLE 2 Rate constant at different initial concentration of cobalt, E=1.8V, pH=7

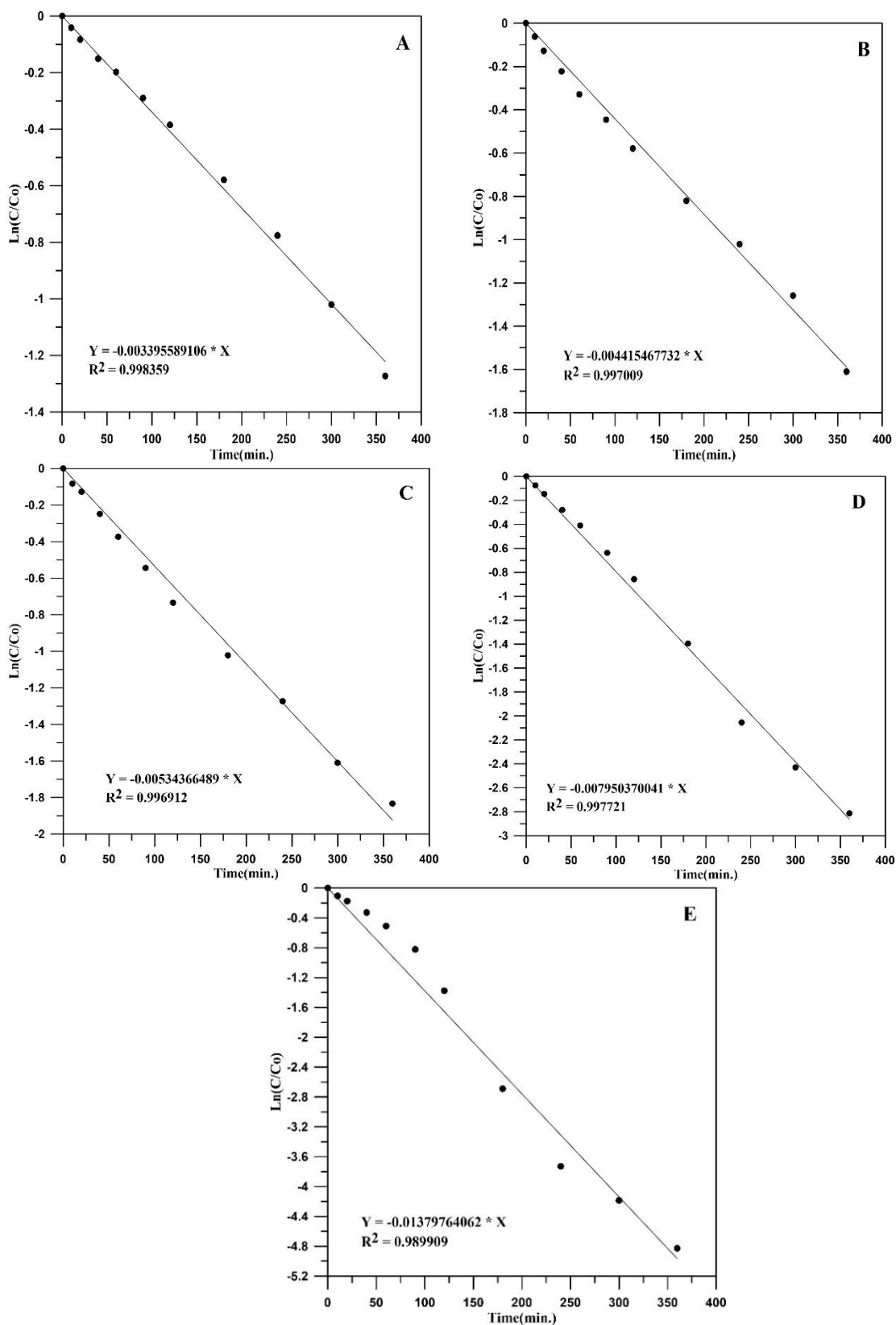| $[Co^{+2}]$, ppm	K(min^{-1})
25	0.013798
50	0.010706
75	0.005599
100	0.004739
125	0.002949

FIGURE 3 Plots of ln(C/Co) against time at different applied voltage:
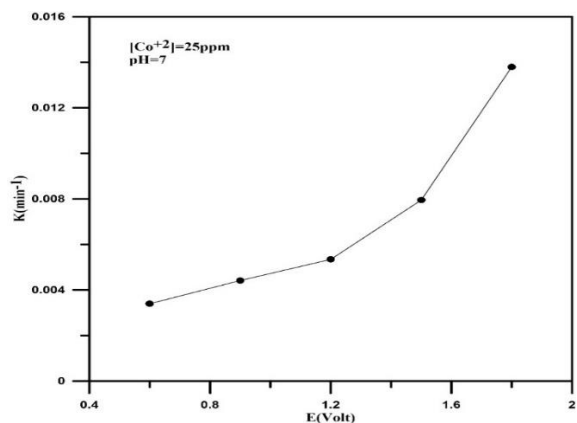A) 0.6V, B) 0.9V, C) 1.2V, D) 1.5V, E) 1.8V. [Co^{+2}]=25ppm,pH=7
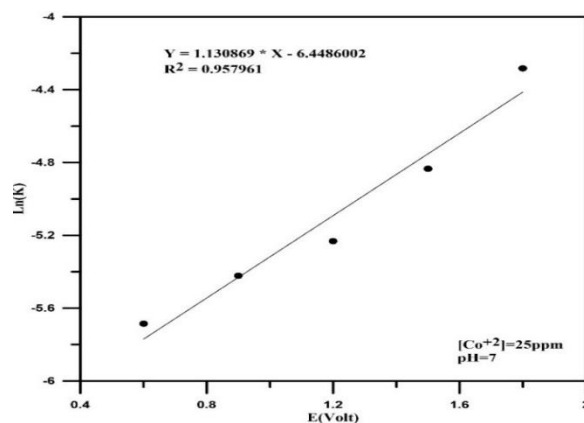
FIGURE 4 Effect of applied voltage on the rate constant (k)

FIGURE 5 Plot of ln(K) against applied voltage

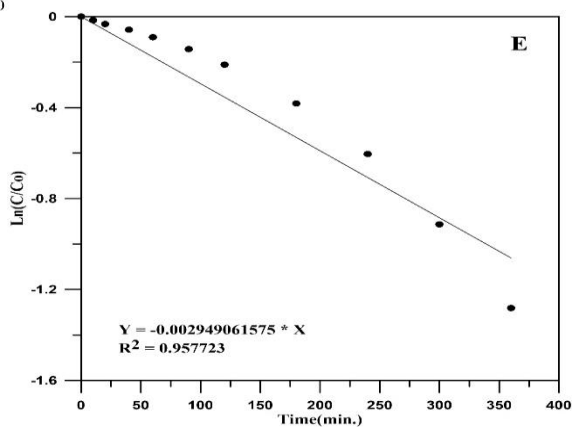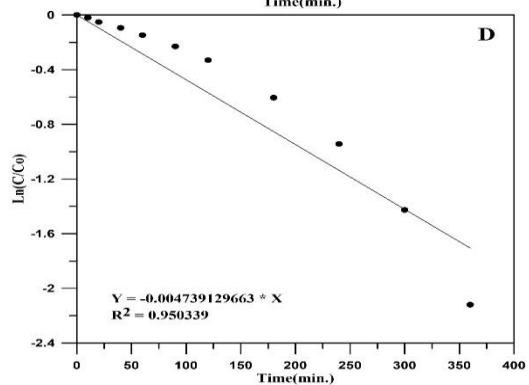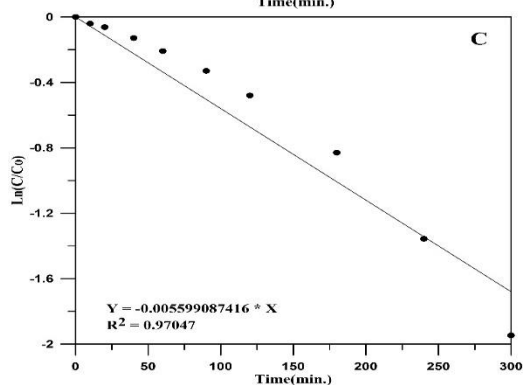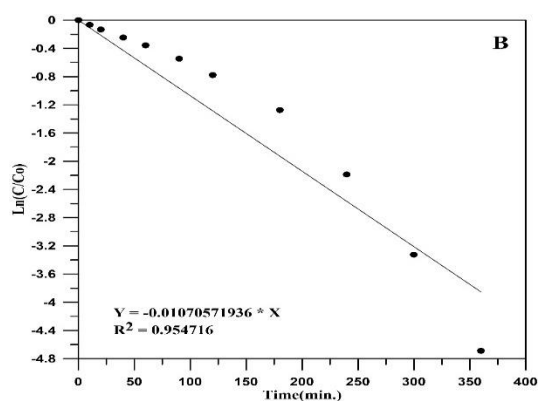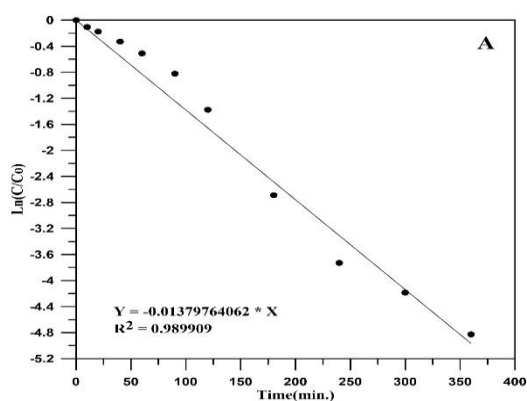**FIGURE 6** Plots of ln(C/Co) against time at different initial concentration:
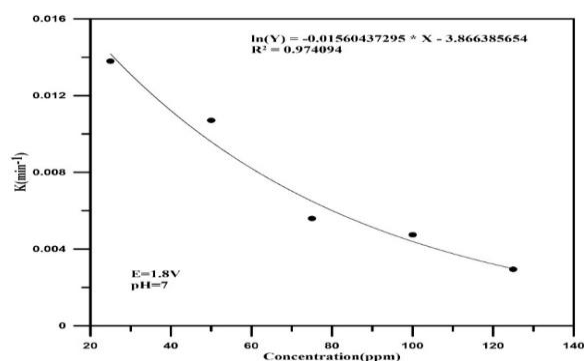A) 25ppm, B) 50ppm, C) 75ppm, D) 100ppm, E) 125ppm. E=1.8V, pH=7

FIGURE 7 Effect of initial concentration of cobalt on the rate constant

3.3   Effect of pH

To demonstrate impact of pH on the rate constant, plots of ln(C/Co) against time at different values of pH were constructed as shown in Figure 8. The effect has been investigated at constant applied voltage of 1.8V and cobalt concentration of 50ppm. From this set of plots, It can be seen that the relation is almost linear with correlation coefficient (R^2) greater than 0.95. Rate constant (k) values at several initial pH values are tabulated in Table 3 and plotted as shown in Figure 9. It was observed that rate constant increased with increasing pH up to a value of 7 then starts to decrease as pH became more alkaline. The interpretation of this behavior depends on effect of hydrogen evolution as a side reaction occurred on the cathode where its rate increases as pH decreased leading to lower transfer of cobalt towards the cathode hence low value of rate constant was observed. At alkaline condition cobalt ions may be precipitated as $Co(OH)_2$ rather than as Co hence rate of cobalt deposition decreased [10]. The effect of pH on cobalt removal up to pH 7 was observed in traditional electrochemical processes [16]. Similar behaviour was observed by Nam and Logan [17] in their work for hydrogen production in two chamber microbial electrolysis cell.

TABLE 3 Rate constant at different initial pH, $[Co^{+2}]$=50ppm, E=1.8V

pH	K(min^{-1})
3	0.003893
5	0.007367
7	0.010706
9	0.008329

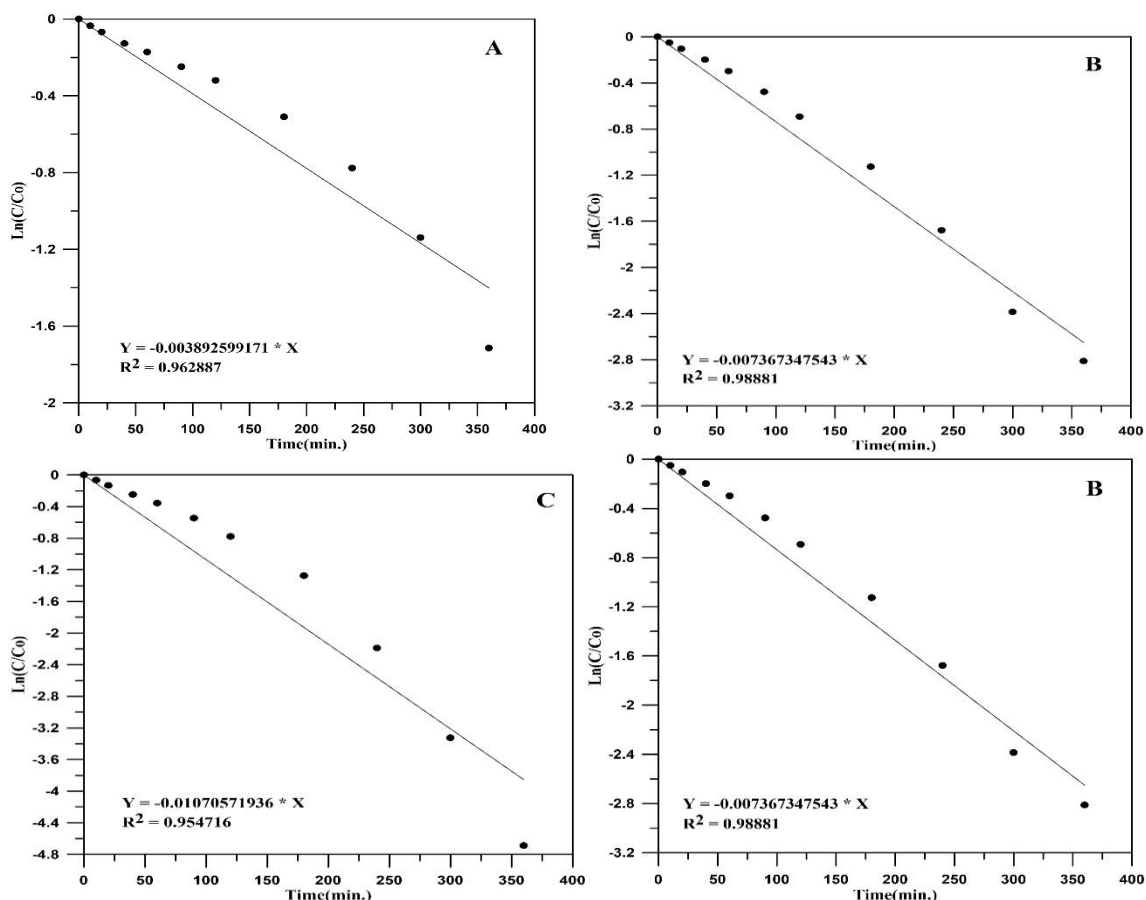**FIGURE 8** Plots of ln(C/Co) against time at different initial pH:
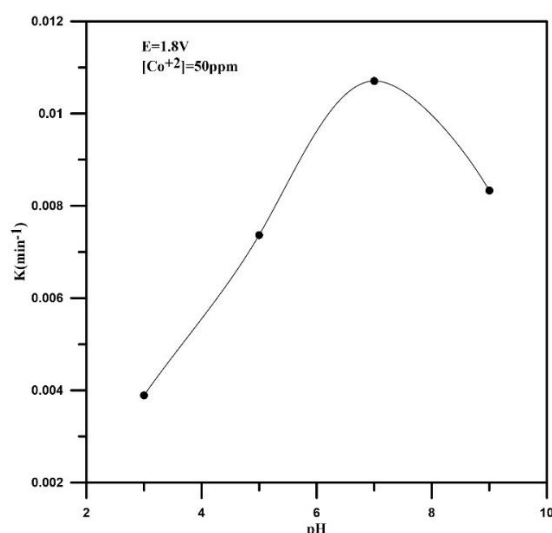A) 3, B) 5, C) 7, D) 9. E=1.8V, $[Co^{+2}]$=50ppm

FIGURE 9 Effect of pH on the rate constant

4. Conclusions

Kinetics of cobalt removal from aqueous solution using a flow-by fixed bed bio-electrochemical reactor were investigated and it was found that cobalt removal at different operating conditions followed a first order kinetic. Results showed that rate constant is affected by initial concentration of cobalt, voltage of cell, and pH. An exponential correlation between rate constant and applied voltage was obtained which is similar to Arrhenius form. The increase in the applied voltage leads to enhancement the rate constant while an increase in concentration has an opposite effect. pH has two dissimilar effects on the rate constant, its increasing from 3-7 leads to an increase in the rate constant while at alkaline condition, the rate constant was found to be declined.

Conflicts of interest
    "There are no conflicts to declare".

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