Efficiency of Two Types of Activated Carbon Columns to Treat Industrial Wastewater: A Case Study

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***Abstract*—**Heavy metals are hazardous elements in aqueous solutions which threaten the living thing organisms. Steel making plant is among the industries which may generate high amounts of pollutants and can possess high values of heavy metals. In this research granular activated carbon material is used in two different types: 1) column made of separate layers of activated carbon and sand 2) column made of mixed layers of activated carbon and sand. Then the removal efficiency of TDS, Turbidity, Fe Concentration, Zn Concentration and Mn Concentration are considered. Based on the results, both systems can efficiently remove heavy metals from this wastewater while they have some minor differences. In the end, the Freundlich and Langmuir isotherms are evaluated for both adsorption columns. These models showed that they can match with experimental results efficiently.

***Keywords*—**Granular Activated Carbon, Adsorption, Freundlich, Langmuir, Removal Efficiency.

I. Introduction

Heavy metals are recognized as toxic and pollutant elements which exhibit metallic properties in the environment and typically possess gravity greater than five. With the rapid development of industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries, pesticides and etc., heavy metals wastewaters are directly or indirectly discharged into the environment increasingly, especially in developing countries [1 , 2]. Steel making plants are among the industries which may generate high amounts of heavy metals if treated partially (or not treated at all) and can seriously threaten the environment and humans lives. Typically major heavy metal pollutants which may exist in this industrial plant include iron, manganese, zinc, cyanic, cobalt and alike.

One main concern relating to steel making plants is their deep dependence on water sources. As an example, Sirajuddin et al reported that in India, on an average each ton of steel production, 25 to 60 cubic meters of water and 4 to 5 tons of other raw materials are consumed. It may be noted that in developed countries the water consumption for each ton of steel production varies from 3 to 6 cubic meters [3]. In another study in China, iron and steel production plant is recognized as a major water consumer, such that iron and steel enterprises are focusing attention on the rationalization of water resources to reduce the fresh water consumption per ton steel. China has the largest steel output in the world, and water consumption by iron and steel industry accounts for about 14% of the total industrial water used in China [4]. Furthermore Beh et al reported that each steel mill in Malaysia uses average of about $18000\ m^3$ of water per day. This large amount of water is mainly used in the steel production for cooling purposes. Among all components existing in the wastewater of steel making plants, iron has the highest concentration depending on the raw material used for steel production [5]. Therefore large amounts of water will get polluted during the steel production procedure and the necessity of an economical and practical method of treatment seems crucial.

Recently there have been introduced several methods to remove heavy metals from aqueous environment but most of them suffer from some restrictions. For instance, electro-coagulation, oxidation/filtration, ion exchange and membrane filtration are all successful methods to remove heavy metals from water or wastewater, but they all suffer from the rapid clogging and pollutant concentration. On the other hand, activated carbon is among the successful treatment materials in the field of water and wastewater treatment. Activated Carbon is a crude form of graphite with a random or amorphous structure, which is highly porous, exhibiting a broad range of pore sizes, from visible cracks, crevices and slits of molecular dimensions. The basis for modern industrial production of Activated Carbons (AC) was established in 1900–1901 to replace bone char in the sugar refining process [6]. ACs adsorptive properties are due to such factors as high surface area (ranges from 500 to 1500 $m^2.g^{-1}$), well-developed internal microporosity, and wide spectrum of surface functional groups [7]. Activated carbon has been used in powder, granular and fiber in water treatment. In the previous studies, Cr (VI) adsorption by activated carbon occurred by two major interfacial reactions: adsorption and reduction, both depending

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on micro-porous structure and surface functionality. Cr (VI) adsorption reached a peak value at pH 5.0–6.0. Cr (III) is less adsorbable than Cr (VI) [6]. In 2011, both powder and granular activated carbon were used for removal of different micro-pollutants [8]. In the other study Phenol is removed by adsorption of activated carbon [9]. In another study lead was successfully removed from aqueous solutions [10].

In this study two types of activated carbon columns (separate layer and mixed later) are described and their efficiency to remove heavy metals, TDS and Turbidity from a case study steel making plant is experimented. In the end the Freundlich and Langmuir isotherms for both columns are introduced.

II. Materials and Methods

A. Simulated Water

In this study, simulated wastewater was applied to activated carbon columns. The characteristics of steel making plant wastewater were obtained from the results of a wastewater in Malaysia. Table 1 shows the characteristic of steel making plant wastewater and Standard B values of Malaysia [6].

Table 1. Characteristic of Steel Making Plant

Parameter	Unit	Before Treatment	Standard B
pH	-	6.3	5.5 – 9.0
Temperature	°C	26.5	40
BOD_5	mg/lit	80.4	50
COD	mg/lit	361	200
TSS	mg/lit	345	100
Cyanide as C_N	mg/lit	$N.D. (< 0.01)$	0.10
Boron as B	mg/lit	0.5	4.0
Phenol	mg/lit	$N.D. (< 0.001)$	1.0
Free Chlorine as Cl_2	mg/lit	$N.D. (< 0.01)$	2.0
Sulphide as S	mg/lit	$N.D. (< 0.01)$	0.50
Oil & Grease	mg/lit	$N.D. (< 0.5)$	10.0
Cadmium as Cd	mg/lit	$N.D. (< 0.001)$	0.02
Chromium as Cr^{+3}	mg/lit	$N.D. (< 0.03)$	1.0
Chromium as Cr^{+6}	mg/lit	$N.D. (< 0.005)$	0.05
Lead as Pb	mg/lit	$N.D. (< 0.01)$	0.5
Copper as Cu	mg/lit	0.83	1.0
Manganese as Mn	mg/lit	1.56	1.0
Nickel as Ni	mg/lit	$N.D. (< 0.01)$	1.0
Zinc as Zn	mg/lit	4.02	2.0
Iron as Fe	mg/lit	23.3	5.0
Mercury as Hg	mg/lit	$N.D. (< 0.001)$	0.05
Arsenic as As	mg/lit	$N.D. (< 0.001)$	0.10
Tin as Sn	mg/lit	$N.D. (< 0.002)$	1.0
Silver as Ag	mg/lit	$N.D. (< 0.02)$	1.0
Aluminium as Al	mg/lit	1.46	15
Fluoride as F	mg/lit	1.44	5
Ammoniacal Nitrogen	mg/lit	1.35	20
Barium as Ba	mg/lit	$N.D. (< 0.05)$	2.0
Formaldehyde	mg/lit	$N.D. (< 0.2)$	2.0

* N.D. means Not Detected

As it can be seen from Table 1, iron ($23.3\ mg/lit$), zinc ($4.02\ mg/lit$) and manganese ($1.56\ mg/lit$) have the highest concentrations which iron precedes other values. According to this table, all other elements meet the standard values except Fe, Mn and Zn. Therefore if only Fe, Mn and Zn concentrations are observed and treated, no threat exists for environment [5]. Therefore the simulated wastewater (containing all elements and mixture in Table 1) will be introduced to the adsorption column and after passing several layers of adsorption, the final concentration of Fe, Mn and Zn will be measure. In addition the value of TDS and Turbidity will be evaluated to check the efficiency of these columns.

B. Materials and Apparatus

In this study the industrial activated carbon (Jacobi from Sweden) is used in two different adsorptive columns. In the first column the layers of granular activated carbon and drainage sand are separately established, while in the second column the materials of granular activated carbon and sand are mixed to form a uniform material. The main reason to study the influence of layering in adsorption column is to find the economical numbers of layers to fully remove the pollutants. Figure 1 schematically shows the difference between two columns.

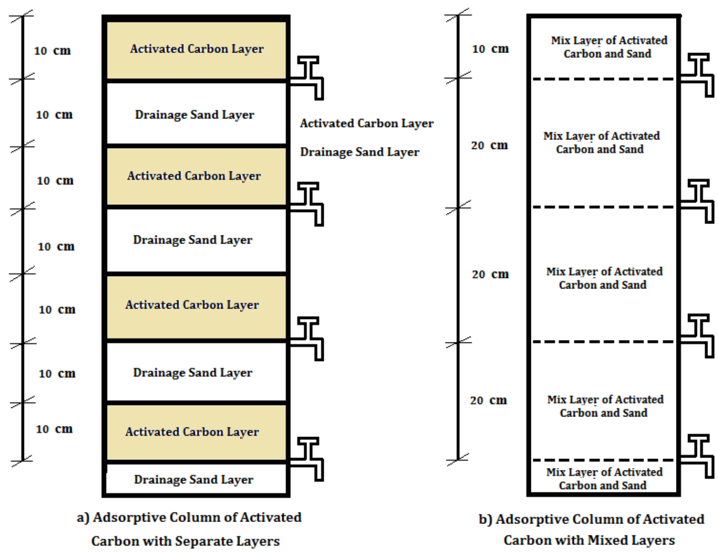

Figure 1. Schematic figure of adsorption columns

In addition Table 2 shows the sieve analysis of granular activated carbon and sand.

Table 2. Comparison of Activated Carbon and Sand Sieving

Mesh Number	Mesh Size	Activated Carbon Percent Passage	Sand Percent Passage
# 4	4.75	100.0	100.0
# 8	2.36	95.2	98.9
# 16	1.18	25.8	32.2
# 30	0.6	1.0	12.1
# 50	0.3	0.3	3.1
# 100	0.15	0.2	0.9
# 200	0.075	0.0	0.0

C. Applied Relations

The adsorption capacity of activated carbon may be determined by the use of an adsorption isotherm. The adsorption isotherm is an equation relating the amount of solute adsorbed onto the solid and equilibrium concentration of the solute in solution at a given temperature. The most commonly used isotherms for the application of activated carbon in wastewater treatment are the Freundlich and Langmuir isotherms, written, respectively as [11]:

$$\frac{X}{M} = k[C]^{1/n} \qquad Eq.(1)$$

$$\frac{X}{M} = \frac{a\,b\,[C]}{1+b\,[C]} \qquad Eq.(2)$$

To measure the heavy metal removal, an initial concentration of the heavy metal was added to the reservoir tank and then pumped into the adsorption columns. The removal efficiency is stated using Eq. (3) where $E(\%)$ is the removal efficiency and C_p and C_0 are the permeate and feed concentration [12]:

$$E(\%) = \left[1 - \frac{C_p}{C_0}\right] \times 100 \qquad Eq.(3)$$

III. Results and Discussions

In the section, the simulated wastewater is introduced to the adsorptive column. In order to find the influence of pH, different pH values (5, 6.5, 8 and 9.5) are applied and finally the optimum pH is achieved. In addition because the influent flow rate is effective, the influence of two different flow rates is considered. Finally because iron has the highest concentration among heavy metals in the influent, thus its concentration has varied to check out the efficiency of these columns. The objective of this study is to consider the removal rate of TDS, Turbidity, Fe concentration, Zn Concentration and Mn concentration. The following tables show the results of the final layer as the best removal efficiency while the measurements were done for each 20cm layer. Because all the following values were achieved for all layers, and this makes a lot of numbers, they are not presented in this section and their final result is just shown.

A. Influence of pH

Table 3 depicts the influence of different pH on the removal efficiency of wastewater. As it can be seen from Table 3, as the wastewater passes through the more layers, the removal efficiency increases for both types of columns. The main reason of this phenomenon is the increase of contact time and contact length of activated carbon and wastewater. As it can be seen, pH=6.5 is the optimum value for most of the parameters in both types of columns. The negative point of separate layer type of column is that if the high efficiency of heavy metal removal is objective, therefore the maximum number of layers is necessary. It means they perform weak when the number of activated carbon layer is minimum. On the contrary, mixed layer column can perform well even if the number of layers is minimum. However after the fourth layer of activated carbon the removal efficiency of heavy metals (Fe, Mn and Zn) , TDS and Turbidity for the separate layer type is higher than mixed layer type. While adsorption columns are effective to remove heavy metals and Turbidity from wastewater, they are not truly efficient to remove TDS in both types of columns.

B. Influence of Influent Flow Rate

Table 4 shows the influence of influent flow rate on the removal efficiencies. All experiments of this section were done at optimum value of pH equals 6.5. In this section two different flow rates (2 and 6 lit per min) were introduced to wastewater. As it can be seen from Table 4, as the flow rate increases, the removal efficiency reduces. The main reason of lower removal efficiencies when the flow rate increases, is that the contact time of activated carbon decreases which results in the lower removal efficiency. In other words, in higher flow rates, the adsorbent materials have lower chance to remove pollutants. In the previous section it was mentioned that removal rates for heavy metals, TDS and Turbidity for separate layer column is a little better than mixed layer, but in higher influent flow rate, these values are much better in the mixed layer column, which emphasizes the power of this column type.

C. Influence of Higher Concentrations of Fe

In this section, the concentration of Fe increases from 23.3 mg/lit to 35 and 50 mg/lit to evaluate the efficiency of activated carbon column to remove heavy metals. All experiments were done at constant value of flow rate equals 2 lit per minute and optimum value of pH=6.5. As the concentration of Fe increases, the adsorptive column will face difficulty to remove pollutants. Table 5 shows the results of higher concentrations of iron. As it can be seen in this Table, adsorptive column could efficiently remove heavy metals (especially iron) without any remarkable difficulty.

Table 3. Influence of pH on Removal Efficiency for the Separate and Mix Layer Adsorption Columns

Column Type	Layer	Mix	Layer	Mix	Layer	Mix	Layer	Mix
Determined Parameter	TDS (mg/lit)	TDS (mg/lit)	C_{Mn} and C_{Zn} (mg/lit)	C_{Mn} and C_{Zn} (mg/lit)	C_{Fe} (mg/lit)	C_{Fe} (mg/lit)	Tu (NTU)	Tu (NTU)
$pH = 5.0,\ \ Q = 2\ lit/min$	33.9 %	23.3 %	100 %	100 %	100 %	100 %	87.6 %	88.3 %
$pH = 6.5,\ \ Q = 2\ lit/min$	42.8 %	22.4 %	100%	100%	100%	100%	90.6 %	92.6 %
$pH = 8.0,\ \ Q = 2\ lit/min$	48.9 %	19.3 %	100 %	100 %	100 %	100 %	91.0 %	89.9 %
$pH = 9.5,\ \ Q = 2\ lit/min$	50.2 %	20.4 %	100%	100%	100%	100%	96.4 %	92.8 %

Table 4. Influence of flow rate on Removal Efficiency for the Separate and Mix Layer Adsorption Columns

Column Type	Layer	Mix	Layer	Mix	Layer	Mix	Layer	Mix
Determined Parameter	TDS (mg/lit)	TDS (mg/lit)	C_{Mn} and C_{Zn} (mg/lit)	C_{Mn} and C_{Zn} (mg/lit)	C_{Fe} (mg/lit)	C_{Fe} (mg/lit)	Tu (NTU)	Tu (NTU)
$pH = 6.5, \quad Q = 2\ lit/min$	42.8 %	22.4 %	42.5 %	22.5 %	100 %	100 %	90.6 %	92.6 %
$pH = 6.5, \quad Q = 6\ lit/min$	22.9 %	23.5 %	22.4 %	22.9 %	100 %	100 %	91.1 %	88.2 %

Table 5. Influence of High Concentrations of Iron on Removal Efficiency for the Separate and Mix Layer Adsorption Columns

Column Type	Layer	Mix	Layer	Mix	Layer	Mix	Layer	Mix
Determined Parameter	TDS (mg/lit)	TDS (mg/lit)	C_{Mn} and C_{Zn} (mg/lit)	C_{Mn} and C_{Zn} (mg/lit)	C_{Fe} (mg/lit)	C_{Fe} (mg/lit)	Tu (NTU)	Tu (NTU)
$pH = 6.5, \quad Q = 2\ lit/min, \quad Con_{Fe} = 23.3$	42.8 %	22.4 %	42.5 %	22.5 %	100 %	100 %	90.6 %	92.6 %
$pH = 6.5, \quad Q = 2\ lit/min, \quad Con_{Fe} = 35$	29.1 %	22.7 %	28.6 %	22.2 %	100 %	100 %	90.3 %	88.5 %
$pH = 6.5, \quad Q = 2\ lit/min, \quad Con_{Fe} = 50$	54.3 %	45.3 %	53.8 %	45.3 %	99.6 %	98.9 %	87.5 %	88.6 %

IV. Freundlich and Langmuir Isotherms

In this section the Freundlich and Langmuir isotherms will be applied to the results of wastewater in both adsorptive columns of separate and mixed layers. These models are done for the concentration of iron as the highest concentration pollutant. These two isotherms were studied due to their popularity for activated carbon and conventionally the other researchers have tried to apply them on their experimental works.

A. Separate Layer

The Freundlich model for Fe in the separate layer is as follow:

$$\frac{X}{M} = 0.19\ C_e^{\,0.396} \qquad Eq.(4)$$

The Langmuir model is as follow:

$$\frac{X}{M} = \frac{0.815\ C_e}{1 + 2.84\ C_e} \qquad Eq.(5)$$

Figure 2 shows the comparison of Freundlich and Langmuir isotherms with the experimental data of wastewater.

As it can be seen from the Figure 2, both models have well matched with the experimental results. Of course Freundlich model was expected to be more accurate due to its nature (being experimental) and it was a bit more accurate in comparison with Langmuir model (which is made theoretically).

B. Mixed Layer

The Freundlich model for Fe in the mixed layer is as follow:

$$\frac{X}{M} = 2.701\ C_e^{\,0.94} \qquad Eq.(6)$$

The Langmuir model is as follow:

$$\frac{X}{M} = \frac{1.607\ C_e}{1 + 5.235\ C_e} \qquad Eq.(7)$$

Figure 3 shows the comparison of Freundlich and Langmuir isotherms with the experimental data of wastewater.

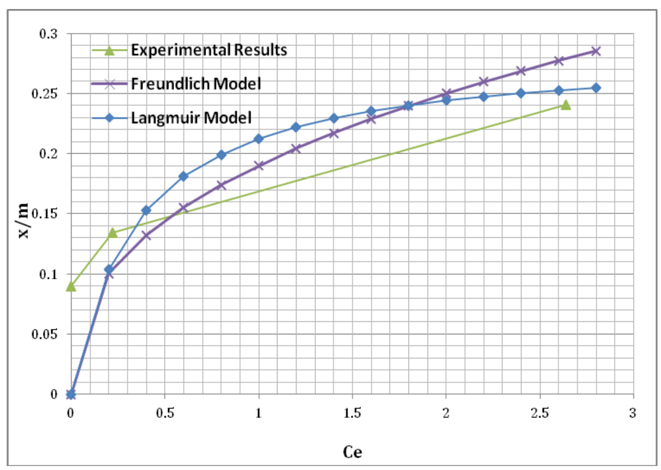

Figure 2. Results of Freundlich and Langmuir Isotherms vs. Experimental Results for the Separate Layer Column

As it can be seen from the Figure 3, both models have well matched with the experimental results. Of course Freundlich model seems to be more accurate.

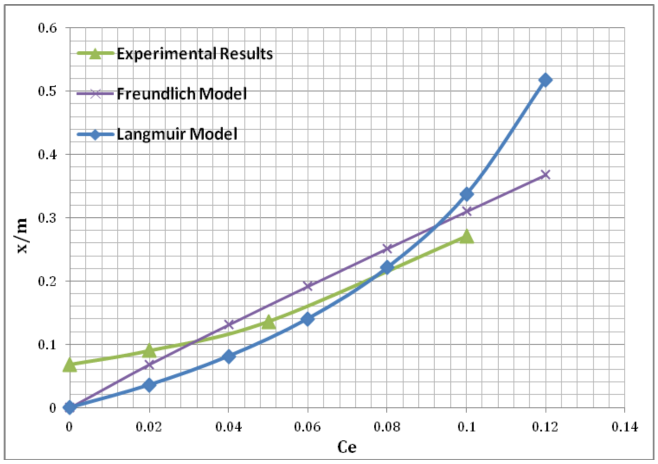

Figure 3. Results of Freundlich and Langmuir Isotherms vs. Experimental Results for the Mixed Layer Column

As a general conclusion for this wastewater, Freundlich model is introduced as a better isotherm to model the wastewater. The main reason may be attributed to the experimental base of Freundlich equation which normally fits better with the experimental studies. The other reason could be the nature of Freundlich model, which is suitable for adsorbents with rough surface while the base of Langmuir equation is for plane surfaces.

V. TDS and EC Relation

In this study the value of EC (Electrical Conductivity) and TDS (Total Dissolved Solid) was evaluated for both columns. Therefore the relation between EC and TDS can be considered and finally we can present a logical relation between them for this wastewater. There exist two reasons to study the relation between EC and TDS. First for many types of wastewaters when the TDS increases to values more than 2000 mg/lit, usually the laboratory tools cannot measure the TDS value. According to this relation, we can guess the value of TDS from the achieved value of EC. Second, this relation can show us if there is any change in the specification of adsorptive columns. It means if the suggested relation doesn't change during the experiment, so it shows the efficiency of this method and no clogging or undesirable occurrence happened.

A. Separate Layer

The values of EC and TDS are plotted against each other and the corresponding relation is obtained. Figure 4 shows the relation between EC and TDS. According to this figure, the corresponding relation is as follow:

$$TDS = 0.5024\ EC \qquad Eq.(8)$$

Equation (8) is within the typical relations of EC and TDS. Normally TDS equals (0.5 - 0.7) of EC for different wastewater.

B. Mixed Layer

For mixed layer the relation between EC and TDS is achieved Figure 5 shows the relation between EC and TDS for this type of column. According to this figure, the corresponding relation is as follow:

$$TDS = 0.5117\ EC \qquad Eq.(9)$$

Equation (9) is again within the normal values.

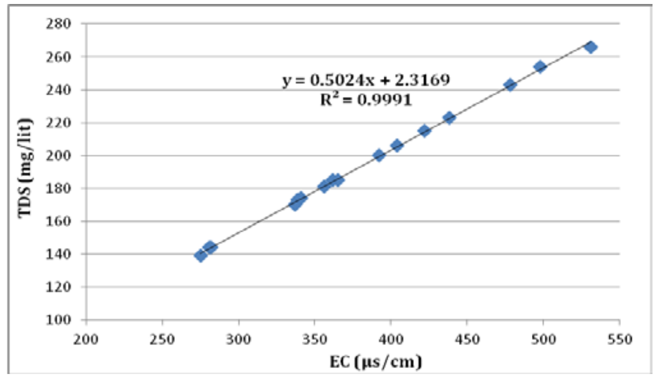

Figure 4. Relation between EC and TDS for the Separate Layer Column

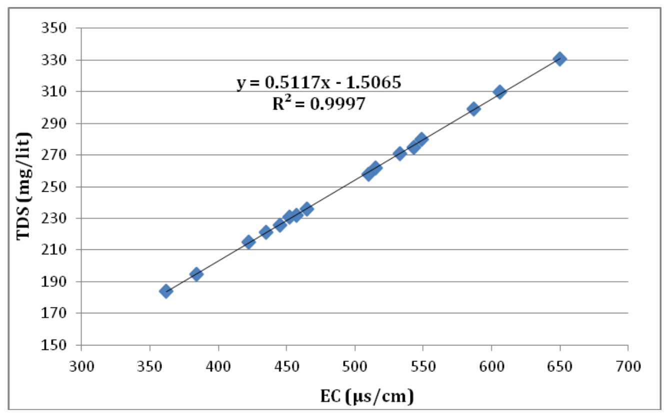

Figure 5. Relation between EC and TDS for the Mixed Layer Column

According to results shown in Figure 4 and 5, we can see that there are valid relations between EC and TDS. Also the relation between EC and TDS has not changed remarkably during the experiment.

VI. Conclusion

In this study the removal efficiency of an industrial wastewater (steel making plant) is considered. TDS, Turbidity, Fe concentration, Mn concentration and Zn concentration are measured as the objectives of this study. In this research two types of adsorptive columns (with separate layers and mixed layers) are considered to evaluate the removal efficiencies of the mentioned parameters. In the first step, optimum pH is evaluated for both adsorptive columns. Then the value of influent flow rate has changed to observe its influence of removal efficiency. Finally the concentration of iron has increased to consider the efficiency of these columns in heavy metal removals. According to the results, both types of columns were able to remove heavy metals with efficiency of more than 99 percent while their ability to remove TDS was not desirable. In addition optimum pH for both types of columns was the constant value of 6.5. Also as the influent flow rate increases, the removal efficiency of all parameters reduces. Furthermore higher concentration of iron did not have any remarkable influence on removal efficiencies.

Freundlich and Langmuir isotherms were applied to this wastewater and it was observed that Freundlich model matches well with the experimental results. The experimental basis of this model can be the reason as well as the concept of this isotherm, which is suitable for rough surfaces adsorption materials. In the end, TDS and EC relation was obtained for both types of columns and it was within the valid values.

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