

Adsorptive Separation of Copper by DION PK208 Ion Exchange Resin

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Abstract– Expanded bed is widening its horizons in continuous operations like adsorption, reaction etc. High density is one of the peculiar characteristics of the adsorbent, desired for using in such operations. So a high density ion exchange resin DION PK208 is selected for in depth understanding in adsorption of copper. Its characterization, equilibrium adsorption, kinetics and thermodynamics of adsorption are reported in this article.

Keywords - Adsorption, Kinetics, Thermodynamics, Ion-exchange resin.

I. Introduction

In recent years industrialization has significantly contributed for upgrading the quality of life. But on the other hand, there are some shortcomings like pollution, which adversely impacted the health of living beings. Trace metals, toxic solvents and other soluble and insoluble impurities contribute to the water pollution. Waste water from manufacturing units like electroplating, printed circuit boards, wire drawing, copper polishing, paint manufacturing, etc. [1] is rich in copper. Although its concentration varies depending on the type of operation, but its intake in the human body may lead to schizophrenia and the Alzheimer kind of diseases. Similarly, it is reported to damage the aquatic life.

Thus, there is a need for efficient processes for removal of such trace metals from wastewater. Various methods like precipitation, electrochemical techniques, and adsorptive separations are reported for isolation of copper from waste water. Each of these techniques has its choosiness depending on the type of wastewater and concentration of copper in it. Adsorption is preferred for a feed of low concentration. Researchers have explored various adsorbents like sawdust, tea waste, banana peel which are cheaper. These are explored as economical option, but high efficiency ion exchange resins are preferred choice for the removal of trace metals from wastewater [2-3].

So in recent years special emphasis was given over developing ion exchange resins and adsorption processes [4-6]. Bentonite is reported to reduce residual concentration of iron and molybdenum below the allowable limits [7-8]. Other ion exchange resins reported in the recent literature are 1500H and 252H for copper adsorption [9], IR-120 for heavy metals like copper, zinc, nickel, cadmium [10] and IRN77 for cobalt [11] etc.

Still, there is a need for more efficient ion exchange resin in adsorptive separation of heavy metals like copper.

In large scale, a fixed bed mode like packed bed with ion exchange resin is used for adsorptive separations. But this method has limitations like need of clear feed. If un-clarified feed passed through it, then it offers higher pressure drop across

the bed. Recently, expanded bed is reported to operate successfully for separation of bio-molecules from un-clarified feedstock [12-14]. So, a new realm of expanded bed process in adsorptive separations in wastewater treatment seems attractive. But these needs adsorbent with characteristics like high density, porosity, and appropriate particle size distribution [16]. So there is a need for studying adsorption characteristics of ion exchange resins suitable for use in expanded bed operation.

In line with this, an ion exchange resin DION PK208 is identified. Its characterization through SEM-EDX, FTIR and XRD are carried out. Also an equilibrium, kinetics and thermodynamics of adsorption at different concentration of copper have been carried out systematically. These studies and its analysis by using various models are reported in this article.

II. Materials and Methodology

A. Physical Characteristics of Adsorbent

The ion exchange resin is characterized through FTIR for functional groups, XRD for crystallinity, SEM for morphology and SEM-EDX for elemental distribution.

B. Equilibrium Studies

Different concentrations of copper sulphate solution (50mL) were taken in a set of 100mL reaction bottles. A fixed volume (5mL) of fresh ion exchange resin i.e. DION PK208 is charged into each bottle. The bottles are kept in a shaking incubator at 200rpm and 30°C for 8 hours. After reaching equilibrium, these are allowed to settle. The liquid is then decanted and analyzed for residual copper.

C. Kinetics Studies

Kinetics of copper adsorption on ion exchange resin DION PK208 is studied at three different feed concentrations of 50, 100 and 150mg/L. A fixed volume, i.e. 400mL of copper sulphate solution is taken in a 500mL three necked round bottom flask. Then 5mL of fresh DION PK208 is charged into it. These adsorbents are kept in suspension by stirring at 600RPM by using a magnetic stirrer. Adsorption is continued for 7 hours and every hour, the residual copper concentration in the liquid phase is analyzed.

D. Thermodynamic Studies

Thermodynamics of copper adsorption on ion exchange resin DION PK208 is studied at three different temperatures of 20°C, 40°C and 60°C and feed concentrations of 50, 100 and 150mg/L. 400mL of copper sulphate solution is taken in a 500mL three necked round bottom flask and 5mL of fresh DION PK208 ion exchange resins is added to it. Resins are kept in suspension by a magnetic stirrer for 7 hours. Residual copper concentration in the liquid phase is analyzed at an interval of one hour.

III. Results and Discussions

A. Physical Characteristics of Adsorbent

The fresh ion exchange resin of DION PK208 is characterized through FTIR, XRD to understand the insights of adsorbent properties. Copper loaded DION PK208 is characterized through

SEM-EDS for morphology, surface structure and surface elemental distribution. For FTIR spectra, resins are grinded and mixed with KBr in the ratio of (2 mg resin/200 mg KBr). Then pellets are made using the mixture and FTIR is taken using PerkinElmer 1750 instrument in 4000-450 cm⁻¹ range. The result is shown in Figure 1.

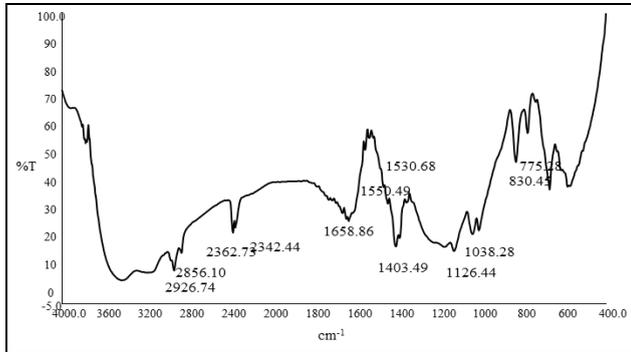


Figure 1: FTIR of DION PK208 ion exchange resin

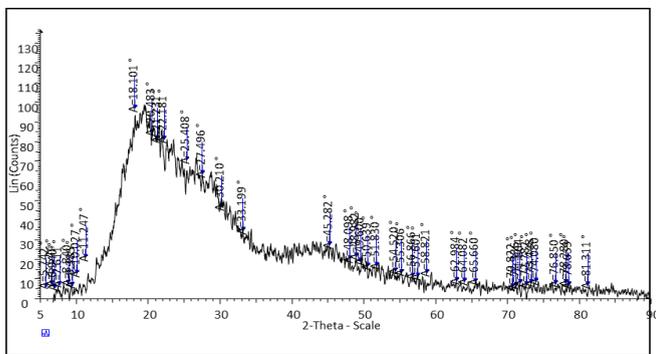


Figure 2: XRD of DION PK208 ion exchange resin

For crystallinity study, grinded fresh resin sample of DION PK208 was subjected to X-Ray diffraction using Bruker D8-Advanced X-Ray diffractometer [17]. Scanning rate for the analysis was 1° min⁻¹ over the range of the diffraction angle (2θ) of 0-100° and the resulting diffraction pattern is shown in Figure 2. No sharp peaks are observed in the diffractogram of DION PK208, indicating its amorphous nature [18].

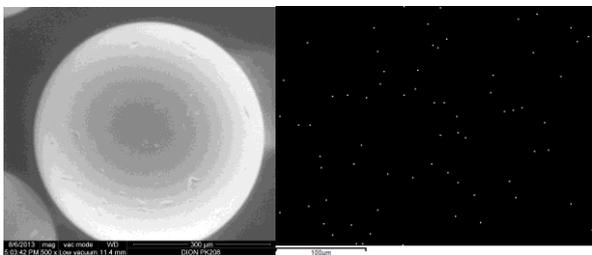


Figure 3: SEM-EDS diffractogram of DION PK208 after copper adsorption.

SEM shows highly spherical ion exchange resin and smooth surface with tiny spots on it. EDS is carried out after the adsorption of copper by the resin. It shows almost uniform distribution of copper on the surface of the resin matrix, as shown in Figure 3 by the white dots in the black matrix.

B. Equilibrium Studies

Adsorption capacity of ion exchange resin is evaluated by equilibrium studies where adsorption is carried out at a different feed concentration and at a constant resin amount and temperature.

Table 1: Isotherm parameters for copper adsorption

| Isotherm | Model | Parameters | Value |
|---------------------------|--|-----------------------|--------|
| Langmuir [20] | $\frac{1}{q_e} = \frac{1}{Q^0} + \frac{1}{bQ^0} \frac{1}{C_e}$ | Q ⁰ (mg/g) | 4.200 |
| | | b (L/mg) | 595.3 |
| | | R ² | 0.991 |
| Freundlich [21] | $q_e = K_F C_e^{1/n}$ | K _F (mg/g) | 3.170 |
| | | n | 2.671 |
| | | R ² | 0.982 |
| Redlich-Peterson [22] | $\frac{C_e}{q_e} = \frac{1}{K_R} + \frac{\alpha_R}{K_R} C_e^\beta$ | K _R (L/g) | 63.07 |
| | | α _R (L/mg) | 9.195 |
| | | β | 0.699 |
| | | R ² | 0.992 |
| Temkin [23] | $q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln(C_e)$ | b | 269.6 |
| | | A (L/g) | 243.3 |
| | | R ² | 0.660 |
| Dubinin-Radushkevich [24] | $\ln q_e = \ln q_s - B \epsilon^2$ | q _s (mg/g) | 70.82 |
| | | ε | 7071.1 |
| | | R ² | 0.738 |

The resultant data are analyzed using various isotherms like Freundlich, Langmuir, Redlich–Peterson, Temkin and Dubinin–Radushkevich. Model parameters are shown in Table 1.

Out of the five isotherms, Langmuir and Redlich-Peterson model shows the best fit for the adsorption. It shows the equilibrium copper adsorption capacity of 4.2 mg/g for DION PK208.

C. Kinetics Studies

Adsorption kinetics is studied for estimating rates of ion uptake on adsorbent, as it controls the equilibrium time [19]. Three different feed concentrations 50, 100 and 150mg/L were used for investigating it. Results are shown in Figure 4. The data are analyzed using pseudo first order, second order and Weiber-Morris model for investigating the adsorption mechanism. It is observed that, initially the rate of adsorption was found to be very high until 60-70% of total ion gets adsorbed. It is then decreased with a reduction in solution concentration. For a feed concentration of 150mg/L, the adsorption curve is almost linear, and decreases in lower feed concentration.

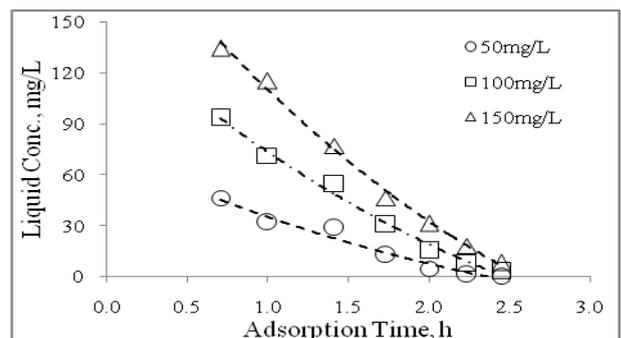


Figure 4: Adsorption of copper on DION PK208 resins

C.1. Pseudo-First-Order Kinetic Model

Pseudo-first-order kinetic model for adsorption is as shown by equation (1) [25].

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (1)$$

When the rate of adsorption varies proportional to time, it can be explained by a single model.

The above equation (1) is a linear equation, and the linear plot of $\log(q_e - q_t)$ versus time explains pseudo first order model. The model for the whole adsorption period gives poor fit compared to the initial period of adsorption for the feed concentrations of 50 and 100mg/L. It fits well for the initial period of adsorption, whereas in case of 150mg/L it explains the whole adsorption period. In case of lower concentration of feed, solution concentration change is significant. So, the later stage of adsorption proceeds at a relatively slower rate. In this stage there is a significant deviation for fitting to the pseudo first order model. In case of feed 150mg/L, residual concentration is significantly higher for a longer period of time. So, the curve is almost linear. Rate constants are calculated from the slopes and intercepts of the plots and found to decrease with increase in initial feed concentration.

Table 2: Kinetic parameters for adsorption of copper on DION PK208 Ion Exchange Resin

| Feed conc. mg/L | Weiber and Moris | | Pseudo first order kinetics | | Pseudo second order kinetics | |
|--------------------|------------------|-------|-----------------------------|-------|------------------------------|-------|
| | k_{id} | R^2 | k_1, h^{-1} | R^2 | $k_2, g/(mg.h)$ | R^2 |
| 50 | 1.936 | 0.863 | 0.115 | 0.933 | 0.053 | 0.975 |
| 100 | 3.667 | 0.951 | 0.092 | 0.976 | 0.018 | 0.981 |
| 150 | 5.298 | 0.988 | 0.085 | 0.995 | 0.014 | 0.984 |

When the rate of ion exchange is proportional to the first power of concentration, it is favoured by surface adsorption. It is found that in the case of feed concentration of 50 and 100 mg/L metal adsorption rate is proportional at the initial period only. In the later stage it decreases, indicating the influence of pore diffusion resistance. Similar results are also reported by Ho and McKay [26] for dyes on peat particles, Rengaraj et al., [9] for copper on 252H and 1500H. But in case of higher concentration of feed i.e. 150mg/L, adsorption rate is proportional to feed concentration in the entire adsorption process.

C.2. Pseudo-Second Order Kinetic Model

In the pseudo-second order model adsorption rate is directly proportional to the number of active sites. So it is dependent on equilibrium adsorption and the surface concentration of solute on the adsorbent's surface [27]. The model equation for pseudo-second order kinetics is by equation (2).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

The initial adsorption rate is as given below.

$$R_i = k_2 q_e^2 \quad (3)$$

From equation (2), t/q_t is plotted against time at different feed concentrations. Its slope and intercept give the values of the model parameters for second order adsorption kinetics as shown in Table 2.

From the correlation co-efficient (R^2), it is observed that low concentration feed follows second order kinetics whereas higher concentration feed follows pseudo first order kinetics. Kinetic constant decreases with feed concentration, but the initial rate increases with the feed concentration. This model agrees well with most of the data, so confirming chemisorption of copper on the resin.

C.3. Adsorption Mechanism

The adsorption process consists of a series of steps, where the entire adsorption is governed by rate limiting step. These are mainly external mass transfer (boundary layer diffusion) or internal mass transfer (intra-particle diffusion). It is also possible that different resistances may control the process at different time period i.e., copper adsorption on ion exchange resins may be controlled by film diffusion at initial stage and later by the particle diffusion. To design a process, it is very important to know the adsorption mechanism and the rate limiting step [28]. Weiber and Morris model [29] as shown in equation (4) is used for determining rate limiting step in the adsorption process.

$$q_t = k_{id} t^{0.5} \quad (4)$$

The plot of q_t versus $(t)^{0.5}$ is shown in Figure 5.

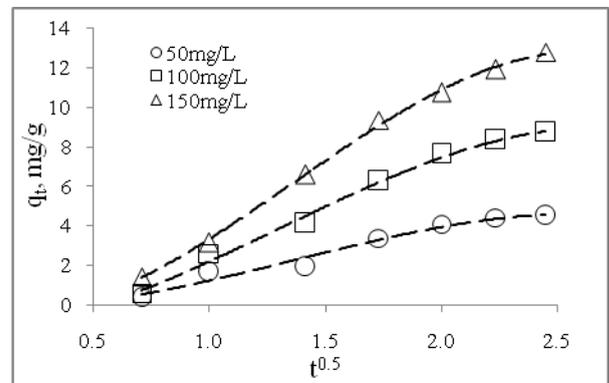


Figure 5: Adsorption kinetics of copper on DION PK208 ion exchange resins

From Figure 5, an initial adsorption period of up to $1.75 h^{0.5}$ is linear for all the studied feed concentrations. So it shows up to $1.75 h^{0.5}$, adsorption process is governed by external surface adsorption. After $1.75 h^{0.5}$, the slope of adsorption curve decreases i.e., from 1.75 to $2.5 h^{0.5}$ there is gentle sloped curve. It shows that the adsorption is governed by intra particle diffusion. So, the gentle-sloped portion from 1.75 to $2.5 h^{0.5}$ is analysed using Weiber and Morris model. The intra particle diffusion coefficient was obtained from the slope of the Weiber and Morris plot and shown in Table 3.

The diffusion resistances are a strong function of the solute concentration. The higher the concentration, lower the diffusion resistance and vice versa. It is confirmed by the slope of Weiber and Moris plot in Figure 5, for different concentrations of the feed. The intra particle diffusion coefficient i.e. k_{id} obtained from the slope of Weiber and Moris plot is shown in Table 3.

Table 3: Weiber and Moris parameter for adsorption of copper on DION PK208 ion exchange resin

| Feed conc., (mg/L) | Intra particle diffusion coefficient, k_{id} | Correlation coefficient, R^2 |
|--------------------|--|--------------------------------|
| 50 | 1.9362 | 0.863 |
| 100 | 3.6671 | 0.951 |
| 150 | 5.2986 | 0.988 |

The intra particle diffusion coefficient is found to increase with increase in feed concentration. It subsequently decreases as adsorption proceeds, because of the lower residual solute concentration in the solution. From Table 3, the correlation coefficient increases with increase in feed concentration. It confirms the role of diffusion resistances in the adsorption of copper on ion exchange resin.

D. Thermodynamic Studies

Adsorption is a temperature dependent process. As it is an exothermic process it is favoured at lower temperature. But, when the process is pore diffusion resistance controlled, then higher temperature also helps to promote diffusion. These two counter effects make adsorption thermodynamics as a process specific parameter, having its own optimized operational window.

Distribution coefficient is the ratio of equilibrium capacity and solute concentration in the raffinate and is given by equation (5).

$$K_d = \frac{q_e}{c_e} \quad (5)$$

Change of molar enthalpy and entropy are related to distribution coefficient as [30].

$$\ln(K_d) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6)$$

Figure 6 shows the influence of temperature on copper adsorption by DION PK208 ion exchange resin at different feed concentrations. The slope and intercept of the plot give thermodynamic parameters as shown in Table 4.

The change of Gibbs free energy is given by [31].

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7)$$

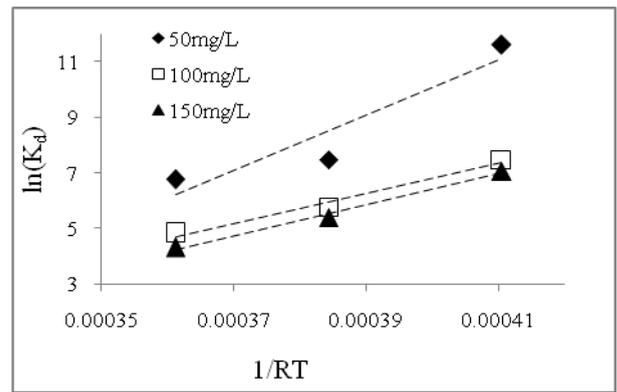


Figure 6: Influence of temperature on adsorption of Cu(II) on DION PK208 ion exchange resin

Table 4: Thermodynamic parameters for adsorption of copper on DION PK208 ion exchange resins

| Feed conc. mg/L | ΔS° kJ/mol.K | ΔH° kJ/mol | ΔG°_{293} kJ/mol | ΔG°_{313} kJ/mol | ΔG°_{333} kJ/mol | R^2 |
|-----------------|---------------------------|-------------------------|-------------------------------|-------------------------------|-------------------------------|-------|
| 50 | -0.248 | -99.8 | -27.1 | -18.0 | -17.1 | 0.953 |
| 100 | -0.133 | -56.1 | -18.0 | -15.5 | -14.4 | 0.995 |
| 150 | -0.123 | -54.1 | -17.1 | -13.1 | -11.8 | 0.999 |

From Table 4, it is clear that ΔG° is negative and increases with increase in adsorption temperature. It reflects reaction is spontaneous and favoured at lower temperature in the range of concentrations studied. Also the change in Gibbs free energy is found to increase with increase in feed concentration. It means the adsorption rate is favoured by the amount of copper ions. The process is exothermic, as shown by the negative value of ΔH° . This is found to increase with increase in feed concentration. It may be due to higher initial adsorption rate, as more ions are available for exchange [32].

IV. Conclusions

Adsorption of copper on DION PK208 follows Redlich–Peterson isotherm with uniform solute distribution on the resin. The adsorption kinetics confirms that major adsorption is governed by surface adsorption. Weiber and Moris model confirms enhanced intra particle diffusion coefficient with an increase in the feed concentration.

Constants

- C_e - Equilibrium concentration (mg/L)
- q_e - Equilibrium adsorption (mg/g)
- q_t - Adsorption at time 't' (mg/g)
- Q_t and b - Langmuir constants
- K_F - Freundlich constant
- K_R, α_R, β - Redlich-Peterson isotherm constants
- k_1 - First order adsorption rate constant (1/h)
- k_2 - Second order adsorption rate constant (g/mg.h)
- k_{id} - Intraparticle diffusion coefficient
- T - Temperature (K)
- R - Universal gas constant (J/mol.K)
- ΔH° - Change in molar enthalpy (J/mol)
- ΔS° - Change in molar entropy (J/mol.K).

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