Removal of aniline from aqueous solution by PVC-CDAE ligand-exchanger

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Abstract

The adsorption of aniline from aqueous solutions onto cobalt(II)-poly(vinyl chloride)-carboxylated diaminoethane (PVC-CDAE) resin has been studied using a mini-column apparatus at $25 \pm 0.1\,^\circ$C. First of all, experimental data obtained from the breakthrough curves were tested by using the Scatchard plot analysis, to have a preliminary prediction about the types of interaction of the resin with aniline. Our aim was to determine the model which best describes the experimental data. The aspect of the Scatchard plot indicated that the aniline adsorption did not follow the Langmuir model and the presence of two types of binding sites for aniline on the resin. However, the dynamics of aniline uptake were represented by the Freundlich model reasonably well. The kinetics of aniline adsorption from aqueous solution on the cobalt(II)-PVC-CDAE have also been tested using continuous column runs and rate-controlling step of the process was determined. In this study, homogeneous diffusion model was adapted to a column system to describe the change in the aniline concentration at the column exit beginning from breakthrough point as a function of time. Kinetic studies revealed that the rate-controlling step of the aniline adsorption was predominately film diffusion controlled rather particle diffusion.
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1. Introduction

Aromatic amines such as aniline and its derivatives are widely used in the manufacturing of rubbers and plastics, azo dyes, agrochemicals, pharmaceuticals and pesticides [1,2]. They are known to be toxic water pollutants and their presence in wastewater even in very low concentrations has been shown to be harmful to aquatic life [3,4]. Although they can easily seep through soil and contaminate groundwater due to their high solubility in water but, unfortunately, these compounds are still being released into the environment directly as industrial residues or indirectly as breakdown products of herbicides and pesticides [5–7]. Consequently, industrial wastewaters contain significant levels of organic pollutant and in order to avoid water pollution treatment is needed before disposal. In view of the importance of these compounds, a rapid and effective method should be developed to remove them from industrial wastes.

There are many processes, such as solvent extraction, activated carbon adsorption and ligand-exchange that can be used for the removal of organic contaminants from wastewater. Although solvent extraction and activated carbon adsorption are the most commonly used processes for this purpose, application of these processes; however, is sometimes restricted because of environmental or technical constraints. Solvent extraction usually produces liquid organic secondary waste which may cause environmental problems and desorption of activated carbon is very difficult because of regeneration costs. Therefore, there is a need for the development of different processes where organic compounds can be removed satisfactorily. Ligand-exchangers are widely used as an adsorbent for the removal of a wide range of pollutants from various matrices because of their

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high adsorption capacity, fast adsorption kinetics and ease of regeneration at low temperature without destroying the materials. We therefore considered the possibility of using a cobalt(II)-PVC-CDAE resin for the removal of aniline from aqueous solution by ligand-exchange process. Any compound that form coordination complex with transition elements can be removed by the ligand-exchange method. Ligand-exchangers have the particular advantage of combining high sorption capacity with high selectivity for the ligand.

The selectivity for the ligand improve by increasing the stability of the metal–ligand complex. Coordinatively saturated complexes are formed in the resin even when the ligand concentration in the external solution is very low [8]. In these processes, ligand-exchange is the most fundamental reaction. It was formally introduced and conceptualized by Helfferich [9,10]. Cu(II)- or Ni(II)-loaded weak acid cation-exchange resins were used by Helfferich to enhance the sorption of various ligands through relatively strong Lewis acid–base interactions. In such ligand-exchange processes, the water molecules (weak ligands) are present at the co-ordination spheres of immobilized Cu(II) and Ni(II) in the cation-exchange resins are replaced by relatively strong ligands, such as ammonia or ethylenediamine.

Although there have been some attempts to describe the attachment of ligands to immobilized cobalt(II)-carboxylated diaminoethane functional groups, the mechanism of adsorption was not well elucidated [11–14]. Therefore, this study was done to investigate the interaction between aniline and the cobalt(II)-PVC-CDAE using the Scatchard plot [15], followed by application of the experimental data to Freundlich isotherm method. To better understand the ligand adsorption processes, it is also necessary to investigate the kinetics of adsorption. In this work, we focused on the dynamic behaviour of the process via breakthrough curves and analyzed the rate-controlling step of the process on the bases of homogeneous diffusion model. Various methods for calculating the breakthrough data have been recently presented by several investigators [16–26]. However, these methods are very complex. We therefore offer a quite simple model to consider carefully the breakthrough curve of single component systems. A detailed investigation of adsorption behaviour of the cobalt(II)-carboxylated diaminoethane functional group is the main goal of this work. Thus, aniline was selected as the solute since its adsorption was previously studied on a similar ligand-exchanger, which has same functional group [13].

2. Experimental

2.1. Materials and apparatus

The commercial PVC with a particle size of 180–200 μm was chosen as a support material for this study. This material was reprecipitated from THF solution by ethanol for several times and finally was dried under vacuum at room temperature for 2 days. All chemicals were purchased from Merck Chemical Company and were of analytical reagents grade. Solutions were prepared using deionized water. Deionized water was used after double distillation in all glass assembly. Aniline was dissolved in deionized water and adjusted to the desired concentration. An Alitea S2 peristaltic pump was used to pump the feed solution. A Shimadzu 160 A UV–vis spectrophotometer was used as a UV detector in the adsorption process.
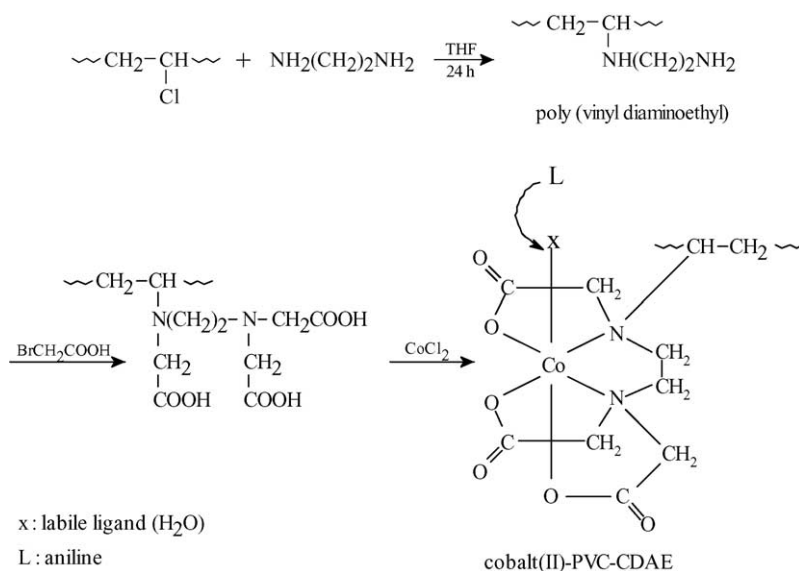
2.2. Modification of poly(vinyl chloride) as ligand-exchanger

The physical properties of the modified PVC with different metal ions and a chelating ligand have been previously studied in detail by Biswas and co-workers [27,28]. However, we here have investigated the adsorption capability of PVC modified with bromoacetic acid, diaminoethane and cobalt(II) ion by similar procedure [27]. Etylenediamine complexes posses a very stable structure with a minor dissociation tendency and act as suitable functional groups for a ligand-exchange matrix. PVC-CDAE which was obtained previously in our laboratory [29] was placed in a reaction vessel, and a 1 M CoCl$_2$ solution was added at pH 6.0. By this way cobalt cations were fixed to the resin matrix. Complex formation steps and ligand-exchange of aniline are illustrated in Scheme 1.

2.3. Column operations

An in-house-constructed column 3 cm in length and 4 mm i.d. was packed with the modified resin and was pre-equilibrated with deionized water. After the column had been conditioned, a solution having a known concentration of aniline was continuously fed into the column at a constant flow rate of 0.15 ml min^{-1} by a peristaltic pump. The column temperature was maintained at $25 \pm 0.1\,^\circ$C using a water jacket connected to a thermostated circulator. The amount of adsorbed ligand was determined by the breakthrough technique, where the aniline content in the effluent was measured by the flow UV–vis spectrophotometer at 280 nm, and was recorded at different time intervals by the data logger. Breakthrough data are acquired by plotting the volume of solution that is passed through a column (or time) versus the concentration of the "breakthrough ligand" as it appears in the effluent. When the concentration of ligand emerging from the bottom of the column is equal to that entering the top of the resin bed, the experiment was terminated. If C_0 is the known concentration of ligand entering the exchanger bed and C is the concentration of the ligand that emerges, then a plot of C/C_0 versus the volume of effluent (or time) gives a typical breakthrough curve [30]. Dynamic adsorption capacity of the column is determined from the breakthrough curve, using the following equation:

$$q_e = \frac{C_0 V}{W} \frac{A_U}{A_U + A_D} \tag{1}$$

Scheme 1. Modification of poly(vinyl chloride) as ligand-exchanger.

where C_0 denotes the initial concentration of the ligands in the aqueous phase, V the volume of the aqueous phase and W is the dry weight of the resin. The amounts of adsorbed and non-retained ligand are proportional to the areas (A_U and A_D) on the left and right side of the breakthrough curves, respectively. In order to determine the dynamic adsorption capacity (q_e), it was necessary to solve the areas of A_U and A_D. This was performed by a computer program which was produced by FIG P Software Corporation Durham, NC, USA. From the breakthrough curve not only equilibrium adsorption data, but also significant information on the kinetics of adsorption can be obtained [12,14]. This technique was used for the acquisition of both the adsorption and the kinetic data in the column runs. The breakthrough curve used in the determination of the adsorption and kinetics data is outlined schematically in Fig. 1.

3. Results and discussion

The adsorption experiments were carried out on cobalt(II)-CDAE-PVC for the removal of aniline from aqueous solution under dynamic conditions. The analysis of the cobalt(II)-CDAE-PVC bed was based on the effluent concentration–time curve, which is called the breakthrough curve. Typical breakthrough curves at three different initial concentrations for the adsorption of aniline on the packed bed are shown in Fig. 2 (also, the total ligand-exchange capacities of the resin for each of all the concentrations of aniline were obtained by breakthrough technique and used in adsorption studies). The general situation of the breakthrough curves was as expected. The effluent concentration first increased gradually and then increased sharply before breakthrough curve reached a stable plateau. It is seen from breakthrough data that aniline underwent significantly high adsorption on
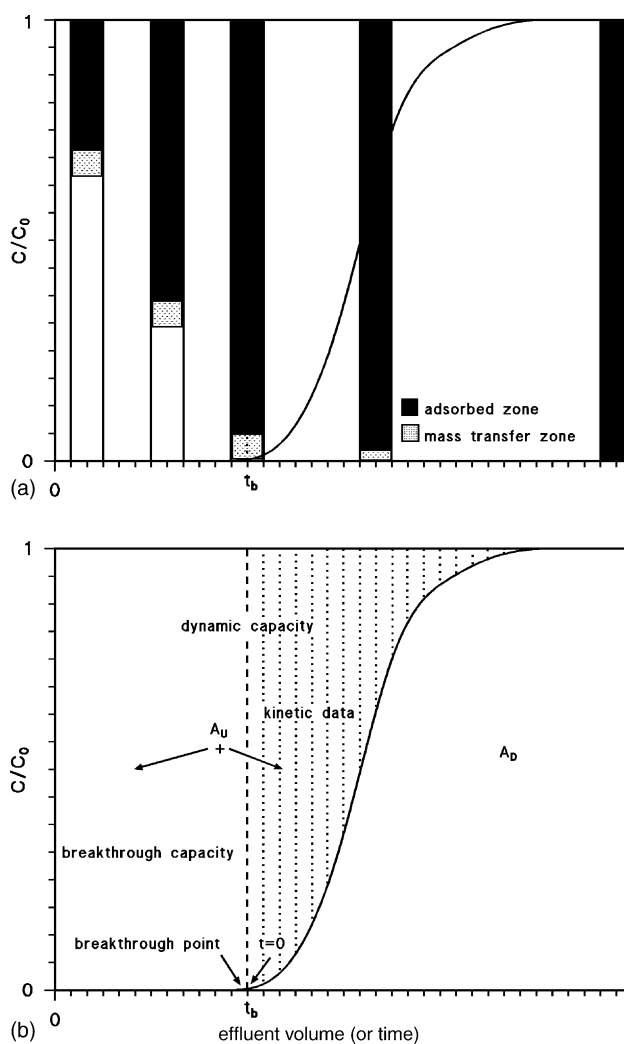

Fig. 1. A schematic view of the technique used in the determination of the adsorption and kinetics data in a column operation.
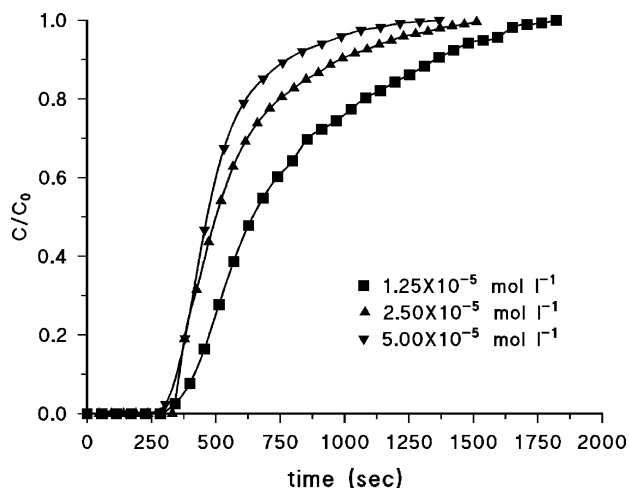
Fig. 2. Experimental breakthrough curves of aniline in the expanded bed of the cobalt(II)-PVC-CDAE at different initial concentrations.

cobalt(II)-PVC-CDAE. However, the adsorbed aniline was easily stripped with water. Hence, the process can be described as a reversible process. To examine the adsorption efficiency of the resin, the loading and regeneration process was repeated for several cycles and this limited number of adsorption–desorption cycles indicated that the adsorption capacity of the resin remained unchanged.

As shown in Fig. 2, the breakthrough data of aniline are seen to be dependent on the concentration of aniline in the external solution. This dependence of breakthrough data on external ligand concentration may help in finding the rate-controlling step of the adsorption process. The data of kinetics and diffusion of adsorption can be obtained from the S-shaped part of the breakthrough curve [31–34], while the dynamic adsorption capacity can be gained from the entire breakthrough curve. The experimental results and the relevant observations were discussed in the following sections.

3.1. Adsorption isotherm

Ligand adsorption depends upon different types of interactions between solute molecules and matrix that is immobilized on a solid phase. Ligand-exchange is one of the most effective interactions which controls the distribution of solutes between solution and solid phases. By ligand-exchange, ligands can be adsorbed from their medium by the formation of complex with the metal attached to the solid support and consequently water or liquid coordinates of the metal will be displaced [35]. However, the interactions between immobilized metal ions and ligands are complex in nature. Ligand retention on a ligand-exchange phase is a combined effect of donor–acceptor complex formation, electrostatic and/or hydrophobic interaction. These interactions often involve multiple-site interactions between a single ligand and a number of individual binding sites distributed on the adsorbent surface. Consequently, it is concluded that the mechanism of ligand adsorption is not only determined by

the complex formation but also by the so called multivalent interaction which is a combined effect of electrostatic, hydrophobic and π-electron donor–acceptor interactions. The optimization of a adsorption process using ligand-exchange technique requires an understanding of the factors that govern the interaction between ligands and a matrix. The complex formation in ligand adsorption are considerably different from conventional adsorption interactions. However, the interactions between ligands and immobilized metal ions can be explained on the basis of various isotherm models applicable to interaction on ligand-exchange matrices. Although, the classical Langmuir isotherm model is applied to account for these interactions as a first approach, in this study, we have used the Scatchard plot in order to obtain more compact information about the binding data [36–39].

A Scatchard linearized form of the Langmuir equation was used here not to determine the adsorption parameters, but to have a preliminary prediction about the types of interaction and resin affinity for aniline.

$$\frac{q_e}{C_e} = q_m K_b - q_e K_b \qquad (2)$$

where q_e is the amount of ligand adsorbed per unit weight, C_e the equilibrium concentration of ligand, K_b and q_m are the adsorption binding constant and maximum ligand capacity, respectively. The shape of the plot of q_e/C_e versus q_e is related to the type of interaction of the ligand with the resin matrix. If the Scatchard plot is linear with a negative slope, it is related to independent interactions between the ligand and the binding sites, which follows the Langmuir model. If it is convex, negative cooperativity is observed. And if q_e/C_e versus q_e plot shows a concave curve, the interaction of the ligand is governed by a positive cooperativity phenomenon between strong and weak binding sites [40–43].

The adsorption behavior of aniline on the cobalt(II)-CDAE-PVC was thoroughly investigated by the Scatchard plot analysis of the experimental data obtained from the column operations. Convex dependency of q_e/C_e versus q_e shows that the interaction between aniline and cobalt(II)-CDAE-PVC did not follow the Langmuir adsorption isotherm but a negative cooperativity was involved in the ligand adsorption process (Fig. 3). Consequently, the interaction with the ligand-exchange matrix is partially a specific one and has occured with the participation of π-electrons of the ligand. The presence of two slopes in a curvilinear Scatchard plot is probably an indication of the existence of two classes of binding sites. In this case, the Freundlich isotherm, which is frequently used to describe the adsorption behavior, can be used since it represents the amount of the adsorbed ligand as the power function of solute concentration.

In the adsorption of aniline, deviation from linearty in the plot of q/C versus q was observed, indicating the presence of multivalent interaction and a non-Langmuirean behaviour (Fig. 3). Therefore, the binding of aniline is considered to have followed more Freundlich model rather than the Langmuirean. To test the fit of data, the Freundlich isotherms equa-
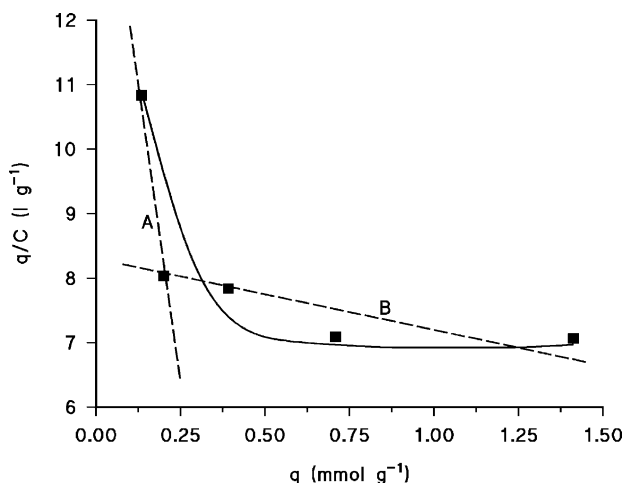
Fig. 3. Scatchard plot of the experimental data for the adsorption of aniline to the cobalt(II)-PVC-CDAE. The solid line represents the concave upward curve. The dotted lines A and B represent the high- and low-affinity binding sites, respectively.

tion was applied.

$$q = kC^{1/n} \tag{3}$$

where k and n are the Freundlich constants. The experimental data were described by the Freundlich isotherm model with a high correlation coefficient (Fig. 4). From Freundlich plots ligand adsorption constants k and n were calculated as 46.18 mmol g^{-1} and 1.16, respectively.

The results indicate that the increase in aniline adsorption is associated with an increase in the aniline concentration. This can be explained by an improvable increase in electrostatic interactions, relative to metal–ligand interactions, of the binding sites with lower affinity for aniline with an increase of the initial aniline concentration.
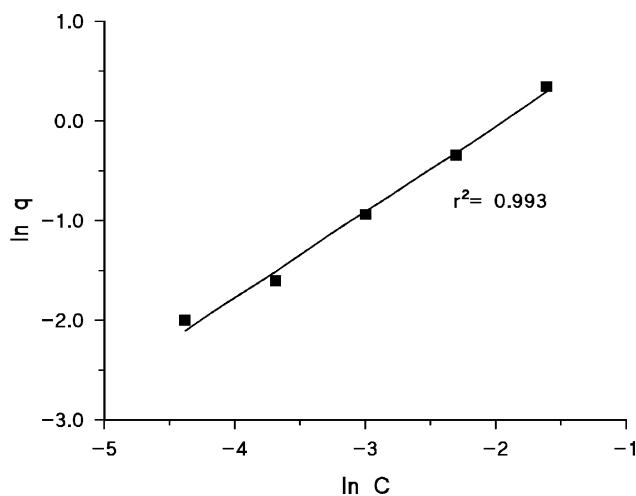

Fig. 4. Freundlich isotherm of the experimental data for the aniline adsorption.

3.2. Kinetic considerations

Ligand-exchange process, as in other heterogeneous reactions between solids and liquids, are mainly controlled by various factors including the following steps: (i) diffusion of ligands through the liquid film surrounding the particle, (ii) diffusion of ions through the polymeric matrix of the resin and (iii) chemical reaction with the functional groups attached to the matrix. One of the steps usually offers much greater resistance than the others, so it can be considered as the rate-controlling step of the process. There are only a few cases in which the rate of ligand-exchange reactions is determined by chemical reaction. When a kinetic study is in its initial stage, it is generally assumed that the chemical reaction is infinitely fast. In this work, kinetic studies describing single solute adsorption in a fixed bed is based on the homogeneous diffusion model. In this model, it is accepted that the resin exchange processes normally are diffusion controlled and not reaction controlled [44]. The rate-controlling mechanism can be diffusion across the liquid film surrounding the resin particle (film diffusion) or diffusion inside the particle (particle diffusion).

The adsorbents are usually used in the fixed bed process because of the ease of operation. In this study, homogeneous diffusion model was adapted to a column system for describing the change in the aniline concentration in the effluent beginning from breakthrough point as a function of time. As the aniline first appeared at the column outlet, the breakthrough curve started to go upward until it reached a stable plateau. This time period, namely, the time required to reach the plateau concentration in the effluent corresponded to the mass transfer zone in the bed (as shown in Fig. 2). The basic idea of this attempt is practically similar to that originally employed by Helfferich for describing the kinetics of batch adsorption systems [44]. In a column system, the batch adsorption conditions are only obtained at the zones of mass transfer beginning from breakthrough point. In these points, a part of aniline in the aqueous solution adsorbs onto the resin, while the others passes through the column and the aniline in solution is infinite for the adsorbent. Thus, the conditions of "zero length column technique" [45], which is used to determine the controlling mechanism of diffusion can be obtained. Note that the amount of aniline being adsorbed at each t time is proportional to the total of each area denoted by punctuated line. By using the homogeneous diffusion model, we have made the following assumption that we have previously tested [12,14] "The kinetic data following after the breakthrough point in a column operation are equivalent to the kinetic data that can be obtained from the batch process". This assumption leads to a new method which can be used for measurement of kinetic data in a column operation that we have named as "equivalent points method".

The breakthrough data for each initial concentration of aniline are seen to be dependent on the ligand concentration in the external solution as shown in Fig. 2. This dependence of the S-shaped parts of the breakthrough curve allows the
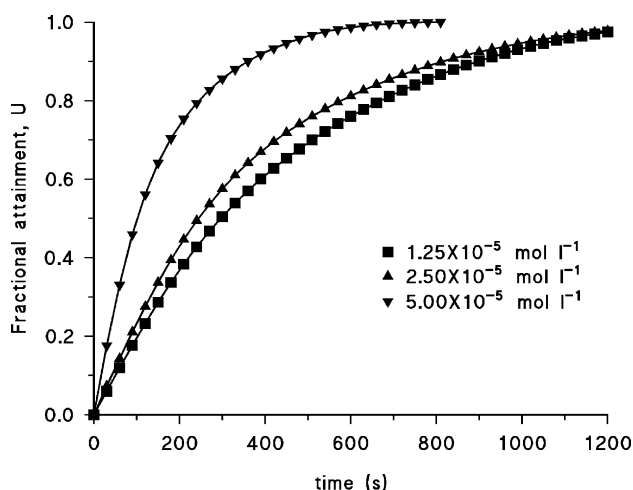
Fig. 5. Rate of adsorption of aniline on the cobalt(II)-PVC-CDAE.

determination of the kinetic behaviour of the adsorption. To test the consistency of our approach we have measured the fractional attainment of equilibrium adsorption for each t time following after the breakthrough point as described in experimental section. The dependence of the fractional attainment on the adsorbate concentration may indicate that the rate-controlling step in the adsorption process is film-diffusion as expressed by Chanda and Rempel [46–49].

The data of fractional attainment of equilibrium adsorption are presented in Fig. 5. From the results given in Fig. 5, it is seen that the rate of attainment of equilibrium adsorption of aniline depends on the ligand concentration in the external solution. This result indicated that film diffusion is the rate-controlling step under the conditions employed.

The homogeneous diffusion model for the batch adsorption system has been extensively used by numerous researchers to describe the uptake of adsorbate by an adsorbent. However, in this work, the adsorption kinetics of aniline in the column system was analyzed using the homogeneous diffusion model which is constructed on the basis of the fact "The ligand concentration in the mobile phase is in equilibrium with the concentration of the adsorbed ligand on the resin surface at each t time after the breakthrough point".

In the case of infinite solution volume, a diffusion-controlled adsorption system can be described by the following equations for film and particle diffusion control, respectively [44,50]:

$$U(t) = 1 - \exp\left(-\frac{3D_\mathrm{f}Ct}{r_0\delta C_\mathrm{r}}\right); \quad -\ln(1-U) = kt$$

$$\text{where } k = \frac{3D_\mathrm{f}C}{r_0\delta C_\mathrm{r}} \tag{4}$$

$$U(t) = 1 - \exp\left(-\frac{D_\mathrm{s}t\pi^2}{r_0^2}\right)^{1/2}; \quad -\ln(1-U^2) = 2kt$$

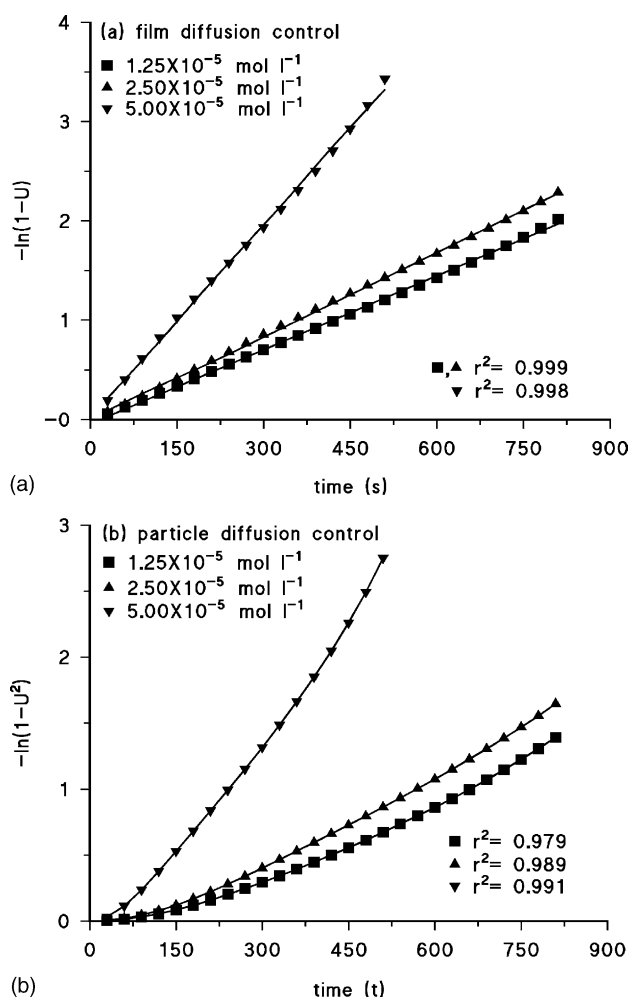$$\text{where } k = \frac{D_\mathrm{s}\pi^2}{r_0^2} \tag{5}$$

Fig. 6. Test of homogeneous diffusion model for the aniline adsorption.

where U is the fractional attainment of equilibrium adsorption at time t, D_f the diffusion coefficient in solution phase, C the total concentration of both exchanging species, δ the liquid film thickness, r_0 the particle radius, C_r the total concentration of both exchanging species in the ligand-exchanger and D_s is diffusion coefficient in solid-phase.

Fig. 6(a) shows the plots of $-\ln(1-U)$ versus t for the adsorption of aniline. The graphs obtained at different concentrations were a straight line, which suggests that fractional attainment of equilibrium adsorption under film diffusion control is observed. Moreover, the graph of $-\ln(1-U^2)$ versus t (Fig. 6(b)) did not give a perfect straight line which implies that adsorption under particle diffusion control has not occured. It can be seen from Fig. 6(a) that the film diffusion model fitted the experimental data very well, with high r^2 values (≥ 0.998) for three different concentration ranges of aniline. This would suggest that the main resistance to aniline adsorption was due to film diffusion when using the lower adsorbate concentration range.

The linearity test of the graphs has been used to distinguish the diffusion mechanisms of the aniline adsorption. Although all results presented upto this point have clearly

demonstrated the dominance of the film diffusion over the the rate-controlling step for the low concentration of aniline, the linearity test of the $-\ln\left(1-U^2\right)$ versus t plots (Fig. 6(b)) reveals that the rate of the reaction may be determined by particle diffusion at high concentrations. This interpretation was based on the correlation coefficients, which implies that the particle diffusion dominates the rate-controlling step, increases linearly with concentration (Fig. 6(b)).

4. Conclusion

This study demonstrates that the cobalt(II)-PVC-CDAE is an effective adsorbent for the removal of aniline from aqueous solution. The adsorption of aniline on the cobalt(II)-PVC-CDAE is essentially due to its specific interaction with the ligand-exchange matrix in the resin phase, which leads to the complex formation of the metal–ligand. However, the adsorption of aniline on this ligand-exchange stationary phase was affected by the electrostatic or hydrophobic interaction at high ligand concentrations. The Scatchard plot reveals that the adsorption process is apparently heterogeneous since the plot of q_e/C_e versus q_e of aniline on the cobalt(II)-PVC-CDAE deviated from linear behavior. Therefore, the experimental data over the whole concentration range could not fit the conventional Langmuir adsorption isotherm. A good fit of the experimental data to the Freundlich adsorption model indicated the presence of heterogeneous binding sites on the resin surfaces. The adsorption performance was strongly affected by the initial concentration of aniline, and results obtained from the breakthrough characteristics of aniline in packed bed of cobalt(II)-PVC-CDAE have indicated that the rate-controlling step of the ligand adsorption was predominately film diffusion controlled rather particle diffusion. Consequently, the breakthrough technique was used in the determination of the rate-controlling step of the adsorption process and a good prediction has been obtained for understanding the effective diffusion type on the ligand adsorption.

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