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# Retention behavior studies for the removal of some hazardous metal ions from waste solutions using polyaniline silicotitanate as composite cation exchanger

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## ABSTRACT

Polyaniline silicotitanate as "organic–inorganic" composite material has been synthesized and utilized as adsorbent for the removal of $Co^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Cs^{+}$, and $Pb^{2+}$ ions from aqueous waste solutions. The experimental data were analyzed by Langmuir, Freundlich, and D–R isotherm models of adsorption. The results suggest that the adsorption of the studied metal ions ($Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, and $Pb^{2+}$ ions) on polyaniline silicotitanate is favorable for the Freundlich isotherm more than Langmuir and D–R isotherms. The numerical values of ($1/n$) for the studied metal ions were found to be smaller than one, which implies heterogeneous surface structure with minimum interaction between the adsorbed atoms. The adsorption energies ($E$) at 25˚C were less than 8 $kJmol^{-1}$ suggesting that the sorption process was dominated by physisorption (physical adsorption). Based on the results obtained, practical separation experiments for the above-mentioned cations on polyaniline silicotitanate column from aqueous waste solutions were carried out.

*Keywords:* Adsorption; Polyaniline silicotitanate; Heavy toxic metals; Sorption isotherm; Separation

## 1. Introduction

Surface water are exposed to pollution from the large quantities of effluent that industry daily discharge into the rivers, sewage works, etc. with the ion of non-ferrous toxic metals such as cobalt, copper, cadmium, cesium, and lead. Several techniques are available for the removal of such ions from wastewater, including precipitation and separation on organic resins, which are widely used in industry [1]. Although, organic ion exchangers can be used due to their uniformity, chemical stability, and control of their ion exchange properties through synthetic methods, they are still limited by their poor thermal and radiation stability than inorganic ion exchangers [2]. Inorganic ion exchangers, besides other advantages and their stability at high temperatures and in radiation fields than the organic [3–9] are still limited because of their non-reproducible character, less stability in high acidic and basic media, and their high cost. Furthermore, inorganic ion exchangers cannot be used in convenient way in case of removing impurities from a large volume.

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Efforts have been made to improve chemical, thermal, and mechanical stabilities of ion exchangers and to make them highly selective for certain metal ions [10,11]. An inorganic ion exchanger based on organic polymeric matrix would be an interesting material having multi-functional groups and mechanical stability due to the presence of organic polymeric species and the basic characteristics of an inorganic ion exchanger regarding its selectivity for some specific metal ions. It was therefore considered to synthesize such composite with a good ion exchange capacity, high stability, and selectivity for heavy metal ions, with high compatibility for the environmental remediation.

In the present paper polyaniline silicotitanate was synthesized in identical conditions. The experimental data were analyzed by Langmuir, Freundlich, and D–R isotherm models of adsorption in order to know the most favorable model for the adsorption of $Co^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Cs^{+}$, and $Pb^{2+}$ ions on polyaniline silicotitanate. The applicability of the prepared exchanger for the removal and separation of the studied metal ions from wastewater was studied.

## 2. Experimental

### 2.1. Chemical reagents and instruments

The main reagents used for the synthesis of the material were obtained from BDH (England) and Loba Chemie (India). All other reagents and chemicals were of analytical reagent grade purity and used without further purification. An atomic absorption spectrophotometer and ICPs-7500 were from Shimadzu, Kyoto, Japan.

### 2.2. Preparation of polyaniline silicotitanate

Polyaniline silicotitanate was prepared as reported earlier [11] using sol–gel technique by mixing the polyaniline as an organic polymer into the inorganic precipitate of silicotitanate. The prepared material was previously characterized by El-Naggar et al. [11].

The water content of polyaniline silicotitanate in the different forms such as $H^{+}$, $Co^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Cs^{+}$, and $Pb^{2+}$ forms were determined by using thermal analysis technique (TG and DTA). The water loss of polyaniline silicotitanate in $H^{+}$, $Co^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Cs^{+}$, and $Pb^{2+}$ forms at 850°C is 51.01, 54.80, 52.07, 52.08, 54.09, and 58.11% w/w, respectively.

The capacity of polyaniline silicotitanate in the $H^{+}$-form for 0.1 ionic strength metal chloride (metal = $Co^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Cs^{+}$, and/or $Pb^{2+}$) solutions was determined by batch experiment technique in a shaker thermostat at 25 ± 1°C. The capacities were found to be 3.95, 3.85, 3.75, 5.31, and 4.44 meq/g for $Co^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Cs^{+}$, and $Pb^{2+}$ ions, respectively.

### 2.3. Sorption Isotherms

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid and the solid phases when the adsorption process reaches an equilibrium state [12,13]. When an adsorbent comes into contact with a metal ion solution, the concentration of metal ions on the surface of the adsorbent will increase until a dynamic equilibrium is reached; at this point, there is a clearly defined distribution of metal ions between the solid and liquid phases [14]. Fitting the isotherm data to different isotherm models is an important step to find the suitable model that can be used for design purposes [12,13].

#### 2.3.1. Langmuir isotherm

Longmuir′s isotherm model suggests that uptake occurs on homogeneous surface by monolayer sorption without interaction between sorbed molecules. The model assumes uniform energies of adsorption onto the surface [12]. The obtained data were applied to Langmuir adsorption isotherm [15,16] using the following linear expression:

$$\frac{C_e}{q_e} = \frac{C_e}{Q} + \frac{1}{bQ} \tag{1}$$

The adsorption results were analyzed by Langmuir adsorption isotherm where $C_e$ is the equilibrium concentration of the adsorbate ions, $q_e$ is the amount of ions sorbed per gram of sorbent (mol/g) at equilibrium while $Q$ and $b$ are the Langmuir constants related to maximum adsorption capacity (monolayer capacity) (meq/g) and heat of adsorption, respectively.

#### 2.3.2. Freundlich isotherm

Freundlich isotherm [17] is the earliest known relationship describing the sorption equation. This isotherm valid for physical adsorption and usually for an adsorbent with very heterogeneous surface [18] and is expressed by the following equation:

$$q_e = K_f {C_e}^{1/n} \tag{2}$$

The equation may be linerized by taking the logarithm of both sides:

$$\log q_e = \log K_f + 1/n \log C_e \tag{3}$$

where $q_e$ is the amount adsorbed at equilibrium (mol/g), $C_e$ is the equilibrium concentration of the adsorbate metal ions, $K_f$ and $n$ are the Freundlich constants, $n$ is giving an indication of how favorable the adsorption process is (adsorption intensity) and $K_f$ (mol/g) $(\text{L/mol})^{1/n}$ is the adsorption capacity of the polyaniline silicotitanate sorbent. $K_f$ is defined as the adsorption or distribution coefficient and represents the quantity of metal ion sorbed onto polyaniline silicotitanate for a unit equilibrium concentration [12].

### 2.3.3. Dubinin–Radushkevich (D–R) isotherm

The Dubinin–Radushkevich (D–R) isotherm [19], which assumes a heterogeneous surface, is expressed as follows:

$$q_e = X_m{}' \exp(-K'\varepsilon^2) \tag{4}$$

where $\varepsilon$ (the polanyi potential) = RT ln (1 + 1/$C_e$), $q_e$ is the amount of ions sorbed per gram of sorbent (mol/g), $X_m{}'$ is the adsorption capacity of the sorbent (meq/g), $C_e$ is the equilibrium concentration of the metal ions in solution, $K'$ is a constant related to the adsorption energy (mol$^2$ kJ$^{-2}$), $R$ is the gas constant (kJ K$^{-1}$ mol$^{-1}$), and $T$ is the temperature (K).

The D–R isotherm can be expressed in a linear form as follows:

$$\ln q_e = \ln X_m{}' - K'\varepsilon^2 \tag{5}$$

The mean adsorption energy ($E$, kJ mol$^{-1}$) can be obtained from the $K'$ values of the D–R isotherm [19] using the following equation:

$$E = (-2K')^{-1/2} \tag{6}$$

### 2.4. Column operations

Chromatographic column breakthrough investigations were conducted as follows; 0.3 g of polyaniline silicotitanate of particle size 0.375 mm was packed in a glass column (0.5 cm diameter and 5 cm heights) to give bed heights of 1.1 cm$^3$ volume. Three hundred and fifty milliliters of the desired natural solutions (pH = 3.45) containing 10$^{-3}$ M of metal chloride {M (Cl)$_x$, where $M$ = one of the ions under investigation, were passed through the column beds at a flow rate of 4–5 drops/min; equal fractions were collected and the concentrations were continuously measured using an atomic absorption spectrophotometer and inductively coupled plasma (ICPS). The values of breakthrough capacity were calculated using the formula;

$$\text{Break through capacity} = V_{(50\%)} \times \frac{C_o}{m}(\text{meq/g}) \tag{7}$$

where $V_{(50\%)}$ is the effluent volume at 50% breakthrough (ml); $C_o$ is the concentration of feed solution (meq/ml); $m$ is the amount of the column bed in (g).

## 3. Results and discussion

The adsorption isotherms were obtained, as it is well known, by a gradual increase in the concentration of sorbate ions in solution and measuring the amount sorbed at each equilibrium concentration. The degree of sorption should therefore be a function of the concentration of sorbate ions only. The adsorption isotherms were investigated for $Co^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Cs^+$, and $Pb^{2+}$ ions on polyaniline silicotitanate in the concentration range from 10$^{-3}$ to 0.1 M at different reaction temperatures (25, 45, and 65 ± 1˚C) at a constant $V/m$ value of 100 ml.g$^{-1}$.

As the concentration of the investigated metal ions increased from 10$^{-3}$ to ~0.1 M, the removal efficiencies decreased from 48.85 to 14.72% for Co(II), 55.57 to 6.16% for Cu(II), 24.85 to 1.24% for Cd(II), 97.20 to 48.3% for Cs(I), and 81.71 to 29.01% for Pb(II). This may be attributed due to the fact that each given mass of adsorbent material has a finite number of adsorption sites, and as the metal concentrations increase, these sites become saturated, producing the maximum adsorption for a given adsorbent mass. Thereafter, adding more metal ions cannot increase adsorption because no more sites are available; all are occupied [14].

The adsorption results were analyzed by Langmuir adsorption isotherm. From Eq. (1), plot of $C_e/q_e$ vs. $C_e$, gives linear relationships, (Figs. 1 and 2) for $Pb^{2+}$ and $Cs^+$ ions (as a sake of brevity); from the slope of these linear plots, the value of $Q$, the saturation capacity of polyaniline silicotitanate for $Co^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Cs^+$, and $Pb^{2+}$ at the investigated temperatures (25, 45, and 65 ± 1˚C, respectively) are calculated and summarized in Table 1. In terms of the saturation capacities, polyaniline silicotitanate seems to be a better sorbent for $Pb^{2+}$ and $Cs^+$ than the other mentioned cations. The adsorption capacity of the hybrid cation exchanger for the studied metal ions increases according to the decrease in the hydrated ionic radii and hydration

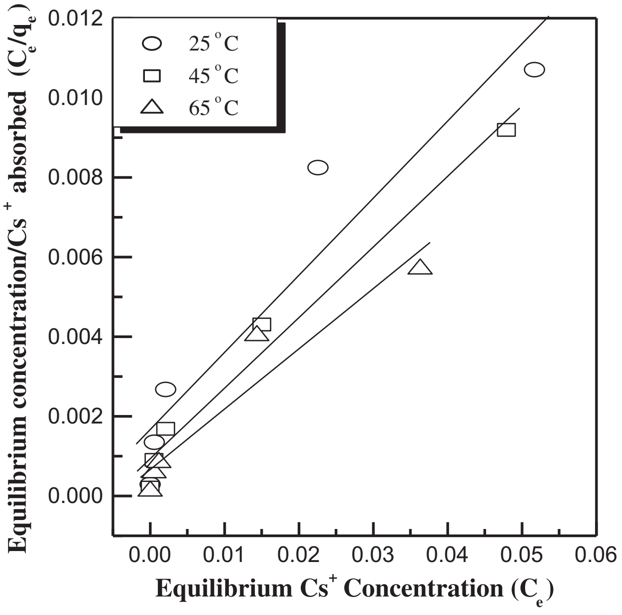

Fig. 1. Langmuir adsorption isotherm for adsorption of Cs$^+$ ion on polyaniline silicotitanate at different reaction temperatures.

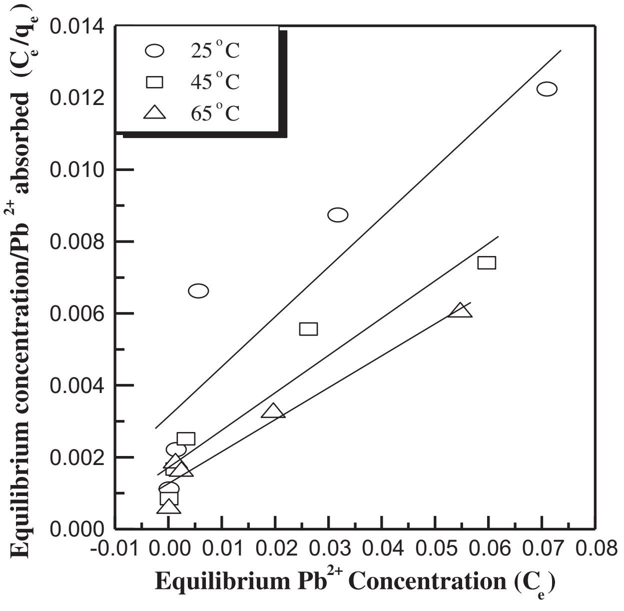

Fig. 2. Langmuir adsorption isotherm for adsorption of Pb$^{2+}$ ion on polyaniline silicotitanate at different reaction temperatures.

energy [11]. Langmuir constants $Q$ and $b$ related to maximum adsorption capacity (monolayer capacity) (meq/g) and heat of adsorption, respectively, increased with increasing temperature.

Table 1 shows that the sorption capacity and intensity of sorption are enhanced at higher temperatures. This suggested that the active surfaces available for sorption have increased with increasing temperature [20]. In addition, the increase in sorption capacity may be due to the increasing kinetic energy of the sorbent metal ions, which increases the frequency of collisions between the adsorbent and metal ions and thus enhances adsorption of metals on the surface of the adsorbent [14].

From Eq. (3), plotting log $q_e$ vs. log $C_e$, gives linear relationships, with a slope of $1/n$ and an intercept of log $K_f$, ((Figs. 3 and 4) for Pb$^{2+}$and Cs$^+$ ions (as a sake of brevity). The corresponding Freundlich isotherm constants $K_f$ and $1/n$ together with the correlation coefficients ($R$) are also listed in Table 1. Values of $K_f$ derived from the Freundlich equation are indicators of the adsorption capacity. The adsorption capacities towards Co$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, Cs$^+$, and Pb$^{2+}$ ions on polyaniline silicotitanate increased with increasing temperatures. The slope ($1/n$) ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [21]. The numerical values of $1/n$ for the studied metal ions were found to be ranging between 0 and 1 ($0 < 1/n < 1$) (Table 1). According to the statistical theory of adsorption [22], when the value of $1/n$ in the adsorption isotherm is less than unity, it implies heterogeneous surface structure with minimum interaction between the adsorbed atoms [23,24]; in this study, the value of $1/n$ for the studied metal ions is smaller than one ($0 < 1/n < 1$), which implies heterogeneous surface structure and favorable Freundlich adsorption processes [24,25]. In another studies the value of $1/n$ was found to be less than unity for the adsorption of (Pb$^{2+}$ 0.34), (Cd$^{2+}$ 0.29), and (Zn$^{2+}$ 0.16) on antimonic acid [26]; (Cu$^{2+}$ 0.82), (Cd$^{2+}$ 0.75), (Zn$^{2+}$ 0.77), and (Ni$^{2+}$ 0.73) on silico antimonate [24]; (Cd$^{2+}$ 0.60) and (Zn$^{2+}$ 0.89) on iron(III) titanate [25]; (Cu$^{2+}$ 0.86), (Co$^{2+}$ 0.83), (Zn$^{2+}$ 0.79), (Cd$^{2+}$ 0.79), (Cs$^+$ 0.86), and (Fe$^{3+}$ 0.71) on magneso-silicate [27]; (Cu$^{2+}$ 0.68), (Co$^{2+}$ 0.59), (Zn$^{2+}$ 0.77), (Cd$^{2+}$ 0.83), (Cs$^+$ 0.86), and (Fe$^{3+}$ 0.77) on magnesium alumino-silicate [27]; and (Cu$^{2+}$ 0.78) on purolite C100-MB [28], and it implies heterogeneous surface structure and favorable Freundlich adsorption processes. These results agree with our finding.

Plotting ln $q_e$ against $\varepsilon^2$ gives a straight line with a slope of $-K^/$ and an intercept of ln $X_m{}^/$ as shown in (Figs. 5 and 6). The regression parameters and correlation coefficients ($R^2$) are also listed in Table 1. Values of $X_m{}^/$ derived from the Dubinin–Radushkevich equation are indicators of the adsorption capacity. The adsorption capacities toward Co$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, Cs$^+$, and Pb$^{2+}$ ions on polyaniline silicotitanate increased with increasing temperatures.

Table 1
Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherm parameters for the sorption of $Co^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Cs^{+}$, and $Pb^{2+}$ onto polyaniline silicotitanate at different reaction temperatures

| | | Langmuir isotherm | | | Freundlich isotherm | | | D–R isotherm | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cation | Reaction temperature (°K) | Q (saturation capacity (meq/g)) | *b* (L/mol) | $R^2$ | 1/*n* | $K_f$(mol/g) $(L/mol)^{1/n}$ | $R^2$ | $X_m'$ (meq/g) | $K'(mol^2\ kJ^{-2}) \times 10^9$ | *E* ($KJmol^{-1}$) | $R^2$ |
| $Pb^{2+}$ | 298 | 7.24 | 44.13 | 0.909 | 0.601 | 28.18 | 0.9995 | 7.39 | 8.58 | 7.63 | 0.9960 |
| | 318 | 9.61 | 60.85 | 0.958 | 0.643 | 48.97 | 0.9996 | 10.59 | 7.78 | 8.01 | 0.9940 |
| | 338 | 11.25 | 69.99 | 0.978 | 0.671 | 81.28 | 0.9982 | 12.18 | 6.68 | 8.65 | 0.9830 |
| $Cs^{+}$ | 298 | 5.15 | 116.27 | 0.949 | 0.513 | 20.09 | 0.9990 | 3.44 | 7.88 | 7.96 | 0.9858 |
| | 318 | 5.65 | 189.90 | 0.988 | 0.552 | 37.67 | 0.9997 | 5.30 | 5.02 | 9.98 | 0.9926 |
| | 338 | 6.62 | 227.15 | 0.959 | 0.614 | 98.85 | 0.9982 | 6.12 | 4.09 | 11.05 | 0.9994 |
| $Co^{+}$ | 298 | 2.75 | 34.30 | 0.963 | 0.658 | 13.49 | 0.9970 | 2.49 | 9.81 | 7.14 | 0.9799 |
| | 318 | 3.93 | 37.97 | 0.950 | 0.618 | 13.99 | 0.9977 | 3.72 | 8.54 | 7.65 | 0.9880 |
| | 338 | 6.80 | 46.53 | 0.978 | 0.619 | 23.23 | 0.9930 | 7.45 | 7.88 | 7.96 | 0.9953 |
| $Cu^{2+}$ | 298 | 1.35 | 58.51 | 0.964 | 0.450 | 3.47 | 0.9990 | 1.61 | 10.06 | 7.05 | 0.9917 |
| | 318 | 2.33 | 69.67 | 0.976 | 0.434 | 5.73 | 0.9940 | 2.96 | 8.93 | 7.48 | 0.9976 |
| | 338 | 4.11 | 135.17 | 0.966 | 0.370 | 8.63 | 0.9920 | 4.76 | 4.84 | 10.16 | 0.9888 |
| $Cd^{2+}$ | 298 | 0.26 | 127.78 | 0.995 | 0.326 | 0.55 | 0.9970 | 0.28 | 7.94 | 7.93 | 0.9954 |
| | 318 | 0.46 | 86.96 | 0.992 | 0.423 | 1.22 | 0.9950 | 0.52 | 6.41 | 8.83 | 0.9977 |
| | 338 | 1.13 | 47.05 | 0.989 | 0.580 | 1.07 | 0.9960 | 1.26 | 5.62 | 9.43 | 0.9975 |

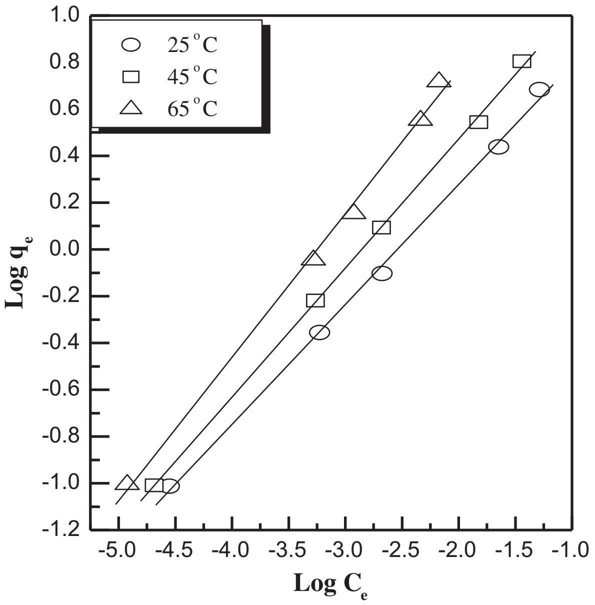

Fig. 3. Freundlich adsorption isotherm for adsorption of $Cs^+$ ion on polyaniline silicotitanate at different reaction temperatures.

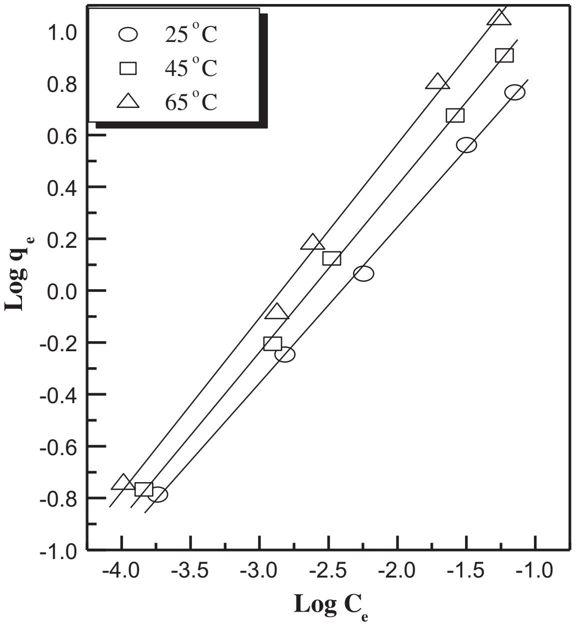

Fig. 4. Freundlich adsorption isotherm for adsorption of $Pb^{2+}$ ion on polyaniline silicotitanate at different reaction temperatures.

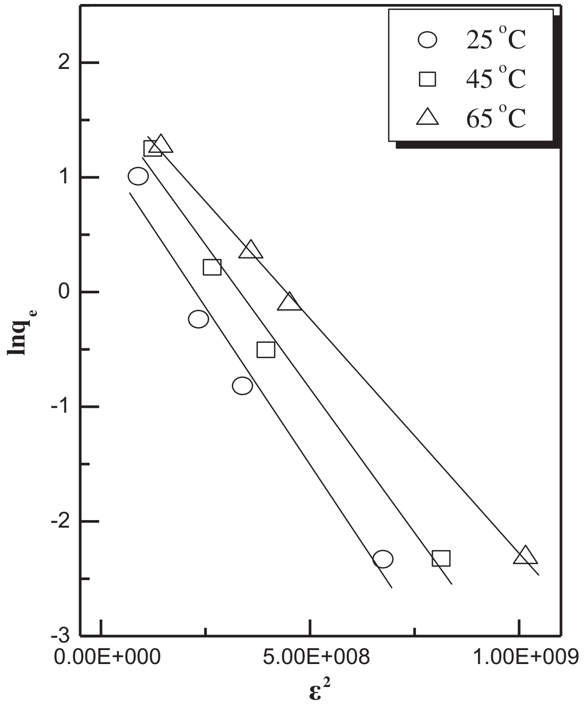

Fig. 5. Linearized D–R isotherms for adsorption of $Cs^+$ ion on polyaniline silicotitanate at different reaction temperatures.

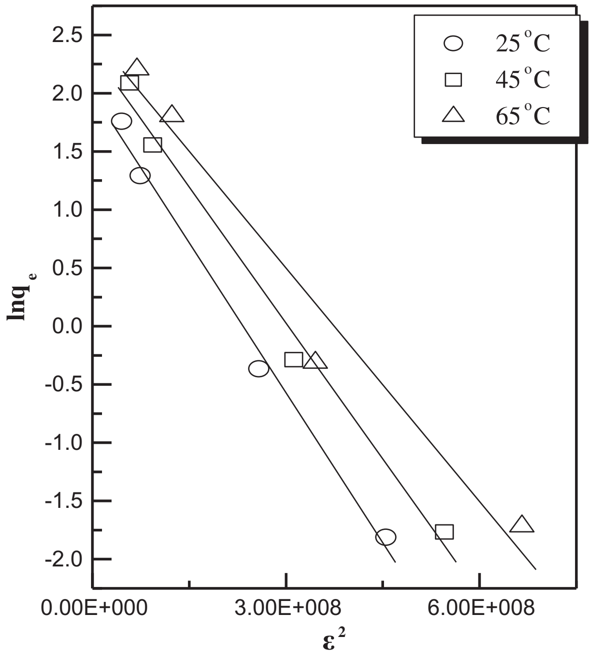

Fig. 6. Linearized D–R isotherms for adsorption of $Pb^{2+}$ ion on polyaniline silicotitanate at different reaction temperatures.

The mean adsorption energy ($E$, kJ mol$^{-1}$) can be obtained from the $K^{/}$ values of the D–R isotherm [19] using Eq. (6). Langmuir isotherm constants do not explain the chemical or physical properties of the adsorption process [14]. However, the mean adsorption energy ($E$) calculated from the D–R isotherm provides important information about these properties [19]. From Table 1 the adsorption energies at 25°C were less than 8 kJ mol$^{-1}$ suggesting that the sorption process was dominated by physisorption [14] at all studied temperatures and this result confirmed that the adsorption of the studied metal ions on polyaniline silicotitanate is favorable for the Freundlich isotherm more than the other adsorption models. In other studies, the value of $E$ was found to be 10.14, 14.11, 13.29, 12.23, and 14.58 kJ mol$^{-1}$ for $Co^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Cs^+$, and $Pb^{2+}$ ions, respectively, sorbed on polyacrylamide Sn(IV) molybdophosphate [23]; 11.4 and 12.5 kJ mol$^{-1}$ for $Cs^+$ and $Sr^{2+}$ ions sorbed on zeolite, respectively [29] confirmed that the adsorption is favorable for the Langmuir isotherm and this result does not agree with our finding.

From the above studies, the results suggest that the adsorption of the studied metal ions ($Co^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Cs^+$, and $Pb^{2+}$ ions) on polyaniline silicotitanate is favorable for the Freundlich isotherm more than Langmuir and D–R isotherm for the following reasons:

1. The correlation coefficient $R^2$ represented from Freundlich isotherm for the studied metal ions is greater than that represented from Langmuir and D–R isotherm (Table 1).
2. The numerical values of $1/n$ for the studied metal ions were found to be ranging between 0 and 1 ($0 < 1/n < 1$) (Table 1); it implies heterogeneous surface structure and favorable Freundlich adsorption processes.
3. From Table 1 the adsorption energies at 25°C ($E$) were $E < 8$ kJ mol$^{-1}$ suggesting that the sorption process was dominated by physisorption mechanism (i.e. physical adsorption) [14].

Confirmation of the experimental data with Freundlich isotherm assumes that sorption occurs on a structurally heterogeneous adsorbent with minimum interaction between the adsorbed atoms. From the above discussion, all the studied elements ($Co^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Cs^+$, and $Pb^{2+}$ ions) are physically adsorbed.

The main theory which explains separation by column chromatography is the plate theory. According to this theory, the column is considered to be divided into a number of equal units called theoretical plates. These units, although entirely hypothetical, give rise to a very useful way for the practical measurements of column efficiency. Investigation were conducted to explore suitable conditions for quantitative loading and sorption of $Co^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Cs^+$, and $Pb^{2+}$ ions in natural media (pH = 3.45) by chromatographic column procedures at room temperatures (25 ± 1°C). As far as the break-through capacity of the column is concerned (Fig. 7) shows curves for $Co^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Cs^+$, and $Pb^{2+}$ ions ($10^{-3}$ M for each) from polyaniline silicotitanate column in the feed solutions. Each break-through curve reflects the percent concentrations of the respective metal ion in the effluent to the feed solution ($C/C_o$ %) vs. effluent volume (V ml). The corresponding uptake for the investigated cations per gram of solid is calculated using Eq. (7).

From the results presented in Fig. 7, it is found that the selectivity of the ions towards polyaniline silicotitanate is in the order:

$$Cs^+ > Pb^{2+} > Co^{2+} > Cu^{2+} > Cd^{2+}$$

The same selectivity order is obtained from batch technique [11]. The break-through capacities for all the metal ions studied are calculated from Fig. 7, and it is found to be 0.101, 0.056, 0.034, 0.710, and 0.215 meq/g for $Co^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Cs^+$, and $Pb^{2+}$ ions, respectively; and the break-through capacities for all the metal ions are low as compared to the ion exchange capacities for the same metal ions obtained from batch technique due to the interference between the five metal ions under study and the break-through capacity for the studied metal ions was calculated before equilibrium while the ion exchange capacity for the same metal ions obtained from batch technique was calculated after equilibrium.

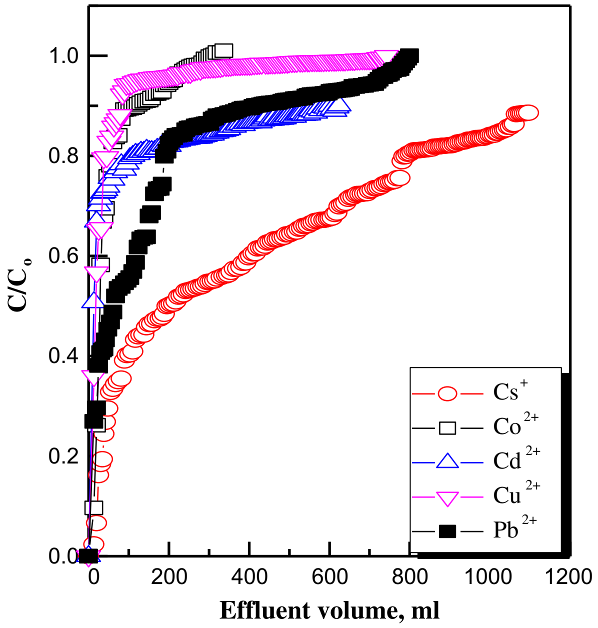

Fig. 7. Break-through curves of mixture of $Co^{2+}$, $Cu^{+2}$, $Cd^{2+}$, $Cs^+$, and $Pb^{2+}$ ions on polyaniline silicotitanate in pH = 3.45 and 25 ± 1°C.

Table 2
Comparison of break-through capacity, values of $Co^{2+}$, $Cu^{+2}$, $Cd^{2+}$, $Cs^+$, and $Pb^{2+}$ ions for various inorganic ion exchangers in DMW

| Inorganic ion exchanger | Break-through capacity (meq $g^{-1}$) | | | | |
|---|---|---|---|---|---|
| | $Cs^+$ | $Pb^{2+}$ | $Co^{2+}$ | $Cu^{2+}$ | $Cd^{2+}$ |
| Polyaniline silicotitanate[a] | 0.710 | 0.215 | 0.101 | 0.056 | 0.034 |
| Cerium(IV) antimonate [30] | 0.060 | – | – | – | – |
| Iron(IV) antimonate [30] | 0.320 | – | – | – | – |
| Silico(IV) antimonate [30] | 0.350 | – | – | – | – |
| Polyacrylamide [23] Sn(IV) molybdophosphate | 0.220 | 0.330 | 0.100 | 0.083 | 0.110 |
| Magnesium silicate [31] | – | – | – | 2.500 | 1.550 |
| Iron(III) titanate [25] | – | – | – | – | 0.120 |
| Zirconium silicate [32] | – | – | 0.230 | – | – |

[a] The material under study.

Table 2 shows the break-through capacity values of polyaniline silicotitanate for the studied metal ions as compared to the other ion exchange materials.

The elution profiles for the investigated cations $Co^{2+}$, $Cu^{2+}$, $Cd^{2+}$, $Cs^+$, and $Pb^{2+}$ ions on polyaniline silicotitanate are given in Fig. 8. The elution of these metal ions is studied in water and nitric acid solutions [0.01–1 M]. Fig. 8 shows that, at water, sharp peaks for $Cu^{2+}$, $Co^{2+}$, and $Cd^{2+}$ ions and small peaks for $Cs^+$ and $Pb^{2+}$ were obtained, at 0.01 M and 0.1 $HNO_3$; sharp peaks for $Cs^+$ and $Pb^{2+}$ were obtained and the peaks of $Cu^{2+}$, $Co^{2+}$, and $Cd^{2+}$ ions were disappeared, and $Cs^+$ and $Pb^{2+}$ ions can be separated at 0.01 and 0.1 M $HNO_3$, at 0.5 and 1 M $HNO_3$; sharp peak for $Cs^+$ was observed and the peaks of $Cu^{2+}$, $Co^{2+}$, $Cd^{2+}$, and $Pb^{2+}$ ions were disappeared, and $Cs^+$ ions can be separated from solutions that contained the studied metal ions at 0.5 and 1 M $HNO_3$.

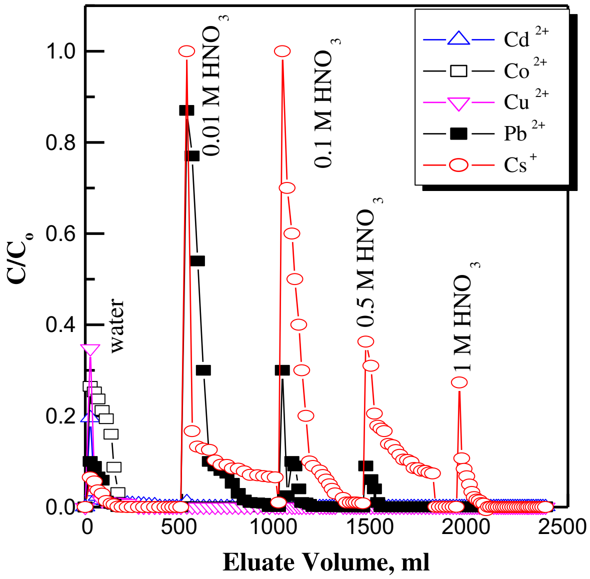

Fig. 8. Elution curves of mixture of $Co^{2+}$, $Cu^{+2}$, $Cd^{2+}$, $Cs^+$, and $Pb^{2+}$ ions with water, 0.01, 0.1, 0.5, and 1 M $HNO_3$ from polyaniline silicotitanate (0.5 cm diameter × 5 cm length and 4–5 drops/min flow rate).

From the presented results, it is clear that the $Cs^+$ ions can be separated from polyaniline silicotitanate column by 0.5 and 1 M $HNO_3$, so we can expect using the column in the regeneration process.

## 4. Conclusions

(1) Polyaniline silicotitanate "organic–inorganic" hybrid cation exchanger was chemically prepared by sol–gel mixing the polyaniline organic polymer into the inorganic precipitate of silicotitanate.

(2) The adsorption of the studied metal ions on polyaniline silicotitanate is favorable for the Freundlich isotherm more than Langmuir and D–R isotherm, all the studied elements are physically adsorbed.

(3) The selectivity of the ions toward polyaniline silicotitanate obtained from column chromatography is in the order: $Cs^+ > Pb^{2+} > Co^{2+} > Cu^{2+} > Cd^{+2}$, this selectivity order is in accordance with that obtained from batch technique.

(4) The break-through capacity for all the metal ions studied is calculated and it is found to be low as compared to the ion exchange capacity for the same metal ions obtained from batch technique.

(5) Cesium metal ions can be separated from polyaniline silicotitanate column by 0.5 and 1 M $HNO_3$.

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