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***EEM2023***

**UNDER THE AUSPICES OF  
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**AND**

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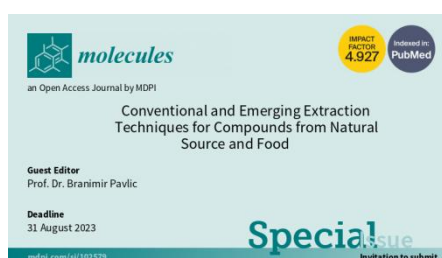
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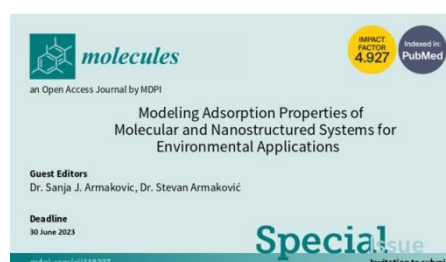
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## KINETICS AND ISOTHERMS MODELING OF SILVER REMOVAL ONTO MACROPOROUS AMINO SORBENT

Tamara T. Tadić<sup>1</sup>, Zvezdana P. Sandić<sup>2</sup>, Sandra S. Bulatović<sup>1</sup>, Bojana M. Marković<sup>1</sup>, Aleksandra B. Nastasović<sup>1</sup>, Antonije E. Onjia<sup>3</sup>

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### Abstract

Silver as one of the most known precious metal is used on a large scale in various industrial branches and the release of silver ions from such industrial activities potentially can cause serious environmental problems. Therefore, the removal of this metal from wastewater is a great challenge, and it is crucial for the quality improvement of the environment. Porous polymer materials with high specific surface areas and other specific physical and chemical characteristics have gained much attention as sorbents in the field of environmental protection. In this paper, macroporous poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) copolymer synthesized by suspension copolymerization and functionalized with diethylenetriamine was employed for silver ions sorption from aqueous solution at unadjusted pH and room temperature. The sorption kinetics and isotherms were studied to establish the mechanisms of sorption process. The kinetic data were modeled with pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich and fractional power (FP) models as well as intraparticle diffusion (IPD) and liquid diffusion model (LFD), while the equilibrium data were analyzed using Langmuir, Freundlich, Sips and Redlich-Peterson isotherm models. Eight error functions such as coefficient of determination ( $R^2$ ), Marquardt's percent standard deviation (MPSD), Chi-square statistic test ( $\chi^2$ ), hybrid fractional error function (HYBRID), the root mean square error (RMSE), the sum of the errors squared (SSE), sum of the absolute errors (SAE), and average relative error (ARE) were used to estimate the error deviations between theoretically predicted and experimental values of sorption capacities. The best kinetic and isotherm models were determined by normalizing eight error functions and finding the sum of normalized error value (SNE). The sorption kinetic studies revealed that the sorption of silver by macroporous amino-functionalized sorbent obeys the PSO kinetic model. In addition, the results indicate that sorption was governed by intraparticle diffusion with the evident influence of liquid film diffusion. The obtained results showed that the sorption isotherm data were satisfactorily fitted to the Redlich-Peterson isotherm model.

**Key words:** silver, macroporous sorbent, error functions, glycidyl methacrylate, sorption

## Introduction

Silver is a very useful precious metal due to its excellent thermal and electrical conductivity, malleability, photosensitivity, and antimicrobial properties and it is abundantly used in the production of mirrors, jewelry, high-quality photography and radiographic films, antimicrobial materials, batteries, and electronic devices (Akgül et al., 2006; Huang et al., 2022; Mao et al., 2023). Power plants, waste incineration, metal smelters, and urban agglomerations are the main source of anthropogenic emissions of silver, while natural sources are windblown dust, volcanic emissions, forest fires, and biogenic and oceanic emissions (Reiman and Fabian, 2022). Silver occurs naturally in the form of insoluble oxides, sulfides and other salts. Rapid industrialization and anthropogenic activities, including modern life habits, have led to high silver concentrations in the environment. When silver reaches the environment, it can be absorbed by biota, and it is toxic to microflora and aquatic organisms as well as humans. The soluble silver compounds may cause some toxic effects such as altering skin, and hair color, argyria, kidney and liver disease, and respiratory disorders (Jintakosol and Nitayaphat, 2016). In rivers and lakes, the silver concentrations are in range between  $0.01 \mu\text{g}/\text{dm}^3$  in unpolluted areas, and  $0.1 \mu\text{g}/\text{dm}^3$  in urban and industrial areas (Causapé et al., 2021). According to the World Health Organization (WHO), the allowable silver ions concentration for drinking water disinfection is  $0.1 \text{ mg}/\text{dm}^3$ , but the U.S. Environmental Protection Agency (EPA) limited the maximum concentration up to  $0.05 \text{ mg}/\text{dm}^3$  (Pelkonen et al., 2003).

Because of the toxicity and strong economical need for silver, there is a growing interest in the removal and recovery of this metal from industrial wastewater. A variety techniques such as precipitation, coagulation, electrolysis, membrane separation, solvent extraction, solid phase extraction, biosorption and sorption have been development for the treatment of silver-contaminated waters (Jintakosol and Nitayaphat, 2016; Virolainen et al., 2015). Among these techniques, sorption has been widely used due to its low cost, simplicity, and high efficiency (Ren et al., 2022). Different economical adsorbents (lignin, chitosan, clay, zeolite, activated carbons, and fly ash) have been used for the removal of silver ions from aqueous solution (Akgül et al., 2006; Çoruh et al., 2011; Jintakosol and Nitayaphat, 2016; Prakoso, 2018). However, this type of adsorbents have some disadvantages such as dissolution in highly acidic solution, poor mechanical and thermal properties, lower adsorption capacity as well as poor reusability (Nitayaphat and Jintakosol, 2015; Ren et al., 2022). Therefore, it was necessary to develop low-cost, energy-efficient, and reusable materials for water treatment. These materials are characterized with large surface area, and the availability of various functional groups ( $-\text{NH}_2$ ,  $-\text{COOH}$ ,  $-\text{OH}$ ) for modification, and with the ability of selectivity and regeneration (Waheed et al., 2021).

Polymeric materials are widely used as metal sorbents due to their specific surface area, high porosity, dimensional stability, high chemical and thermal stability, and reusability (Suručić et al., 2023). Among the polymeric sorbents, glycidyl methacrylate (GMA) based polymers are very interesting because of the presence of epoxy groups which offer numerous modification possibilities and therefore have versatile applications (Marković et al., 2021; Suručić et al., 2023; Tadić et al., 2022).

In this work, the macroporous GMA based copolymer, PGME-deta, was tested as a potential Ag(I) sorbent from aqueous solutions. Kinetic data were analyzed using six kinetic models to determine the nature of sorption kinetics and the rate-controlling step for silver sorption by PGME-deta. The isotherm parameters were also evaluated from the equilibrium experimental data.

## Materials and Methods

Macroporous poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) copolymer, PGME-deta, was prepared by suspension copolymerization and functionalized with

diethylenetriamine as described previously (Ekmešćić et al., 2019). The solution of silver ions was prepared using  $\text{AgNO}_3$  (Sigma-Aldrich, USA).

The sorption studies of silver ions from aqueous solutions were carried out in batch static conditions at unadjusted pH and room temperature. Kinetic experiment was performed by adding 0.5 g of PGME-deta to  $0.05 \text{ dm}^3$  of  $50 \text{ mmol/dm}^3$  Ag(I) solution with contact time ranging from 0 to 180 min. The residual concentrations of Ag(I) ions were determined by using inductively coupled plasma optical emission spectrometry (ICP-OES) (model Thermo Scientific iCAP 6500, Waltham, MA, USA). The sorption capacity at contact time,  $Q_t$  (mmol/g), was obtained according to the following equation:

$$Q = \frac{(C_i - C_t) * V}{m} \quad (1)$$

where  $C_i$  ( $\text{mmol/dm}^3$ ) and  $C_t$  ( $\text{mmol/dm}^3$ ) are the initial and final concentrations of Ag(I) ions in aqueous solutions,  $V$  ( $\text{dm}^3$ ) is the volume of aqueous solution and  $m$  (g) is the weight of polymer sorbent.

The equilibrium study was examined using 0.1 g of PGME-deta added to  $0.01 \text{ dm}^3$  of initial Ag(I) ion concentrations (10 - 100  $\text{mmol/dm}^3$ ) for 3 h at room temperature. The equilibrium sorption capacity,  $Q_e$  (mmol/g), was calculated according to the following equation:

$$Q = \frac{(C_i - C_e) * V}{m} \quad (2)$$

where  $C_e$  ( $\text{mmol/dm}^3$ ) is the equilibrium concentrations of Ag(I) ions in aqueous solutions.

## Results and Discussion

The sorption kinetics of Ag(I) ions by PGME-deta was investigated using four surface-reaction models (pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich, fractional power (FP) models) (Nastasović et al., 2022). The non-linear analysis was used to fit the experimental data to determine the best-fit kinetic model. To estimate the error deviations between theoretically predicted and experimental values of sorption capacities, eight error functions are used (Shahmohammadi-Kalalagh and Babazadeh, 2014). The coefficient of determination ( $R^2$ ), Marquardt's percent standard deviation (MPSD), Chi-square statistic test ( $\chi^2$ ), hybrid fractional error function (HYBRID), the root mean square error (RMSE), the sum of the errors squared (SSE), sum of the absolute errors (SAE), and average relative error (ARE) are the error functions that have been employed for analysis. The best kinetic models were determined by normalizing eight error functions and finding the sum of normalized error value (SNE). The calculated kinetic parameters and error functions data for four surface-reactions models are presented in Table 1 to Table 4, while fitting curves are portrayed in Figure 1.

Based on the obtained results, it is noted that the HYBRID error function showed the best fit giving the lowest SNE value for the PFO and FP kinetic model, while SAE and  $\chi^2$  produced the best fit for PSO and Elovich kinetic models, respectively. The highest  $R^2$  value and the lowest values of SSE, SAE, ARE, HYBRID, MPSD,  $\chi^2$  and RMSE indicate the PSO model is the most suitable model for Ag(I) sorption onto PGME-deta. Also, the sorption capacity at the equilibrium value obtained by the PSO model ( $Q_e^{cal} = 1.09 \text{ mmol/g}$ ) agrees very well with the experimental sorption capacity ( $Q_e^{exp} = 1.12 \text{ mmol/g}$ ) confirming that Ag(I) sorption process predominantly followed the pseudo-second-order kinetic model.

Table 1. The PFO parameters with error functions analysis.

|                      | $R^2$  | SSE    | SAE    | ARE    | HYBRID       | MPSD   | $\chi^2$ | RMSE   |
|----------------------|--------|--------|--------|--------|--------------|--------|----------|--------|
| $k_1$ , 1/min        | 0.12   | 0.12   | 0.11   | 0.11   | <u>0.12</u>  | 0.14   | 0.44     | 0.12   |
| $Q_e^{cal}$ , mmol/g | 1.06   | 1.07   | 1.07   | 1.07   | <u>1.06</u>  | 1.03   | 0.95     | 1.07   |
| $R^2$                | 0.852  | 0.852  | 0.851  | 0.851  | 0.851        | 0.842  | 0.669    | 0.852  |
| SSE                  | 0.092  | 0.092  | 0.094  | 0.094  | 0.093        | 0.100  | 0.261    | 0.092  |
| SAE                  | 0.487  | 0.488  | 0.460  | 0.460  | 0.513        | 0.645  | 1.146    | 0.488  |
| ARE                  | 11.060 | 11.133 | 10.590 | 10.590 | 11.482       | 13.078 | 18.706   | 11.133 |
| HYBRID               | 3.146  | 10.054 | 3.196  | 3.196  | 3.133        | 3.197  | 6.181    | 3.141  |
| MPSD                 | 27.585 | 27.555 | 27.838 | 27.838 | 27.445       | 27.319 | 33.016   | 27.555 |
| $\chi^2$             | 0.715  | 0.704  | 0.772  | 0.772  | 0.671        | 0.593  | 0.291    | 0.704  |
| RMSE                 | 0.115  | 0.115  | 0.116  | 0.116  | 0.115        | 0.119  | 0.193    | 0.115  |
| SNE                  | 5.613  | 6.287  | 5.670  | 5.670  | <b>5.596</b> | 5.779  | 8.390    | 5.599  |

Table 2. The PSO parameters with error functions analysis.

|                      | $R^2$  | SSE    | SAE          | ARE    | HYBRID | MPSD   | $\chi^2$ | RMSE   |
|----------------------|--------|--------|--------------|--------|--------|--------|----------|--------|
| $k_2$ , g/mmol min   | 0.19   | 0.19   | <u>0.19</u>  | 0.27   | 0.23   | 0.41   | 0.42     | 0.19   |
| $Q_e^{cal}$ , mmol/g | 1.12   | 1.12   | <u>1.12</u>  | 1.11   | 1.09   | 0.99   | 1.04     | 1.12   |
| $R^2$                | 0.866  | 0.866  | 0.866        | 0.848  | 0.863  | 0.811  | 0.822    | 0.866  |
| SSE                  | 0.082  | 0.082  | 0.082        | 0.094  | 0.084  | 0.126  | 0.114    | 0.082  |
| SAE                  | 0.617  | 0.616  | 0.082        | 0.575  | 0.659  | 0.998  | 0.744    | 0.616  |
| ARE                  | 12.214 | 12.211 | 12.211       | 11.833 | 12.595 | 15.523 | 13.043   | 12.211 |
| HYBRID               | 2.429  | 2.431  | 2.431        | 2.658  | 2.403  | 2.754  | 2.894    | 2.431  |
| MPSD                 | 23.093 | 23.092 | 5.332        | 23.256 | 22.638 | 21.849 | 23.245   | 23.092 |
| $\chi^2$             | 0.260  | 0.257  | 0.257        | 0.179  | 0.226  | 0.186  | 0.152    | 0.257  |
| RMSE                 | 0.108  | 0.108  | 0.108        | 0.116  | 0.109  | 0.134  | 0.127    | 0.108  |
| SNE                  | 6.691  | 6.77   | <b>5.378</b> | 6.538  | 6.618  | 7.542  | 6.968    | 6.677  |

Table 3. The parameters of Elovich kinetic model with error functions analysis.

|                       | $R^2$  | SSE    | SAE    | ARE    | HYBRID | MPSD   | $\chi^2$     | RMSE   |
|-----------------------|--------|--------|--------|--------|--------|--------|--------------|--------|
| $\alpha$ , mmol/g min | 2.29   | 2.29   | 2.38   | 2.38   | 1.70   | 1.60   | <u>1.96</u>  | 2.29   |
| $\beta$ , mmol/g      | 6.73   | 6.73   | 7.16   | 7.16   | 6.44   | 6.48   | <u>6.47</u>  | 6.73   |
| $R^2$                 | 0.860  | 0.860  | 0.832  | 0.844  | 0.857  | 0.851  | 0.859        | 0.960  |
| SSE                   | 0.086  | 0.086  | 0.099  | 0.099  | 0.088  | 0.093  | 0.087        | 0.086  |
| SAE                   | 0.739  | 0.739  | 0.719  | 0.719  | 0.754  | 0.763  | 0.734        | 0.739  |
| ARE                   | 10.470 | 10.468 | 9.732  | 9.732  | 10.469 | 10.576 | 10.200       | 10.468 |
| HYBRID                | 1.693  | 1.693  | 1.774  | 1.774  | 1.633  | 1.666  | 1.692        | 1.692  |
| MPSD                  | 16.147 | 16.145 | 15.635 | 15.635 | 15.391 | 15.249 | 16.070       | 16.145 |
| $\chi^2$              | 0.106  | 0.106  | 0.126  | 0.126  | 0.109  | 0.117  | 0.105        | 0.106  |
| RMSE                  | 0.111  | 0.111  | 0.119  | 0.119  | 0.112  | 0.115  | 0.111        | 0.111  |
| SNE                   | 7.543  | 7.543  | 7.799  | 7.813  | 7.534  | 7.702  | <b>7.506</b> | 7.543  |

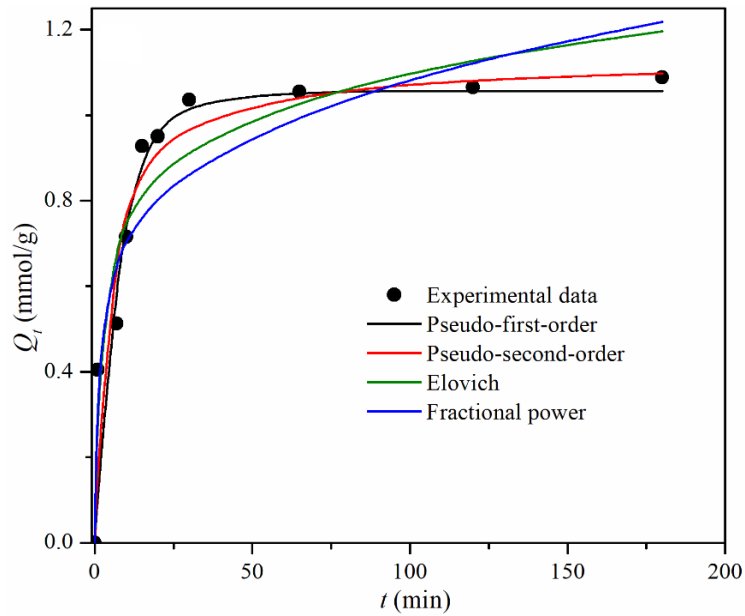


Figure 1. Non-linear fitting kinetic curves for Ag(I) sorption onto PGME-deta.

Table 4. The parameters of FP kinetic model with error functions analysis.

|                       | $R^2$  | SSE    | SAE    | ARE    | HYBRID       | MPSD   | $\chi^2$ | RMSE   |
|-----------------------|--------|--------|--------|--------|--------------|--------|----------|--------|
| $k_{FP}$ , mmol/g min | 0.51   | 0.51   | 0.49   | 0.40   | <u>0.46</u>  | 0.42   | 0.48     | 0.51   |
| $\nu$ , 1/min         | 0.17   | 0.17   | 0.16   | 0.23   | <u>0.19</u>  | 0.21   | 0.18     | 0.17   |
| $R^2$                 | 0.819  | 0.819  | 0.807  | 0.762  | 0.809        | 0.790  | 0.815    | 0.819  |
| SSE                   | 0.116  | 0.116  | 0.128  | 0.164  | 0.125        | 0.142  | 0.120    | 0.116  |
| SAE                   | 0.918  | 0.918  | 0.888  | 1.013  | 0.931        | 0.982  | 0.928    | 0.918  |
| ARE                   | 13.939 | 13.914 | 13.123 | 12.504 | 12.755       | 12.567 | 13.471   | 13.914 |
| HYBRID                | 2.352  | 2.346  | 2.380  | 2.503  | 2.135        | 2.244  | 2.250    | 2.346  |
| MPSD                  | 19.568 | 19.520 | 18.785 | 16.860 | 16.893       | 16.292 | 18.405   | 19.520 |
| $\chi^2$              | 0.149  | 0.149  | 0.169  | 0.179  | 0.154        | 0.173  | 0.146    | 0.149  |
| RMSE                  | 0.129  | 0.129  | 0.135  | 0.153  | <u>0.133</u> | 0.142  | 0.131    | 0.129  |
| SNE                   | 7.230  | 7.223  | 7.319  | 7.688  | <b>7.038</b> | 7.323  | 7.117    | 7.223  |

In order to define the rate-determining step of the Ag(I) sorption by macroporous PGME-deta sorbent, two diffusion kinetic models (intra-particle-diffusion (IPD) and liquid film diffusion (LFD) models) were utilized and the results are shown in Table 5. The higher  $R^2$  values ( $> 0.900$ ) for IPD revealed that sorption is more particle diffusion controlled than LFD ( $R^2 = 0.736$ ). However, the IPD shows three diffusion stages, indicating that IPD is not the only rate-controlling step of Ag(I) sorption process.

Table 5. Kinetic diffusion models parameters for Ag(I) sorption by PGME-deta

| Intra-particle diffusion model        |       |       | Liquid film diffusion model |                              |       |
|---------------------------------------|-------|-------|-----------------------------|------------------------------|-------|
| Stage                                 | I     | II    | III                         |                              |       |
| $k_{id}$ (mmol/g min <sup>0.5</sup> ) | 0.17  | 0.07  | 0.01                        | $k_{LFD} \cdot 10^3$ (1/min) | 2.72  |
| $C_{id}$ (mmol/g)                     | 0.19  | 0.65  | 1.01                        | $C_{LFD}$                    | -1.16 |
| $R^2$                                 | 0.908 | 0.971 | 0.974                       | $R^2$                        | 0.736 |

For determining potential interactions between PGME-deta and Ag(I) ions and predicting the mechanisms of the sorption process, the four isotherm models were used. The experimental equilibrium data were fitted with Langmuir, Freundlich, Sips, and Redlich–Peterson isotherm models using non-linear regression analysis (Nastasović et al., 2022). The best-fitting model was determined by normalizing eight error functions ( $R^2$ , MPSD,  $\chi^2$ , HYBRID, RMSE, SSE, SAE,



and ARE) and finding the sum of normalized error value (SNE). Isotherm parameters and error function data are presented in Table 6 to Table 9, while isotherm fitting curves are showed in Figure 2.

Table 6. The parameters of Langmuir isotherm model with error functions analysis

|                       | $R^2$ | SSE    | SAE   | ARE   | HYBRID | MPSD  | $\chi^2$     | RMSE  |
|-----------------------|-------|--------|-------|-------|--------|-------|--------------|-------|
| $Q_{max, L}$ , mmol/g | 1.22  | 1.22   | 1.24  | 1.25  | 1.23   | 1.50  | <u>2.14</u>  | 1.22  |
| $K_L$ , $dm^3/mmol$   | 0.38  | 0.38   | 0.33  | 0.32  | 0.36   | 0.10  | <u>0.13</u>  | 0.38  |
| $R^2$                 | 0.958 | 0.958  | 0.950 | 0.949 | 0.958  | 0.958 | 0.961        | 0.958 |
| SSE                   | 0.008 | 0.008  | 0.010 | 0.010 | 0.008  | 0.008 | 0.008        | 0.008 |
| SAE                   | 0.166 | 0.166  | 0.144 | 0.140 | 0.160  | 0.160 | 0.135        | 0.166 |
| ARE                   | 4.503 | 4.502  | 3.452 | 3.383 | 4.196  | 4.196 | 3.196        | 4.502 |
| HYBRID                | 0.432 | 4.644  | 0.486 | 0.491 | 0.421  | 0.421 | 0.371        | 0.431 |
| MPSD                  | 6.925 | 6.923  | 6.878 | 6.905 | 6.623  | 6.623 | 5.989        | 6.923 |
| $\chi^2$              | 0.009 | 0.009  | 0.010 | 0.010 | 0.009  | 0.009 | 0.008        | 0.009 |
| RMSE                  | 0.064 | 0.064  | 0.071 | 0.071 | 0.064  | 0.064 | 0.064        | 0.062 |
| SNE                   | 7.431 | 16.008 | 7.587 | 7.583 | 7.226  | 7.226 | <b>6.549</b> | 7.402 |

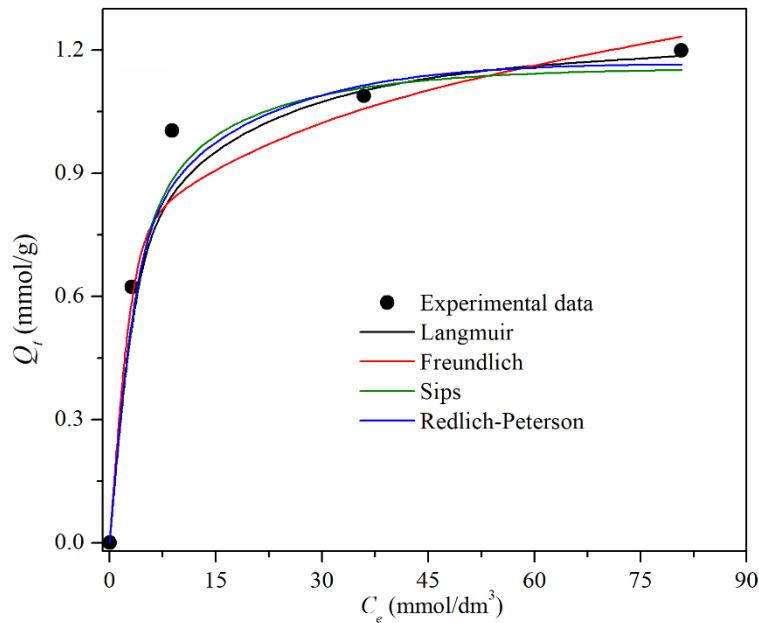


Figure 2. Non-linear fitting isotherm curves for Ag(I) sorption onto PGME-deta

Table 7. The parameters of Freundlich isotherm model with error functions analysis

|                               | $R^2$  | SSE          | SAE    | ARE    | HYBRID | MPSD   | $\chi^2$ | RMSE   |
|-------------------------------|--------|--------------|--------|--------|--------|--------|----------|--------|
| $K_F$ , $dm^3 \text{ mmol/g}$ | 0.61   | <u>0.61</u>  | 0.62   | 0.49   | 0.58   | 0.55   | 0.61     | 0.61   |
| $n$                           | 6.30   | <u>6.29</u>  | 6.70   | 4.53   | 5.73   | 5.30   | 6.12     | 6.29   |
| $R^2$                         | 0.854  | 0.854        | 0.848  | 0.780  | 0.848  | 0.834  | 0.853    | 0.854  |
| SSE                           | 0.032  | 0.032        | 0.034  | 0.055  | 0.034  | 0.038  | 0.032    | 0.032  |
| SAE                           | 0.286  | 0.286        | 0.281  | 0.317  | 0.292  | 0.299  | 0.293    | 0.286  |
| ARE                           | 8.654  | 8.651        | 8.685  | 7.534  | 8.317  | 8.061  | 8.741    | 8.651  |
| HYBRID                        | 1.970  | 1.969        | 2.075  | 2.670  | 1.865  | 1.938  | 1.948    | 1.969  |
| MPSD                          | 15.993 | 15.983       | 16.415 | 16.161 | 14.715 | 14.366 | 15.771   | 15.983 |
| $\chi^2$                      | 0.039  | 0.039        | 0.042  | 0.066  | 0.041  | 0.045  | 0.039    | 0.039  |
| RMSE                          | 0.127  | 0.127        | 0.130  | 0.165  | 0.130  | 0.137  | 0.127    | 0.127  |
| SNE                           | 6.552  | <b>6.551</b> | 6.685  | 7.760  | 6.479  | 6.634  | 6.565    | 6.551  |

Table 8. The parameters of Sips isotherm model with error functions analysis

|                               | $R^2$ | SSE   | SAE   | ARE   | HYBRID | MPSD         | $\chi^2$ | RMSE  |
|-------------------------------|-------|-------|-------|-------|--------|--------------|----------|-------|
| $Q_{m,s}$ , mmol/g            | 1.16  | 1.16  | 1.21  | 1.21  | 1.16   | <u>1.16</u>  | 1.16     | 1.16  |
| $K_s$ , dm <sup>3</sup> /mmol | 0.21  | 0.21  | 0.21  | 0.21  | 0.20   | <u>0.20</u>  | 0.20     | 0.21  |
| $n_s$                         | 0.66  | 0.66  | 0.69  | 0.69  | 0.64   | <u>0.63</u>  | 0.65     | 0.66  |
| $R^2$                         | 0.962 | 0.962 | 0.954 | 0.954 | 0.961  | 0.961        | 0.960    | 0.962 |
| SSE                           | 0.007 | 0.007 | 0.009 | 0.009 | 0.008  | 0.008        | 0.008    | 0.007 |
| SAE                           | 0.165 | 0.165 | 0.150 | 0.150 | 0.162  | 0.160        | 0.160    | 0.165 |
| ARE                           | 4.248 | 4.248 | 4.009 | 4.009 | 4.001  | 3.977        | 3.851    | 4.248 |
| HYBRID                        | 0.743 | 0.743 | 0.911 | 0.911 | 0.725  | 0.728        | 0.734    | 0.743 |
| MPSD                          | 6.188 | 6.187 | 6.845 | 6.845 | 5.926  | 5.940        | 5.871    | 6.187 |
| $\chi^2$                      | 0.007 | 0.007 | 0.009 | 0.009 | 0.007  | 0.007        | 0.007    | 0.007 |
| RMSE                          | 0.061 | 0.061 | 0.068 | 0.068 | 0.062  | 0.062        | 0.063    | 0.061 |
| SNE                           | 7.282 | 7.282 | 7.847 | 7.847 | 7.156  | <b>7.148</b> | 7.169    | 7.282 |

As can be seen from the presented results, the  $\chi^2$  error function indicated the best correlation for the two isotherm models (Langmuir and Redlich-Peterson), followed by the SSE and MPSD error function for Freundlich and Sips isotherm models, respectively. Also, based on the SNE values, the best-fitted isotherm models for the sorption of Ag(I) onto PGME-deta were arranged as: Redlich-Peterson > Langmuir > Freundlich > Sips. These results suggest that the surface of PGME-deta is homogenous and the Ag(I) sorption is a monolayer.

Table 9. The parameters of Redlich-Peterson isotherm model with error functions analysis

|                             | $R^2$ | SSE   | SAE   | ARE   | HYBRID | MPSD  | $\chi^2$     | RMSE  |
|-----------------------------|-------|-------|-------|-------|--------|-------|--------------|-------|
| $A$ , dm <sup>3</sup> /g    | 0.40  | 0.40  | 0.40  | 0.40  | 0.38   | 0.36  | <u>0.38</u>  | 0.40  |
| $B$ , dm <sup>3</sup> /mmol | 0.29  | 0.29  | 0.29  | 0.29  | 0.26   | 0.23  | <u>0.25</u>  | 0.29  |
| $g$                         | 1.03  | 1.03  | 1.03  | 1.03  | 1.05   | 1.06  | <u>1.05</u>  | 1.03  |
| $R^2$                       | 0.975 | 0.975 | 0.959 | 0.960 | 0.975  | 0.975 | 0.975        | 0.975 |
| SSE                         | 0.005 | 0.005 | 0.008 | 0.008 | 0.005  | 0.005 | 0.005        | 0.005 |
| SAE                         | 0.111 | 0.111 | 0.091 | 0.091 | 0.109  | 0.108 | 0.107        | 0.111 |
| ARE                         | 2.553 | 2.553 | 2.093 | 2.089 | 2.457  | 2.448 | 2.398        | 2.553 |
| HYBRID                      | 0.422 | 0.422 | 0.745 | 0.729 | 0.420  | 0.422 | 0.421        | 0.422 |
| MPSD                        | 4.343 | 4.343 | 5.849 | 5.788 | 4.315  | 4.335 | 4.308        | 4.343 |
| $\chi^2$                    | 0.004 | 0.004 | 0.007 | 0.007 | 0.004  | 0.004 | 0.004        | 0.004 |
| RMSE                        | 0.049 | 0.049 | 0.064 | 0.063 | 0.049  | 0.049 | 0.049        | 0.049 |
| SNE                         | 6.263 | 6.263 | 7.617 | 7.531 | 6.199  | 6.191 | <b>6.174</b> | 6.263 |

## Conclusions

The sorption kinetic studies revealed that the sorption of silver by macroporous amino-functionalized sorbent, PGME-deta, obeys the PSO kinetic model. According to results, sorption was governed by intra particle diffusion with the evident influence of liquid film diffusion. The obtained results showed that the sorption isotherm data were satisfactorily fitted to the Redlich-Peterson isotherm model, suggesting a monolayer sorption at specific homogenous sites.

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