**Supplementary materials**

# Extended Rate Constants Distribution (RCD) Model for Sorption in Heterogeneous Systems: 2. Importance of Diffusion Limitations for Sorption Kinetics on Cryogels in Batch

**Irina Malakhova[1], Alexey Golikov[1], Yuliya Azarova[1] and Svetlana Bratskaya[1]***

[1] Institute of Chemistry, Far Eastern Branch of Russian Academy of Sciences, 159, prosp.100-letiya Vladivostoka, Vladivostok 690022, Russia

* Correspondence: sbratska@ich.dvo.ru (S.B.), azarova87@mail.ru (Yu.A.)

Linearization of the pseudo-first-order (PFO) rate expression (1)

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t) \tag{1}$$

is given as equation (2):

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{2}$$

where Qe and Qt are the adsorbed amounts of the adsorbate at equilibrium and at time t, respectively, and $k_1$ is the rate constant of pseudo-first order adsorption.

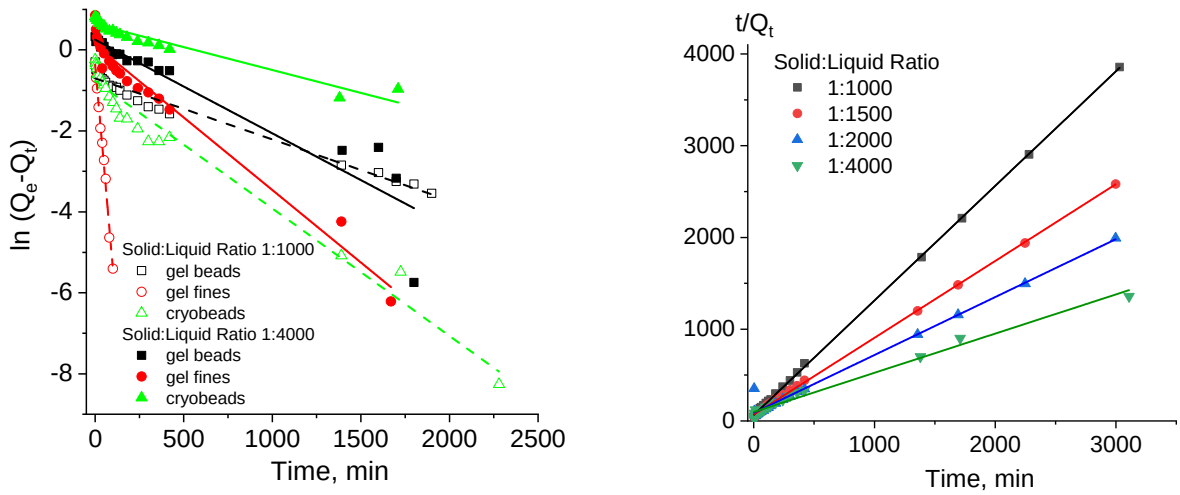
The pseudo-second-order (PSO) rate expression (3), can be transformed to equation (4) and it's linear form (5):

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \tag{3}$$

$$Qt = \frac{Q_e^2 k_2 t}{Q_e k_2 t + 1} \tag{4}$$

$$\frac{t}{Qt} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \tag{5}$$

where $Q_e$ and $Q_t$ are the adsorbed amounts of the adsorbate at equilibrium and at time t, respectively, and k2 is the rate constant of pseudo-second order adsorption.




(**a**) (**b**)

**Figure 1S.** Linear PFO model for Cu(II) ions adsorption kinetics of PEI-gels and PEI cryobeads (a) and linear PSO model for Cu(II) ions adsorption kinetics of PEI-cryobeads (b).

**Table 1S.** The parameters of PFO model for kinetic curves of Cu(II) ions sorption on PEI cryogels and gels - $k_1$ is rate constant of pseudo-first- order adsorption, $Q_e$ is Cu(II) adsorbed amounts at quasi-equilibrium

| **Sorbent** | **Solid:liquid ratio** | **$R^2$** | **$k_1$, $min^{-1}$** | **Qe, mmol/g** |
|---|---|---|---|---|
| PEI-gel | 1:1000 | 0,97 | 0,00151 | 0,49 |
| PEI-gel, fines | 1:1000 | 0,99 | 0,05039 | 0,69 |
| PEI-cryobeads | 1:1000 | 0,96 | 0,00315 | 0,46 |
| PEI-gel | 1:4000 | 0,88 | 0,00231 | 1,28 |
| PEI-gel, fines | 1:4000 | 0,96 | 0,00358 | 1,12 |
| PEI-cryobeads | 1:4000 | 0,92 | 0,00113 | 1,88 |

**Table 2S.** The parameters of PSO model for kinetic curves of Cu(II) ions sorption on PEI cryogels and gels - $k_2$ is rate constant of pseudo-second-order adsorption, $Q_e$ is Cu(II) adsorbed amounts at quasi-equilibrium

| Sorbent | Solid:liquid ratio | $R^2$ | $k_2$, $g \cdot mmol^{-1} min^{-1}$ | Qe, mmol/g |
|---|---|---|---|---|
| PEI-gel, beads | 1:1000 | 0,99 | 0,01194 | 0,76 |
| | 1:1500 | 0,99 | 0,00655 | 0,96 |
| | 1:2000 | 0,99 | 0,00542 | 1,18 |
| | 1:4000 | 0,97 | 0,00237 | 1,61 |
| PEI-gel, beads (t=100 min) | 1:1000 | 0,98 | 0,16579 | 0,38 |
| | 1:1500 | 0,97 | 0,13191 | 0,38 |
| | 1:2000 | 0,93 | 0,18806 | 0,46 |
| | 1:4000 | 0,47 | 0,02641 | 0,58 |
| PEI-cryobeads | 1:1000 | 0,99 | 0,02409 | 0,80 |
| | 1:1500 | 0,99 | 0,00996 | 1,20 |
| | 1:2000 | 0,98 | 0,00452 | 1,58 |
| | 1:4000 | 0,99 | 0,00189 | 2,32 |
| PEI-cryobeads (t=100 min) | 1:1000 | 0,98 | 0,05159 | 0,63371 |
| | 1:1500 | 0,94 | 0,02602 | 0,88339 |
| | 1:2000 | 0,98 | 0,01356 | 1,1976 |
| | 1:4000 | 0,94 | 0,03052 | 0,91075 |
| PEI-gel, fines | 1:1000 | 0,99 | 0,10369 | 0,83 |
| | 1:1500 | 0,99 | 0,06905 | 1,192 |
| | 1:2000 | 0,99 | 0,04156 | 1,59 |
| | 1:4000 | 0,99 | 0,01013 | 2,43 |
| PEI-gel, fines (t=100 min) | 1:1000 | 0,99 | 0,09258 | 0,84746 |
| | 1:1500 | 0,99 | 0,11845 | 1,14943 |
| | 1:2000 | 0,99 | 0,07871 | 1,47493 |
| | 1:4000 | 0,99 | 0,05793 | 1,81403 |

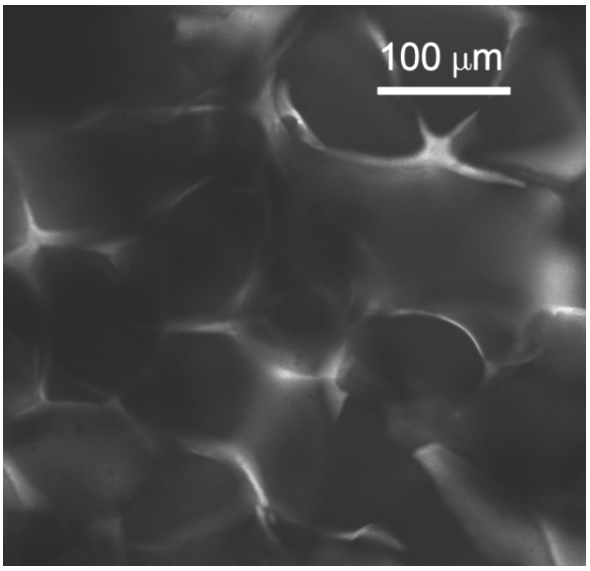



**Fig. 2S.** Confocal laser scanning microscopy (CLSM) images of PEI-cryogels stained with fluorescein.