**Mechanisms and adsorption capacities of natural and eco-friendly nanoparticles for heavy metals and phosphate ions from water using DSD approach**

**Autors:** Jovana Jokić Govedaricaa, Dragana Tomašević Pilipovića\*, Vesna Gvoićb, Đurđa Kerkeza, Anita Leovac Maćeraka, Nataša Slijepčevića, Milena Bečelić-Tomina

a University of Novi Sad, Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection, Trg Dositeja Obradovića 3, 21000, Novi Sad, Serbia

b University of Novi Sad, Faculty of Technical Sciences, Department of Graphic Engineering and Design, Trg Dositeja Obradovića 6, 21000, Novi Sad, Serbia

\***Corresponding author:** Dragana Tomašević Pilipović, Phone: +381 21 485 27 34; Fax: +381 21 454 065; e-mail address: [dragana.tomasevic@dh.uns.ac.rs](mailto:djurdja.kerkez@dh.uns.ac.rs); Postal address: Trg Dositeja Obradovica 3, 21000 Novi Sad, Serbia

**List of Figure Captions**

**Figure S1.** Diagnostic plots: a) cadmium - Actual vs Predicted; b) cadmium - Residual by Predicted; c) phosphate - Actual vs Predicted; d) phosphate - Residual by Predicted

**Figure S2:** Pareto chart for: a) cadmium removal; b) phosphate removal

**Figure S3.** Diagnostic plots: a) nickel - Actual vs Predicted; b) nickel - Residual by Predicted; c) phosphate - Actual vs Predicted; d) phosphate - Residual by Predicted

**Figure S4:** Pareto chart for: a) nickel removal; b) phosphate removal

**Figure 5. a)** effect of reaction time on adsorption of Cd (II) and Ni (II) in the presence of phosphate on oak-nZVI b) kinetic model pseudo-first-order c) kinetic model pseudo-second-order

Figure 4.tif

**Figure S1.** Diagnostic plots: a) cadmium - Actual vs Predicted; b) cadmium - Residual by Predicted; c) phosphate - Actual vs Predicted; d) phosphate - Residual by Predicted

Figure 5.tif

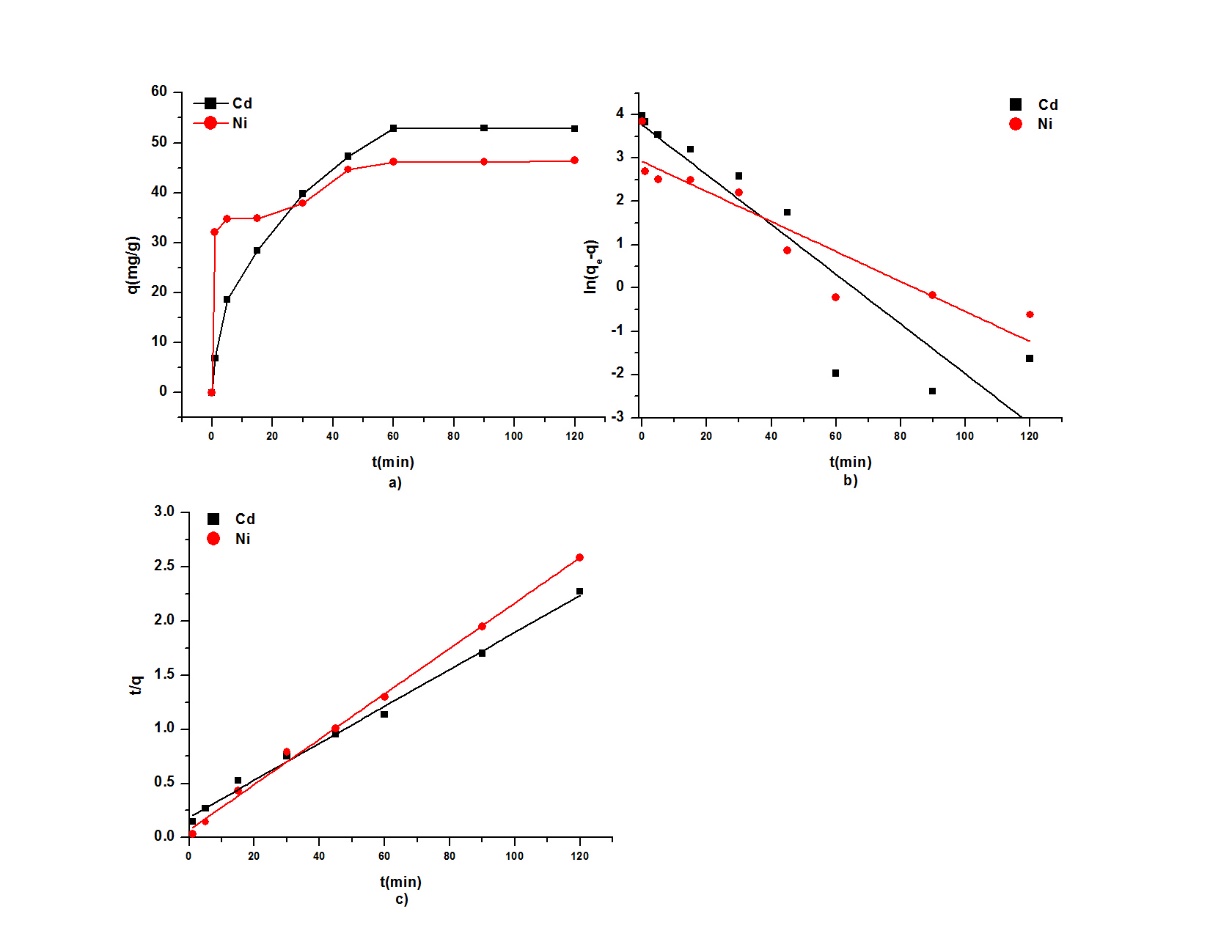
**Figure S2:** Pareto chart for: a) cadmium removal; b) phosphate removal

Figure 8.tif

**Figure S3.** Diagnostic plots: a) nickel - Actual vs Predicted; b) nickel - Residual by Predicted; c) phosphate - Actual vs Predicted; d) phosphate - Residual by Predicted

Figure 5.tif

**Figure S4:** Pareto chart for: a) nickel removal; b) phosphate removal



**Figure S5: a)** effect of reaction time on adsorption of Cd (II) and Ni (II) in the presence of phosphate on oak-nZVI b) kinetic model pseudo-first-order c) kinetic model pseudo-second-order

**List of Tables**

**Table S1.** Process variables with experimental levels

**Table S2.** DSD experimental design layout

**Table S3.** Adsorption efficiency (%) for the removal of cadmium and phosphate

**Table S4.** Standard selection criteria for the regression models (cadmium and phosphate)

**Table S5.** ANOVA and "Lack of fit "test (cadmium and phosphate)

**Table S6.** Experimental verification of optimized processes for cadmium and phosphate removal

**Table S7.** Adsorption efficiency (%) for the removal of nickel and phosphate

**Table S8.** Standard selection criteria for the regression models (nickel and phosphate)

**Table S9.** ANOVA and "Lack of fit"test – nickel and phosphate removal

**Table S10.** Experimental verification of optimized processes

**Table S11.** Parameters of kinetic models for describing the adsorption of cadmium and nickel in the presence of phosphate on oak-nZVI

**Table S1. Process variables with experimental levels**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Variables** | **Unit** | **Symbol coded** | **Levels** | | |
| -1 | 0 | +1 |
| **Metal concentration** | mgL-1 | X1 | 1 | 5 | 9 |
| **Ion concentation** | mgL-1 | X2 | 1 | 5 | 9 |
| **pH** | - | X3 | 2 | 6 | 10 |
| **oak-nZVI concentration** | ml | X4 | 2 | 9 | 16 |

**Table S2. DSD experimental design layout**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Run** | **Metal concentration** | **Ion concentration** | **pH** | **oak-nZVI concentration** |
| **1** | 9 | 9 | 10 | 9 |
| **2** | 1 | 1 | 2 | 9 |
| **3** | 1 | 5 | 10 | 16 |
| **4** | 9 | 5 | 2 | 2 |
| **5** | 5 | 1 | 2 | 16 |
| **6** | 5 | 9 | 10 | 2 |
| **7** | 1 | 9 | 6 | 16 |
| **8** | 9 | 1 | 6 | 2 |
| **9** | 9 | 9 | 2 | 16 |
| **10** | 1 | 1 | 10 | 2 |
| **11** | 9 | 1 | 10 | 16 |
| **12** | 1 | 9 | 2 | 2 |
| **13** | 5 | 5 | 6 | 9 |
| **14** | 9 | 9 | 10 | 9 |
| **15** | 1 | 1 | 2 | 9 |
| **16** | 1 | 5 | 10 | 16 |
| **17** | 9 | 5 | 2 | 2 |
| **18** | 5 | 1 | 2 | 16 |
| **19** | 5 | 9 | 10 | 2 |
| **20** | 1 | 9 | 6 | 16 |
| **21** | 9 | 1 | 6 | 2 |
| **22** | 9 | 9 | 2 | 16 |
| **23** | 1 | 1 | 10 | 2 |
| **24** | 9 | 1 | 10 | 16 |
| **25** | 1 | 9 | 2 | 2 |
| **26** | 5 | 5 | 6 | 9 |
| **27** | 5 | 5 | 6 | 9 |
| **28** | 5 | 5 | 6 | 9 |

**Table S3. Adsorption efficiency (%) for the removal of cadmium and phosphate**

|  |  |  |
| --- | --- | --- |
| **Run** | **Cadmium** | **Phosphate** |
| **1** | 91.06 | 64.67 |
| **2** | 90.02 | 82.00 |
| **3** | 96.63 | **29.00** |
| **4** | 85.94 | 71.56 |
| **5** | 57.54 | 75.00 |
| **6** | 95.86 | 81.40 |
| **7** | 98.96 | 73.00 |
| **8** | 26.02 | 76.22 |
| **9** | 91.90 | 66.89 |
| **10** | **15.44** | **97.00** |
| **11** | 24.85 | 81.00 |
| **12** | **99.01** | 69.00 |
| **13** | 89.61 | 83.20 |
| **14** | 92.59 | 64.22 |
| **15** | 90.47 | 87.00 |
| **16** | 96.71 | 34.00 |
| **17** | 86.09 | 71.89 |
| **18** | 59.56 | 76.40 |
| **19** | 95.64 | 79.80 |
| **20** | 98.91 | 69.00 |
| **21** | 39.83 | 76.89 |
| **22** | 91.90 | 66.33 |
| **23** | 91.13 | 91.00 |
| **24** | 33.14 | 79.00 |
| **25** | 98.87 | 65.00 |
| **26** | 91.95 | 81.80 |
| **27** | 91.47 | 82.60 |
| **28** | 92.19 | 82.20 |

**Table S4.** **Standard selection criteria for the regression models (cadmium and phosphate)**

|  |  |  |
| --- | --- | --- |
| **Descriptive factor** | **Cadmium** | **Phosphate** |
| **R2** | 0.823 | 0.737 |
| **R2 adj** | 0.761 | 0.626 |
| **AIC** | 241.184 | 223.199 |
| **BIC** | 243.174 | 223.580 |
| **RMSE** | 12.886 | 8.779 |

**Table S6. ANOVA and "Lack of fit "test (cadmium and phosphate)**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Source** | **aDF** | **bSS** | **cMS** | **F parameter** |
|  | **Cadmium** | | | |
| **Model** | 7 | 15480.632 | 2211.520 | 13.318 |
| **Error** | 20 | 3321.069 | 166.050 | **Prob>F** |
| **C. Total** | 27 | 18801.701 | - | **<0.0001** |
| **Lack of Fit** | 5 | 319.399 | 63.880 | 0.319 |
| **Pure Error** | 15 | 3001.669 | 200.111 | **Prob>F** |
| **Total Error** | 20 | 3321.069 | - | **0.894** |
|  | **Phosphate** | | | |
| **Model** | 8 | 4107. 143 | 513.393 | 6.661 |
| **Error** | 19 | 1464.501 | 77.079 | **Prob>F** |
| **C. Total** | 27 | 5571.644 | - | **0.0003** |
| **Lack of Fit** | 4 | 1399.634 | 349.908 | 80.9137 |
| **Pure Error** | 15 | 64.867 | 4.324 | **Prob>F** |
| **Total Error** | 19 | 1464.501 | - | **0.966** |

aDegrees of freedom;bThe sum of square; cVariance (mean of square)

**Table S6. Experimental verification of optimized processes for cadmium and phosphate removal**

|  |  |  |
| --- | --- | --- |
| **Run** | **Cadmium** | **Phosphate** |
| **1** | 98.90 | 89.28 |
| **2** | 99.66 | 87.38 |
| **3** | 98.98 | 87.42 |
| **4** | 98.77 | 87.92 |
| **5** | 98.93 | 88.02 |
| **6** | 99.08 | 87.16 |
| **7** | 99.09 | 87.66 |
| **8** | 98.99 | 87.44 |
| **95% confidence interval** | **98.83 - 99.27%** | **87.29 - 87.86%** |

**Table S7. Adsorption efficiency (%) for the removal of nickel and phosphate**

|  |  |  |
| --- | --- | --- |
| **Run** | **Nickel** | **Phosphate** |
| **1** | 92.08 | 95.76 |
| **2** | **13.96** | 49.40 |
| **3** | 91.35 | 58.00 |
| **4** | 91.59 | 95.99 |
| **5** | 67.39 | 75.20 |
| **6** | 85.98 | 63.02 |
| **7** | 87.59 | 71.90 |
| **8** | 60.31 | **97.70** |
| **9** | 76.55 | 80.84 |
| **10** | 76.32 | 75.50 |
| **11** | 65.18 | 90.34 |
| **12** | 76.16 | **13.10** |
| **13** | 93.69 | 83.58 |
| **14** | 85.39 | 95.73 |
| **15** | 87.09 | 48.70 |
| **16** | 89.03 | 56.10 |
| **17** | 93.05 | 95.93 |
| **18** | 90.50 | 74.14 |
| **19** | 87.01 | 63.86 |
| **20** | 88.93 | 71.20 |
| **21** | 66.93 | 97.66 |
| **22** | 79.99 | 80.74 |
| **23** | **97.38** | 80.30 |
| **24** | 71.32 | 90.82 |
| **25** | 79.69 | 13.30 |
| **26** | 94.69 | 83.52 |
| **27** | 95.11 | 83.50 |
| **28** | 94.86 | 83.28 |

**Table S8. Standard selection criteria for the regression models (nickel and phosphate)**

|  |  |  |
| --- | --- | --- |
| **Descriptive factor** | **Nickel** | **Phosphate** |
| **R2** | 0.715 | 0.910 |
| **R2 adj** | 0.546 | 0.872 |
| **AIC** | 246.007 | 218.047 |
| **BIC** | 241.194 | 218.428 |
| **RMSE** | 11.286 | 8.008 |

**Table S9. ANOVA and "Lack of fit"test – nickel and phosphate removal**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Source** | **DF** | **SS** | **MS** | **F parameter** |
|  | **Nickel** | | | |
| **Model** | 10 | 5421.248 | 542.125 | 4.256 |
| **Error** | 17 | 2165.324 | 127.372 | **Prob>F** |
| **C. Total** | 27 | 7586.574 | - | **0.0044** |
| **Lack of Fit** | 15 | 2165.235 | 144.39 | 3234.107 |
| **Pure Error** | 2 | 0.089 | 0.045 | **Prob>F** |
| **Total Error** | 17 | 2165.324 | - | **0.906** |
|  | **Phosphate** | | | |
| **Model** | 8 | 12307.914 | 1538.49 | 23.993 |
| **Error** | 19 | 1218.335 | 64.12 | **Prob>F** |
| **C. Total** | 27 | 13526.249 | - | **<0.0001** |
| **Lack of Fit** | 17 | 1218.299 | 71.665 | 4041.240 |
| **Pure Error** | 2 | 0.0355 | 0.018 | **Prob>F** |
| **Total Error** | 19 | 1218.3347 | - | **0.925** |

**Table S10. Experimental verification of optimized processes**

|  |  |  |
| --- | --- | --- |
| **Run** | **Nickel** | **Phosphate** |
| **1** | 93.77 | 96.20 |
| **2** | 94.85 | 96.92 |
| **3** | 95.14 | 96.82 |
| **4** | 94.65 | 96.75 |
| **5** | 93.73 | 97.12 |
| **6** | 94.02 | 97.06 |
| **7** | 94.56 | 97.03 |
| **8** | 94.45 | 96.41 |
| **95% confidence interval** | **93.97 - 94.83%** | **96.51-97.06%** |

**Table S11. Parameters of kinetic models for describing the adsorption of cadmium and nickel in the presence of phosphate on oak-nZVI**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Pseudo-first order | | | | |
| Metal | ***R2*** | ***qe***  **(mg/g) exp** | ***k1***  **(min−1)** | ***qe* (mg/g) cal1** |
| Cd | 0.815 | 53 | 0.96 | 43.3 |
| Ni | 0.839 | 47 | 0.977 | 18.6 |
| Pseudo-second order | | | | |
| Metal | ***R2*** | ***qe* (mg/g) exp** | ***k2*·10-3**  **(q mg−1 min−1)** | ***qe* (mg/g) cal2** |
| Cd | 0.957 | 53 | 1.89 | 55.1 |
| Ni | 0.996 | 47 | 6.48 | 47.7 |