**Supporting Information**

**Preparation and adsorption performance of nano-hydroxyapatite-enhanced acrylamide hydrogel adsorbent**

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**Kinetic Model Fitting**

Pseudo-first-order model:

(1)

Pseudo-second-order model:

(2)

Intraparticle diffusion model:

(3)

where *q*e (mg/g) is the sorbed metal quantity at equilibrium; *q*t (mg/g) is the sorbed quantity at time *t*; *k*1 (L/min), *k*2 (g/(mg∙min)) and *k*p (min-1) are the corresponding adsorption rate constants.

**Adsorption Modeling**

(4)

(5)

where*C*e (mg/L) is the equilibrium concentration of metal ions, *q*e (mg/g) is the equilibrium sorption capacity, *q*max (mg/g) is the maximum monolayer metal ions coverage capacity per unit weight of adsorbent, *K*L (L/mg) and *K*F (mg1-n·Ln/g) are the corresponding adsorption equilibrium constants, *n* is the adsorption intensity.

**Adsorption Thermodynamics**

= (6)

(7)

(8)

(9)

where *K*c is the equilibrium constant; *q*e and *C*e are equilibrium concentrations (mg/L) of heavy metal ions on the sorbent and in the solution, respectively; *T* is the absolute temperature (K) and *R* is the universal gas constant.

(10)

(11)

(12)

where *q*max (mol/g) is the D-R maximum adsorption capacity, *kdr* (mol2/kJ2) is the constant related to the adsorption energy, the Polanyi sorption potential *ε* (J/mol) is the amount of energy required to pull adsorbed molecule from its sorption site and *E* is the free energy (kJ/mol)











Fig. S1 Fitting effect diagram of intra-particle diffusion model, Lead ion (a-c), Nickel ion (d-f), 5% MB (g-i)





Fig.S2 Adsorption isotherms (ac) of Pb(II)(a), Ni(II)(b) and MB(c) at different temperatures (293K, 303 K and 313 K) on hydroxyapatite composite hydrogels. m/V = 1g/L, initial pH = 5±0.1.

 

Fig. S3 The non-linear curves of ε2 and qe of Ni(II) (b) /Pb(II) (a) and MB(c) on the hydroxyapatite composite hydrogels

Table S1. Isotherm parameters of three pollutants on hydroxyapatite-hydrogel.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Model |  | Parameters | Pb | | | Ni | | | MB | | |
| 293K | 303K | 313K | 293K | 303K | 313K | 293K | 303K | 313K |
| Langmuir | 1% | *Q*m | 318.91 | 332.73 | 349.39 | 206.10 | 217.19 | 223.33 | 318.22 | 337.40 | 361.30 |
| *K*L | 0.3559 | 0.2349 | 0.2134 | 0.5061 | 0.3642 | 0.5198 | 0.1893 | 0.1710 | 0.1508 |
| R2 | 0.9532 | 0.9615 | 0.9575 | 0.9305 | 0.9412 | 0.9447 | 0.9518 | 0.8904 | 0.9342 |
| Freundlich | *K*F | 129.61 | 120.87 | 122.94 | 94.56 | 90.66 | 97.15 | 101.24 | 103.27 | 100.93 |
| *1/n*F | 0.1753 | 0.1964 | 0.2022 | 0.1626 | 0.1811 | 0.1766 | 0.2342 | 0.2418 | 0.2666 |
| R2 | 0.6808 | 0.7052 | 0.6925 | 0.7766 | 0.7794 | 0.7471 | 0.7286 | 0.6981 | 0.7810 |
| Langmuir | 3% | *Q*m | 336.53 | 344.19 | 355.16 | 214.11 | 219.47 | 225.03 | 328.69 | 336.57 | 350.68 |
|  | *K*L | 0.2123 | 0.2113 | 0.2086 | 0.5202 | 0.5504 | 0.3013 | 0.1610 | 0.2280 | 0.2080 |
|  | R2 | 0.9575 | 0.9818 | 0.9564 | 0.9469 | 0.9263 | 0.9248 | 0.9222 | 0.9477 | 0.9231 |
| Freundlich | *K*F | 120.09 | 119.71 | 123.27 | 96.19 | 98.95 | 93.21 | 95.05 | 113.22 | 120.99 |
|  | *1/n*F | 0.1993 | 0.2072 | 0.2054 | 0.1670 | 0.1660 | 0.1914 | 0.2508 | 0.2278 | 0.2276 |
|  | R2 | 0.7193 | 0.7571 | 0.6926 | 0.7717 | 0.7248 | 0.8124 | 0.6697 | 0.7536 | 0.8459 |
| Langmuir | 5% | *Q*m | 337.45 | 354.70 | 359.24 | 218.34 | 223.11 | 226.75 | 333.12 | 348.70 | 365.17 |
|  | *K*L | 0.2376 | 0.1720 | 0.2626 | 0.3859 | 0.3406 | 0.5174 | 0.1709 | 0.1787 | 0.1445 |
|  | R2 | 0.9645 | 0.9450 | 0.9726 | 0.9552 | 0.9767 | 0.9838 | 0.8893 | 0.8838 | 0.9525 |
| Freundlich | *K*F | 125.10 | 117.89 | 135.98 | 90.10 | 89.66 | 95.06 | 98.41 | 100.56 | 101.37 |
|  | *1/n*F | 0.1942 | 0.2117 | 0.1930 | 0.1836 | 0.1911 | 0.1865 | 0.2463 | 0.2559 | 0.2705 |
|  | R2 | 0.7436 | 0.7078 | 0.7503 | 0.7691 | 0.8286 | 0.8074 | 0.6323 | 0.6425 | 0.8257 |

Table S2 Parameters of thermodynamic

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | *T* (K) | Pb | | |  | | Ni | | |  | MB | | |
| Δ*G*0 (kJ/mol) | Δ*S*0  (J/(mol K)) | Δ*H*0 (kJ/mol) | |  | Δ*G*0  (kJ/mol) | Δ*S*0  (J/(mol K)) | Δ*H*0 (kJ/mol) |  | Δ*G*0 (kJ/mol) | Δ*S*0  (J/(mol K)) | Δ*H*0 (kJ/mol) |
| 1% | 293 | -0.07 | 19.38 | 5.61 | |  | -0.08 | 20.06 | 5.80 |  | -1.51 | 49.46 | 12.98 |
| 303 | -0.26 |  | -0.28 |  | -2.00 |
| 313 | -0.45 |  | -0.48 |  | -2.50 |
| 3% | 293 | -0.29 | 12.88 | 3.48 | |  | -0.22 | 17.65 | 4.95 |  | -1.63 | 46.38 | 11.96 |
| 303 | -0.42 |  | -0.40 |  | -2.10 |
| 313 | -0.55 |  | -0.58 |  | -2.56 |
| 5% | 293 | -0.34 | 18.40 | 5.05 | |  | -0.28 | 19.55 | 5.45 |  | -1.69 | 49.46 | 12.81 |
| 303 | -0.52 |  | -0.47 |  | -2.18 |
| 313 | -0.71 |  | -0.67 |  | -2.68 |

Table S3 Parameters of Dubinin–Radushkevich (D-R) isotherm.

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | *T* (K) | Pb | | |  | Ni | | |  | MB | | |
| *k* (mol2/kJ2) | *E* (kJ/mol) | R2 |  | *k* (mol2/kJ2) | *E* (kJ/mol) | R2 |  | *k* (mol2/kJ2) | *E* (kJ/mol) | R2 |
| 1% | 293 | 4.61×10-9 | 10.41 | 0.9559 |  | 4.56×10-9 | 10.47 | 0.9020 |  | 5.00×10-9 | 10.00 | 0.9868 |
| 303 | 4.98×10-9 | 10.02 | 0.9802 |  | 5.18×10-9 | 9.83 | 0.9284 |  | 7.37×10-9 | 8.24 | 0.9772 |
| 313 | 5.04×10-9 | 9.96 | 0.9806 |  | 4.65×10-9 | 10.37 | 0.9205 |  | 4.92×10-9 | 10.08 | 0.9381 |
| 3% | 293 | 5.93×10-9 | 9.18 | 0.9915 |  | 7.47×10-9 | 8.18 | 0.9258 |  | 6.11×10-9 | 9.05 | 0.9789 |
| 303 | 4.53×10-9 | 10.51 | 0.9939 |  | 7.31×10-9 | 8.27 | 0.9340 |  | 4.75×10-9 | 10.26 | 0.9721 |
| 313 | 4.27×10-9 | 10.83 | 0.9371 |  | 6.04×10-9 | 9.10 | 0.9210 |  | 4.97×10-9 | 10.03 | 0.9574 |
| 5% | 293 | 5.20×10-9 | 9.81 | 0.9759 |  | 5.28×10-9 | 9.73 | 0.9460 |  | 7.18×10-9 | 8.35 | 0.9855 |
| 303 | 6.16×10-9 | 9.01 | 0.9684 |  | 4.03×10-9 | 11.14 | 0.9792 |  | 6.88×10-9 | 8.52 | 0.9804 |
| 313 | 4.05×10-9 | 11.11 | 0.9894 |  | 3.49×10-9 | 11.97 | 0.9483 |  | 5.23×10-9 | 9.78 | 0.9727 |
| 313 | 5.24×10-9 | 9.77 | 0.9391 |  | 4.66×10-9 | 10.36 | 0.9554 |  | 5.72×10-9 | 9.35 | 0.9355 |

Table S4 Comparisons of various adsorbents in terms of adsorption capacity.

|  |  |  |
| --- | --- | --- |
| Adsorbents | Adsorption condition | Adsorption capacity  (mg/g) |
| PVA/PAA hydrogels 1 | Pb(II) pH 4.0 | 194.99 |
| Chitosan nanofibrils2 | Pb(II) pH 5.0 | 118.0 |
| Cellulose (Glycidyl methacrylate)3 | Ni(II) pH 4.0 | 48.5 |
| CSTEC fiber4 | Pb(II) pH 5.0 | 144.93 |
| Cellulose Hydrogel5 | Pb(II) pH 5.0 | 382.80 |
| Acrylic grafted hydroxyethyl cellulose 6  Activated carbon7  Chitosan and chitosan derivate8 | Pb(II) pH 5.0  Ni(II) pH 5.0  Ni(II) pH 4.5 | 63.0  62.5  58.09 |
| Cellulosic okra fibers9 | Pb(II) pH 5.0 | 268.32 |
| Graphene oxide10 | Pb(II) pH 5.0 | 312.5 |
| (Hydroxyapatite-hydrogel) | pH 5.0 | 359.24 (Pb)  226.75 (Ni)  365.17 (MB) |

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