**Supplementary Information**

**for**

**The removal of Pb (II) and Cd (II) with hydrous manganese dioxide: Mechanism on zeta potential and adsorption behavior**

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**Table 1**. The number of HMO with different ZP values

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| MnO4-/Mn2+ | 1:1 | 1:1.1 | 1:1.2 | 1:1.3 | 1:1.4 | 1:1.5 | 1:1.6 | 1:1.7 | 1:1.8 | 1:1.9 | 1:2 |
| ZP value(mV) | -51.7 | -49.0 | -44.6 | -42.2 | -40.8 | -38.6 | -35.4 | -32.6 | -29.6 | -26.3 | -21.8 |

**Table 2**. The BET analysis of HMOs

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | 1-HMO | 3-HMO | 5-HMO | 7-HMO | 9-HMO | 11-HMO |
| Zeta potential(mV) | -51.7 | -44.6 | -40.8 | -35.4 | -29.6 | -21.8 |
| Surface area(m2/g) | 66.88 | 64.80 | 62.00 | 60.00 | 59.00 | 58.21 |
| Average pore size(nm) | 5.39 | 7.20 | 7.55 | 8.28 | 12.10 | 15.53 |

**Table 3** The parameter of linear function for Pb (II) and Cd (II)

|  |  |  |  |
| --- | --- | --- | --- |
|  | Slope | Intercept | R2 |
| Pb (II) | -7.68 | 75.12 | 0.99 |
| Cd (II) | -2.65 | 0.29 | 0.99 |

**Table 4** The parameters of Langmuir and Freundlich isotherm model

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| heavy metal | Temperature/K | Langmuir | | |  | Freundlich | | |
| Qm (mg/g) | KL | R2 |  | KF | 1/n | R2 |
| Pb | 293.15 | 469.1 | 4.3 | 0.99 |  | 365.6 | 0.06 | 0.90 |
| 303.15 | 475.4 | 131.1 | 0.97 |  | 416.4 | 0.05 | 0.66 |
| 313.15 | 487.0 | 118.7 | 0.99 |  | 435.7 | 0.04 | 0.64 |
| Cd | 293.15 | 128.2 | 20.5 | 0.99 |  | 115.1 | 0.05 | 0.79 |
| 303.15 | 140.3 | 6.2 | 0.98 |  | 117.0 | 0.06 | 0.92 |
| 313.15 | 154.6 | 3.9 | 0.99 |  | 120.2 | 0.06 | 0.94 |

**Table 5** The comparison of the Langmuir maximum adsorption capacity onto various adsorbents for Pb (II) and Cd (II)

|  |  |  |  |
| --- | --- | --- | --- |
| Heavy metal ion | Adsorbents | *qm* (mg/g) | Refs. |
| Pb (II) | chitosan functionalized magnetic nanoparticles | 498.6 | [1] |
| HMO | 475.4 | This study |
| sulphuric acid-treated cashew nut shell | 408.6 | [2] |
| surface modified Strychnos potatorum seeds | 166.7 | [3] |
| β-MnO2 | 13.6 | [4] |
| Cd (II) | MnO2 nanosheet | 348 | [5] |
| freshly synthesized hydrous manganese dioxide | 168.4 | [6] |
| HMO | 140.3 | This study |
| polying alcohol/polyacrylic acid double network gel | 115.9 | [7] |
| Surface modified Eucalyptus seeds | 71.2 | [8] |

**Table 6** Thermodynamic parameters for the adsorption of Pb (II) and Cd (II)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | Initial con. (mg/L) | ΔH (kJ/mol) | ΔS (J/mol/K) | ΔG (kJ/mol) | | |
|  | 293.15 | 303.15 | 313.15 |
| Pb | 90 | 164.4 | 596.2 | -10.6 | -16.6 | -22.5 |
| 100 | 61.3 | 239.8 | -9.3 | -11.7 | -14.1 |
| 110 | 24.2 | 107.9 | -7.6 | -8.7 | -9.8 |
| Cd | 20 | 28.8 | 149.7 | -15.1 | -16.6 | -18.1 |
| 30 | 9.5 | 60.7 | -8.3 | -8.9 | -9.5 |
| 40 | 5.0 | 35.8 | -5.5 | -5.8 | -6.2 |

**Table 7** The kinetic model constants and correlation coefficients for Pb (II)

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | pseudo-first order model | | | pseudo-second order model | | | intraparticle diffusion model | | |
|  |  | *qe*(mg/g) | *k1*(s-1) | R2 | *qe*(mg/g) | *k2*(g/mg\*s) | R2 | *kp*(mg/g min1/2) | *C* | R2 |
| Pb | 1-HMO | 465.7 | 0.22 | 0.83 | 467.3 | 0.0069 | 0.99 | 12.06 | 405.7 | 0.95 |
| 3-HMO | 419.7 | 0.39 | 0.82 | 421.9 | 0.0056 | 0.99 | 21.19 | 321.1 | 0.74 |
| Cd | 1-HMO | 135.3 | 0.12 | 0.90 | 135.9 | 0.0201 | 0.99 | 2.02 | 122.4 | 0.85 |
| 3-HMO | 123.7 | 0.20 | 0.73 | 124.5 | 0.0135 | 0.99 | 3.86 | 100.1 | 0.58 |



**Fig. 1** The relationship between ZP value and ratio of KMnO4 and MnSO4



**Fig. 2** The XRD spectrum of HMOs with different Zeta potential



**Fig. 3** The SEM images of 1-HMO (a), 6-HMO (b) and 11-HMO (c) and TEM images of 1-HMO (d) and 11-HMO (e)



**Fig. 4** The correlation between zeta potential and adsorption capacity (a) and removal rate (b)



**Fig. 5** Effect of pH on Pb (II) and Cd (II) removal by 1-HMO



**Fig. 6** Isotherm adsorption of Pb (II) and Cd (II) on 1-HMOin (a-d)



**Fig. 7** Thermodynamic study



**Fig. 8** The kinetic study of Pb (II) and Cd (II) on 1 and 3-HMO



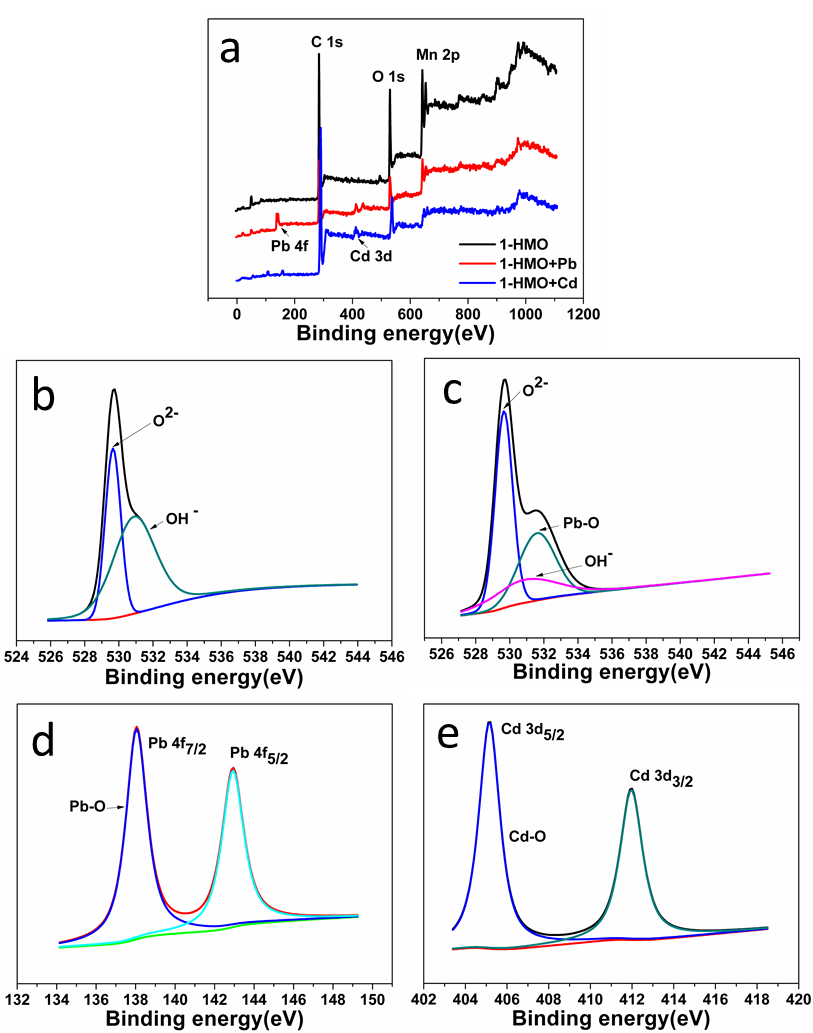
**Fig. 9** Intraparticle diffusion model



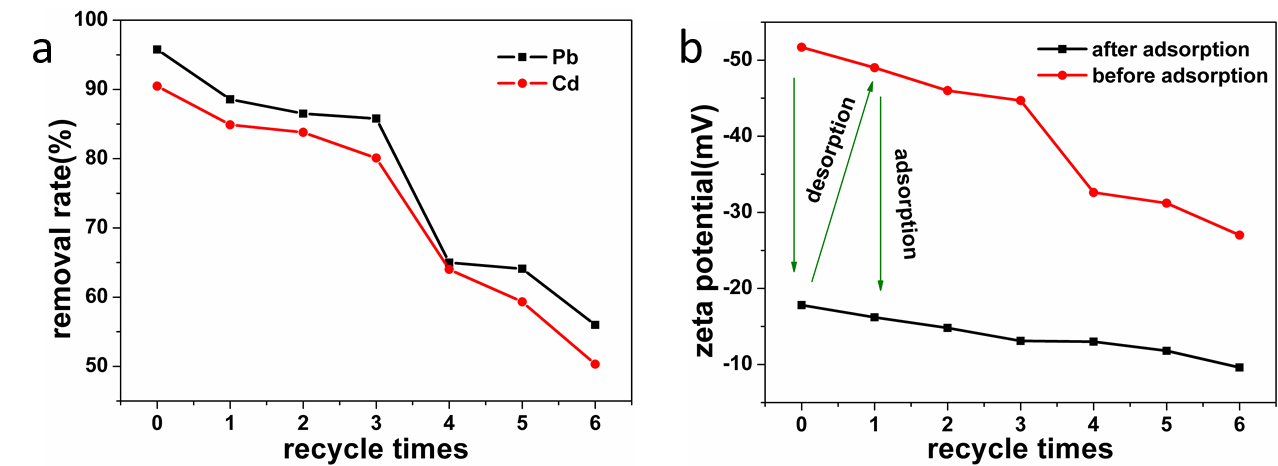
**Fig. 10** SEM-EDS spectra of HMO nanoparticles before and after adsorbing Pb (II) and Cd (II)



**Fig. 11** The FT-IR spectrum of 1-HMO adsorbent before and after adsorbing Pb (II) and Cd (II)



**Fig. 12** The XPSfull spectrum of 1-HMO before and after adsorption of Pb (II) and Cd (II) (a); O (1s) spectra before adsorption (b) and after adsorption of Pb (II) (c); Pb (4f) spectra (d) and Cd (3d) spectra of 1-HMO after adsorption



**Fig. 13** the removal efficiency of heavy metal ion and ZP value versus recycle times of HMO

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