SUPPLEMENTARY MATERIAL TO

**A New** **Thiamine Functionalized Silica Microparticules as a Sorbent for Removal of Lead, Mercury and Cadmium Ions in Aqueous Media**

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*Adsorption Isotherms*

In adsorption studies the interaction between adsorbate and adsorbent is described by adsorption isotherms1. They are critical in optimizing the use of adsorbents. When the adsorbent is in contact with surrounding solution with certain composition, adsorption takes place and after sufficiently time adsorbent and surrounding fluid reaches equilibrium2. Langmuir and Freundlich adsorption models were fitted to the data obtained from the adsorption isotherm. The Langmuir equation (1) was the simplest theoretical model for monolayer adsorption and the Langmuir model was developed to represent the adsorption on adsorbent. The ideal Langmuir model generally gives an appropriate representation of the system behavior at low sorbate concentration. However, the Freundlich equation (2) is an empirical approach for adsorbents with very uneven adsorbing surfaces. This model is applicable for an adsorption of a single solute system within a fixed range of concentration3. The equations of the above two types of sorption isotherms are expressed as follows:

 $q\_{e}= \frac{Q\_{m} . k\_{L} . C\_{e}}{1+ k\_{L} . C\_{e}}$ (1)

 $ln q\_{e}=lnK\_{F}+ \frac{1}{n} (lnC\_{e})$ (2)

where qe is equilibrium uptake capacity of M3APS, Ce is the concentration of metal ions in the supernatant after sorption, n and KF are empirical constants, Qm and kL are Langmuir’s constant related to the capacity and energy of the adsorption respectively.

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*Recovery and Reuse*

Many of adsorbents can be reused several times for practical applications. The adsorption and desorption processes were repeated 5 times to examine uptake capacity of M3APS. The desorption study was studied with acidic solutions. First, M3APS was loaded with metal ions at optimum conditions. Then, metal ions were desorbed by using 0.1 mol L-1 HNO3 and the results are given in Table S-I. Table S-I showed that the regeneration procedure, and the desorption efficiency was generally high and M3APS could be used 5 times without loss of their adsorption capacities.

TABLES**-**I. Adsorption and desorption capacity of M3APS

|  |  |  |  |
| --- | --- | --- | --- |
| Cycle | Pb(II) | Hg(II) | Cd(II) |
| Adsorption, mg g-1 | Desorption, % | Adsorption, mg g-1 | Desorption, % | Adsorption, mg g-1 | Desorption, % |
| 1 | 39.4 | 98.1 | 30.9 | 97.2 | 9.5 | 94.5 |
| 2 | 38.9 | 97.3 | 30.2 | 96.5 | 8.3 | 93.4 |
| 3 | 38.2 | 96.1 | 29.7 | 96.1 | 7.6 | 92.6 |
| 4 | 37.2 | 95.1 | 28.8 | 95.2 | 7.1 | 92.1 |
| 5 | 36.6 | 94.9 | 27.4 | 94.4 | 6.6 | 91.8 |

*The Gibbs Free Energy*

The Gibbs free energy of the adsorption was calculated by the following equation:

 $∆G= -RT lnK\_{L}$ (3)

Where *ΔG* is the Gibbs free energy (kJ mol-1), *R* is the ideal gas constant (8.314 mol-1 K-1), *T* is the solution temperature (K), and *KL*is the Langmuir constant (L mol-1) 4,5,6. The values of *ΔG* for adsorption of Pb(II), Hg(II) and Cd(II) were ­-25.3, -21.6 and -16.5 kJ mol-1, respectively. The negative value for Gibbs free energy shows that the adsorption process of Pb(II), Hg(II) and Cd(II) on M3APS is spontaneous in nature and feasibility of the process.

*Comparison with Some of Other Adsorbents*

A comparison of the proposed systems with other systems is given in Table S-II. Some parameters obtained were comparable to those presented by other described in the literature. As seen from the data in Table S-II, the proposed method by using M3APS has relatively high adsorption capacities and high pH values in comparison with other methods which are using modified silica gels as an adsorbent.

TABLES-II Comparative data from recent studies for adsorption of metal ions by using M3APS

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| System | Studied metal | pH | Adsorption capacities, mg g-1 | Reference |
| Modified almond shell  | Pb(II), Cd(II) | 5 | 7.00 – 9.00 | 6 |
| Urea functional hydrogel | Pb(II), Cd(II) | 5 | 26.0 | 7 |
| P(VIM/AAc/HEMA) hydrogels | Pb(II) | 4.5 | 30.38 | 8 |
| 1,3,4-trithiane | Hg(II), Sb(III), Cd(II), Pb(II) | 5 | 9.50 – 35.5 | 9 |
| Dithizone modified silica gel | Cu(II), Pb(II), Ni(II), Fe(III), Cd(II), Zn(II) Co(II) | 1 - 6 | 2.06 – 8.28 | 10 |
| Resacetophenone modified silica gel | Cu(II), Pb(II), Ni(II), Fe(III), Cd(II), Zn(II) Co(II) | 5.5 - 7.5 | 6.5 – 15.2 | 11 |
| Gallic acid modified silica gel | Pb(II), Cu(II), Cd(II), Ni(II) | 3 - 7 | 4.62 – 15.38 | 12 |
| Silica gel phase functionalized by choline | Pb(II), Hg(II), Cd(II), Cu(II), Ni(II), Co(II) | 7 | 11.7 ­­– 60.1 | 13 |
| Pyrazol-3-ylimine modified silica gel | Pb(II), Cd(II), Cu(II), Zn(II) | 2 – 8 | 0.96 – 74.89 | 14 |
| Vitamin B1 modified 3-aminopropyl silica gel | Pb(II), Hg(II), Cd(II) | 5 | 9.54 – 39.4 | This work |

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