

COMPETITIVE ADSORPTION OF AQUEOUS METAL IONS ON SURFACE FUNCTIONALITY IN A NANOPOROUS OXIDIZED ACTIVATED CARBON

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Introduction Activated carbons have well developed porous structures with specific surface chemical properties, and are widely used in industry for the removal of many organic compounds from both liquid and gas phases. However, they also have hydrophilic functional groups as well as hydrophobic graphene layers. This makes activated carbons versatile adsorbents with a wide range of possible applications. The interaction of aqueous metal ions with surface functionality of activated carbons plays a crucial role in adsorption of aqueous metal ions. Two important mechanisms, ion exchange and metal coordination to functional groups, are primarily involved [1,2] depending on the acidic/basic properties of carbon surface functional groups present and the experimental conditions, such as pH etc. Previous studies have shown that the surface functionalities have different affinities to various metal ions. The competitive interaction of various metal ions with surface functionalities takes place in the adsorption of binary metal ion mixtures and this is related to the characteristic adsorption of individual metal ions. In this investigation, the competitive adsorption of aqueous metal ions on the surfaces of nanoporous activated carbons with oxygen functionalities was studied and a physical model for competitive adsorption, where the accessibility of species to the porous structure varied, was developed.

Experimental A nitric acid oxidized carbon GN was used in this study [1]. Carbon G209 (Pica, France) was refluxed in HNO_3 solution (7.5 M) for 48 hours to give oxidized carbon GN. The product was filtered and washed before Soxhlet extraction with distilled water until the solution pH was constant. The carbon was dried at 383 K. The total and micropore volumes were determined by adsorption of N_2 (77 K) and CO_2 (273 K), respectively. The surface functionalities of carbon GN were characterized by FTIR, Raman spectroscopy, XRD, XANES, TPD, Boehm titrations and pH_{PZC} .

Adsorption studies of Hg^{2+} (aq), Pb^{2+} (aq), Ca^{2+} (aq) and Cd^{2+} (aq) ions were carried out at 298 K. Surface metal ion concentrations were determined from the difference of the M^{2+} (aq) concentration before and after adsorption and were measured using a Unicam 701 inductively coupled plasma (ICP) spectrometer. The initial molar ratios of binary metal ions in systems Cd^{2+} (aq)/ Ca^{2+} (aq), Pb^{2+} (aq)/ Ca^{2+} (aq), Pb^{2+} (aq)/ Cd^{2+} (aq), Hg^{2+} (aq)/ Ca^{2+} (aq), Hg^{2+} (aq)/ Cd^{2+} (aq) and Hg^{2+} (aq)/ Pb^{2+} (aq) were 0.5, 1.0 and 2.0. The solution pH after adsorption was in the range 2.42 – 3.90 for the mixtures.

Results and Discussion The micropore and total pore volumes of carbon GN were 0.266 and 0.366 cm^3g^{-1} , respectively. The characteristic average half width of slit shaped pores of carbon GN determined by the DS method was 0.47 nm [3]. Nitric acid oxidation did not change the pore structure characteristics to a large extent. XRD showed that carbon GN had structural parameters, $L_a \sim 3.3$ nm, $L_c \sim 1.2$ nm and $L_c/d_{002} \sim 3.2$. This indicates that small basic structural units (BSUs) with poor stacking order are present in carbon GN. Nitric acid oxidation incorporated the oxygen functional groups (oxygen analysis = 22.36 wt%daf), which result in lower pH at point of zero charge ($\text{pH}_{\text{PZC}} = \sim 2.5$) than that of the original carbon ($\text{pH}_{\text{PZC}} \sim 8.1$). The FTIR, XANES, TPD and Boehm titration analyses indicate the presence of carboxylic, lactone/lactol and phenolic groups in GN. The relative intensity ratio of the D and G bands in the Raman spectra do not change markedly with metal species adsorption or surface oxidation and also indicated the absence of nitrate ions associated with adsorbed metal ion species. The enhanced ($\times \sim 30$) adsorption of metal ion species on GN compared with G209 is directly related to the surface functional groups of GN since the porous structure does not change markedly. The speciation of $\text{M}^{2+}(\text{aq})$ in solution also needs to be considered in relation to adsorption on carbon GN.

The model of Koopal *et al.* based on a Langmuir-Freundlich (LF) analysis was used for analysis of the $\text{M}^{2+}/\text{H}^+(\text{aq})$ single metal ion systems. The results showed that the binary systems i) follow the Langmuir isotherm, ii) behave as though the surface is homogeneous; iii) the adsorption constant for metal ions K_M can be regarded as constant over the pH range used; iv) the adsorption constant for protons K_H is much smaller than K_M ; v) the Langmuir parameters obtained from the conventional Langmuir and competitive adsorption models are identical within experimental error and vi) the isotherms for metal ion adsorption are directly related to the corresponding isotherms for proton displacement even where complex speciation occurs in solution.

A typical example of the competitive adsorption of metal ions where one of the metal ions is displaced is shown in Figure 1.

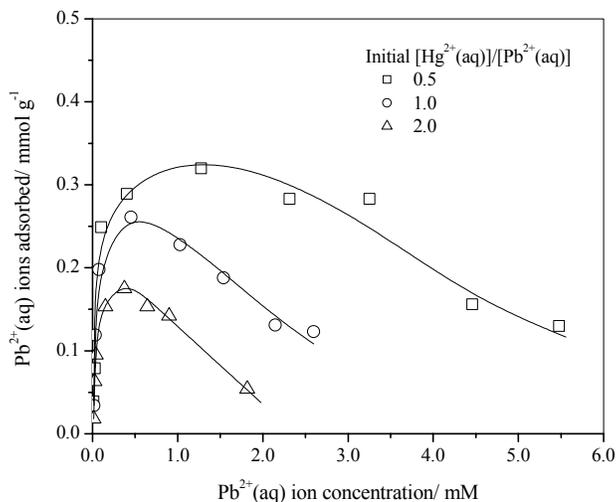


Figure 1 Competitive adsorption isotherms of $\text{Hg}^{2+}(\text{aq})$ and $\text{Pb}^{2+}(\text{aq})$ ions on carbon GN at various initial molar fractions of $[\text{Hg}^{2+}(\text{aq})]/[\text{Pb}^{2+}(\text{aq})]$

The values of K_H were small, the surface characteristics of GN were homogeneous etc., for adsorption of single metal ions, allowing the competitive adsorption of the ternary A (strong), B (weak) and H^+ system to be described by a simpler binary metal ion model based on ideal Langmuir behavior neglecting K_H . Therefore, a model for competitive adsorption of binary metal ions involving the ion exchange of metal ions was developed and expressed as follows,

$$A_T = \frac{K_{AH}(A_m - B_m)C_A}{1 + K_{AH}C_A} + \frac{\varphi K_{BHA}B_m C_B}{1 + K_{BHA}C_B + \varphi(K_{BHA} - K_{BA})C_B} \quad (1)$$

$$B_T = \frac{K_{BHA}B_m C_B}{1 + K_{BHA}C_B + \varphi(K_{BHA} - K_{BA})C_B} \quad (2)$$

$$\text{with } \varphi = \frac{K_{AHB}C_A + K_{AB}C_A K_{BHA}C_B}{K_{BHA}C_B + K_{AHB}C_A K_{BA}C_B}$$

where A_T (B_T) is the total amount of A (B) adsorbed, A_m (B_m) is the maximum amount of A(B) adsorbed, C_A (C_B) is the concentration of A(B) in solution, K_{AH} is the adsorption constant for non-competitive exchange of A with surface proton sites, K_{AHB} (K_{BHA}) is the adsorption constant for competitive exchange of A (B) with surface proton sites in the presence of species B (A), and K_{AB} (K_{BA}) is the adsorption constant for exchange of A (B) with adsorbed B (A).

Equations (1) and (2) can be combined with the data on ion exchange and proton displacement to allow for different accessibilities to the porous structure, providing a good fit for the experimental data from all the binary metal ion systems, for example, see Figure 2. The results for the values of K_{AB} and K_{BA} are shown in Table 1. The values of K_{AB} are expected to be higher when the differences in the competitive adsorption are greatest. The results for K_{AB} given in Table 1 indicate the competitive order: $Hg^{2+}(aq) > Pb^{2+}(aq) > Cd^{2+}(aq) > Ca^{2+}(aq)$.

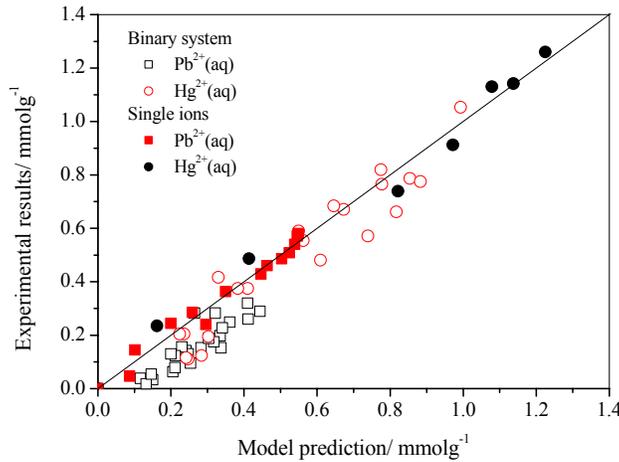


Figure 2. Comparison of experimental results and model prediction for $Hg^{2+}(aq)/Pb^{2+}(aq)$ binary metal ion systems.

Table 1. Parameters obtained from equations (1) and (2).

Binary system (A/B)	K_{AB} , Lmmol ⁻¹	Chi ² /DoF
Cd ²⁺ (aq)/Ca ²⁺ (aq)	1.41 ± 0.29	0.002
Pb ²⁺ (aq)/Ca ²⁺ (aq)	8.52 ± 1.31	0.002
Pb ²⁺ (aq)/Cd ²⁺ (aq)	5.12 ± 1.05	0.003
Hg ²⁺ (aq)/Ca ²⁺ (aq)	2.30 ± 0.33	0.006
Hg ²⁺ (aq)/Cd ²⁺ (aq)	1.54 ± 0.20	0.010
Hg ²⁺ (aq)/Pb ²⁺ (aq)	1.42 ± 0.19	0.018

K_{BA} was < 10⁻¹⁰ Lmmol⁻¹ in all cases.

The order for competitive adsorption is the same as that obtained from the maximum amounts adsorbed for the adsorption of single metal ions.

Conclusions. The competitive adsorption of all binary metal ion mixtures were studied and modeled using dynamic equilibrium methods combined with the displacement of protons to allow for different accessibilities to the porous structure. The Langmuir parameters obtained from single metal ion adsorption and parameters for ion exchange between components of the binary metal ion mixture were used in the model. The model only requires a single additional parameter for the ion exchange of the more strongly adsorbed species in solution with the more weakly adsorbed species since the other ion exchange parameter, for exchange of the more weakly adsorbed component in solution and the more strongly adsorbed species, was very small. The metal ion selectivity is related to electrostatic effects, multiple speciation of the ions in solution, accessibility of the porous structure to the species present in solution and the stability constants for interaction with the surface species.

References

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