

ZINC ADSORPTION IN BENTONITE CLAY: PARTICLE SIZE AND pH INFLUENCE

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Abstract - In environmental studies is important to know the adsorption process of heavy metals in clay minerals, since they are able to immobilize these metals. Knowing the cations adsorption is influenced for several factors, the objective of this research was to study the zinc adsorption process by bentonite clay and to evaluate the particle size of clay and pH influence on this process. In order to quantify the adsorbed zinc, 2 g of bentonite clay, dried at room temperature and sieved at 0.5 and 2-mm-mesh, were equilibrated for 24 hours with 20 mL of water containing different quantities of zinc (10, 15, 20, 30, 50, 100, 150 and 200 mg L⁻¹) as background solutions of pH values 4 and 6. Langmuir's adsorption equation in its linearized form was applied and the values of the maximum capacity and those of the constant related to the bonding energy were obtained. The results showed that Langmuir equation was adequate to describe zinc adsorption at different pH values and particle size of bentonite clay. Zinc adsorption in bentonite clay depended on pH and particle size, decreasing as they increased. The maximum retention capacity, 3.24 mg g⁻¹, was obtained in pH 4 using particle size of bentonite clay < 0,5 mm.

Keywords: heavy metal, Langmuir, granulometry

ADSORÇÃO DE ZINCO POR ARGILA BENTONITA: INFLUÊNCIA DO TAMANHO DA PARTÍCULA E DO pH

Resumo - Em estudos ambientais é importante se conhecer o processo de adsorção de metais pesados em minerais argilosos, uma vez que eles são capazes de imobilizar estes metais. Sabendo-se que a adsorção de cátions é influenciada por vários fatores, o objetivo desta pesquisa foi estudar o processo de adsorção de zinco pela argila bentonita e avaliar a influência do tamanho das partículas de argila e pH da solução sobre este processo. A fim de quantificar o zinco adsorvido, 2 g de argila bentonita, seca à temperatura ambiente e passada em peneira de malha de 0,5 e 2,0 mm de diâmetro, foram equilibradas durante 24 horas com 20 ml de água contendo diferentes quantidades de zinco (10, 15, 20, 30, 50, 100, 150 e 200 mg L⁻¹), ajustadas a pH 4 e 6. Os dados experimentais foram ajustados à equação de adsorção de Langmuir, na sua forma linearizada, obtendo-se assim, os valores da capacidade máxima de adsorção e da constante relacionada com a energia de ligação. Os resultados mostraram que a equação de Langmuir foi adequada para descrever a adsorção de zinco nos diferentes valores de pH e tamanhos de partículas da argila bentonita. A adsorção de zinco pela argila bentonita variou com o pH e com o tamanho das partículas, diminuindo à medida em que estes aumentaram. A capacidade máxima de adsorção de 3,24 mg g⁻¹, foi obtida em pH 4 usando as partículas de argila bentonita com tamanho < 0,5 mm.

Palavras-chave: metal pesado, Langmuir, granulometria

INTRODUCTION

Heavy metals can be introduced into agricultural soils by industrial emissions and by a variety of agricultural treatments, including fertilizers, liming materials, manure, sewage sludges, and composts (KABATA- PENDIAS & PENDIAS, 2001). Several studies on soil chemistry have demonstrated the zinc (Zn) concentration increases in certain agricultural soils as the

result of the use of those materials (KABATA-PENDIAS & PENDIAS, 2001). The phytotoxic threat of Zn and the risk of its contaminating surface or groundwater depend on its concentration in the soil solution, which is related to its adsorption and desorption from soil colloids.

Owing to their adsorption capacity, aluminosilicate and oxide minerals are capable of removing many metals over a wider pH range representing an efficient way for the remediation of contaminated soils.

Extensive research has assessed the metal adsorption characteristics of natural or modified clays and oxides and has demonstrated that pH variation influences zinc adsorption. Lacin et al. (2005) found the pH has positive effects on zinc adsorption by bentonite clay. Usually, arising pH increases the capacity for zinc adsorption (CASAGRANDE et al., 2004; ARIAS et al., 2005). The increase in adsorption is probably due to cation hydrolysis, since hydroxyl complexes are adsorbed preferentially over uncomplexed cations or to the increase in the negative surface charge of the adsorbent related to the increase in the concentration of hydroxyl ions, leading to an increase in attraction for cation in solution (SÁNCHEZ et al., 1999).

The same way, the surface area of the adsorbent can influence in the adsorption process. Bentonite exhibits an enormous surface area when it is hydrated in water. It consists of numerous microscopic platelets, each with negative charges on flat surfaces and positive charges on edges. Hydration causes these platelets to separate into a porous structure containing both positive and negative charges. It is known that the ionic charge and the porous structure give bentonite the ability to adsorb the toxins (ZHU et al., 1998). Numerous researches have been conducted on natural bentonite to examine its potential for the removal of heavy metal ions. It is found that natural bentonite could be used effectively for the removal of zinc ions from aqueous solutions (MELLAH; CHEGROUCHE, 1997).

The aim of the present work was to investigate the possibility of using bentonite clay to retain zinc and the influence of pH and particle size of bentonite clay in the adsorption process.

METHODOLOGY

Samples of bentonite clay were collected from Primavera deposit of Boa Vista, Paraíba State, Brazil. The

samples were dried at room temperature, sieved at 0.5 and 2-mm-mesh, homogenized, and stored pending analysis.

For the adsorption studies, 2 g of bentonite clay, with different granulometry, were equilibrated for 24 h at room temperature (22 ± 2 °C) with 20mL of solutions with concentration of 10, 15, 20, 30, 50, 100, 150 and 200 mg L⁻¹ of Zn which were prepared with pure water from standard solutions of 1000 mg Zn L⁻¹. Before equilibration between bentonite clay and solution the lots received either HCl 0.1 N or NaOH 0.1 N to obtain pH values 4 and 6. After 24 h the supernatant was drawn off and filtered through Whatman 540 paper, and its Zn content was measured using atomic absorption spectrophotometry. Adsorbed Zn was calculated as the difference between the amount added initially and the amount remaining in solution after equilibration. All assays were carried out in triplicate and only mean values are presented. Langmuir equation was adjusted for describing zinc adsorption:

$$C/(x/m) = 1/(kb) + C/b \quad (1)$$

where C is the equilibrium solution concentration in mg L⁻¹, x/m is the amount of Zn sorbed in mg g⁻¹ of clay, b is the sorption maximum in mg g⁻¹, and k is the bonding energy constant in L g⁻¹. A higher k indicates that a larger adsorption of a solute by the solid surface exists at very low equilibrium solute concentrations.

RESULTS AND DISCUSSION

The Langmuir equations for zinc adsorption by different particle size of bentonite clay and pH values are listed in Table 1. The values observed in the laboratory of zinc adsorbed on bentonite and the curves got from the values estimated by Langmuir model are shown in Figure 1. The approximation between the curves and the values observed show that Zn adsorption on bentonite was well described by Langmuir model according to Ayuso & Sánchez (2003).

Table 1. Results of fitting the model Langmuir equation to data for adsorption Zn by bentonite clay

Particle size	pH	Equation
< 0,5 mm	4	$x/m = (0,04 \times 3,24 \times C) / (1 + 0,04 C)$
	6	$x/m = (0,15 \times 2,11 \times C) / (1 + 0,15 C)$
0,5 – 2,0 mm	4	$x/m = (0,06 \times 2,38 \times C) / (1 + 0,06 C)$
	6	$x/m = (0,16 \times 2,08 \times C) / (1 + 0,16 C)$

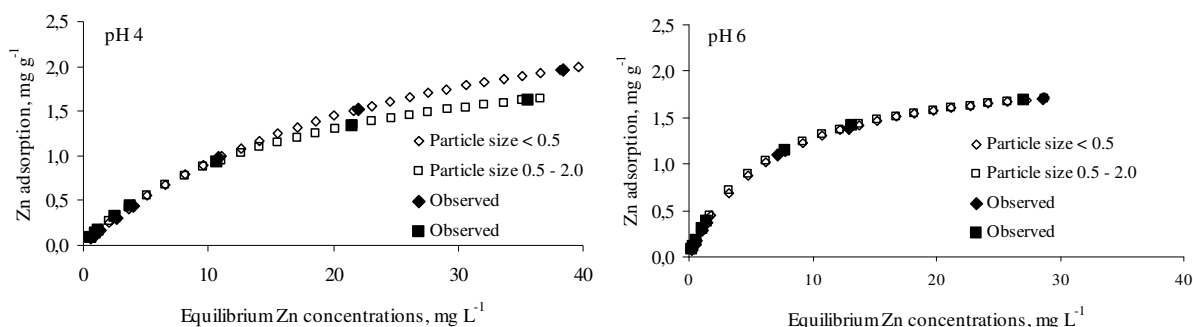


Figure 1. Relationship between the equilibrium solution concentration zinc and adsorbed zinc amount on bentonite by Langmuir model for different particle size, pH values and observed points in laboratory

The curves were very similar for both sizes of particle analyzed, mainly at pH 6 (Figure 1). Zinc adsorption increased as Zn was added. The inclination of the adsorption curves, mainly, in the pH 6, showed that the increase in zinc adsorption was higher at the lowest concentration of the metal. As the concentration increased, the increase in the adsorption was less pronounced. With the increase in the metal concentration, more sites were filled and Zn retention became more difficult. This confirms the fact of the isotherms are L type (L-Langmuir), characterized by a slope decline. At the lower concentration of added Zn, all Zn was adsorbed by bentonite.

The parameters b and K obtained by Langmuir equations have been used to evaluate the maximum adsorption and the binding energy, respectively (Table 2). The values of these parameters presented the effect of pH and particle size on Zn adsorption on bentonite.

Table 2. Parameters of Langmuir equation that were fitted to the Zn adsorption data

Particle size (mm)	K		b	
	(L mg ⁻¹)		(mg g ⁻¹)	
	pH 4	pH 6	pH 4	pH 6
< 0.5	0.04	0.15	3.24	2.11
0.5 – 2.0	0.06	0.16	2.38	2.08

Considering the b parameter of the Langmuir equation, it is observed that the maximum retention capacity is obtained in pH 4 for both particle sizes, although with lower bonding energy (K) suggesting the possibility of Zn ions to be easy released to solution. The lowest values of b at pH 6 appear to contradict reports that arising pH increases the capacity for zinc adsorption. However, using NaOH to raise the pH of the solution may have occurred precipitation of zinc hydroxides being unavailable to be adsorbed on bentonite clay surface

according to Adriano et al. (2004). Despite the maximum retention capacity of Zn at pH 6 has been lower, Zn adsorbed on the bentonite surface, in this condition, is retained with higher bonding energy (K), decreasing your release to solution. As the particle size of bentonite decreases, adsorption increases (Table 2) according to Sánchez et al. (1999). This can be explained in terms of the active surface area of the adsorbent and probability of solid-solution interaction. With the increase in particle size, a longer interaction time would become necessary to obtain similar results, since diffusion must occur through the aggregates.

As can be observed in Table 2, the b parameter of Langmuir equation indicates a capacity ranging from 2.08 to 3.24 mg g⁻¹, which is close to the levels of the Zn pollution in the soils (ranging up to 3000 mg kg⁻¹). Therefore, the bentonite clay, probably, can be used to remediation of contaminated soil with Zn.

CONCLUSION

The results showed that Langmuir equation was adequate to describe zinc adsorption at different pH values and particle size of bentonite clay. Zinc adsorption in bentonite clay depended on pH and particle size, decreasing as they increased. The maximum retention capacity, 3.24 mg g⁻¹, was obtained in pH 4 using particle size of bentonite clay < 0.5 mm.

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