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TESIS DE DOCTOR EN QUÍMICA

ADSORCIÓN Y DESORCIÓN DE METALES PESADOS EN MATERIALES ARCILLOSOS DE LA NORPATAGONIA

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RESUMEN

En el desarrollo de esta tesis se caracterizó una bentonita (CATAE) y seis minerales arcillosos constitutivos de las escombreras de las canteras de bentonita (DTN2, DTN3, MP2, MP4, LE1 y LE18) pertenecientes a la región de Cinco Saltos (Provincia de Río Negro) en sus aspectos mineralógicos, fisicoquímicos y mecánicos. Referente a los aspectos físicos y mecánicos se determinó: la densidad aparente, el límite líquido, la capacidad de hinchamiento y la conductividad hidráulica. Respecto a las propiedades químicas evaluadas, se enfatizó en las relacionadas al comportamiento de adsorción de los minerales. Se determinó la capacidad de intercambio catiónico, la naturaleza de los cationes intercambiables, el área superficial específica, la densidad de carga superficial permanente y la densidad de carga dependiente del pH, el punto de carga cero, el punto isoeléctrico y la composición elemental.

Se evaluó la capacidad de sorción y de desorción de tres minerales arcillosos caracterizados (CATAE, DTN2 y DTN3), para seis iones metálicos: Cd^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Pb^{2+} y Zn^{2+}. Se trabajó con una técnica en "batch" empleando materiales naturales y purificados, en solución acuosa y a temperatura ambiente, a tres valores de pH 3,5; 6,5 y 9,5 y a fuerzas iónicas variables. Las desorciones se realizaron con HCl y HNO_3 (0,1 %) por extracción simple y en etapas sucesivas. En todos los casos la cuantificación del ion metálico remanente en solución, se determinó por Espectrometría de Emisión Atómica (ICP-AES).

El estudio mineralógico puso de manifiesto que los minerales arcillosos (provenientes de escombreras) contienen proporciones variables de montmorillonita (82 a 87 %) e illita (5 a 9 %), mientras que la bentonita regional está formada principalmente por esmectita (97 %) y los minerales acompañantes son $CaCO_3$ (calcita) y óxidos u oxohidróxidos amorfos de Fe.

Para igual tiempo de contacto, la bentonita (CATAE) adsorbió concentraciones significativamente mayores de especies iónicas metálicas que las arcillas comunes DTN2 y DTN3. La adsorción de cada ion metálico fue superior cuando los minerales arcillosos estaban libres de impurezas acompañantes, presentando el Cu^{2+} el comportamiento inverso. Los porcentajes de retención alcanzados fueron: 100 % para especies iónicas de Cr y Pb, 96 % para especies iónicas de Cd, 93 % para especies

iónicas de Zn y 90 % para especies iónicas de Ni. El ion Cu^{2+} se adsorbe casi en su totalidad sobre el mineral natural y sólo el 55 % cuando la bentonita está libre de oxohidróxidos de Fe y carbonatos.

La adsorción para cada ión metálico es más lenta cuando los iones compiten por los mismos sitios activos del adsorbente, ya que la pendiente en la etapa inicial de las isotermas se atenúa. Si bien la secuencia de afinidades se mantuvo con las soluciones múltiples ensayadas ($Cr^{3+} > Cd^{2+} > Pb^{2+}$) y ($Zn^{2+} > Ni^{2+} > Cu^{2+}$), la capacidad de retención disminuyó para los iones bivalentes. Para la solución conteniendo Zn^{2+}, Ni^{2+} y Cu^{2+}, el proceso de adsorción se modificó. Mientras que el Cu^{2+} fue adsorbiéndose en forma gradual desde los primeros minutos de contacto con la arcilla, Ni^{2+} y Zn^{2+} reaccionaron de forma tardía.

La desorción en tres etapas sucesivas fue más efectiva que la desorción simple, llegando en algunos casos a triplicar la cantidad de ion metálico removido de la superficie. La solución de HNO_3 (0,1 %) resultó ser más efectiva que la solución de HCl (0,1 %) en la remoción de la mayoría de los iones metálicos. Respecto a las arcillas comunes, las diferencias entre ambos ácidos no fueron significativas; aunque cabe destacar que, los iones metálicos se desorbieron con mayor facilidad de las arcillas comunes que de la bentonita. El proceso de desorción se modificó cuando a la solución multicatiónica se le agregó un electrolito inerte para generar un efecto salino determinado. Así, para una solución 0,1 M de KNO_3 ambas soluciones ácidas removieron el 100 % del Cd^{2+}, Ni^{2+} y Zn^{2+} inmovilizado por la arcilla. Del Cr^{3+} retenido sólo se desorbió el 2 %, mientras que para Cu^{2+} y Pb^{2+} los porcentajes alcanzados fueron 68 % y 78 % respectivamente.

Respecto a las propiedades mecánicas de los minerales estudiados y acorde a lo establecido en la reglamentación internacional vigente, para la elaboración de membranas geotextiles (GCLs), destinadas a la impermeabilización de sitios de disposición final de residuos peligrosos, sólo la bentonita regional (CATAE) y las arcillas comunes DTN2 y DTN3 cumplen las especificaciones para ser utilizadas en la fabricación de GCLs.

ABSTRACT

During the development of this thesis a bentonite (CATAE) and six claystones (denoted as DTN2, DTN3, MP2, MP4, LE1 and LE18) which are the main constituent of the tailings from the quarries of bentonite and belonging to the region of Cinco Saltos (Province of Río Negro) were characterized in their mineralogical, physicochemical and mechanical aspects. Regarding the physical and mechanical aspects the bulk density, the liquid limit, the swelling capacity and the hydraulic conductivity were determined. The chemical properties evaluated, are related to the adsorption behavior of minerals. The cation exchange capacity, the nature of the exchangeable cations, the specific surface area, the surface charge density of permanent charge and pH-dependent charge, the point of zero charge, the isoelectric point and the elemental composition were determined.

Sorption and desorption capacity for three clay minerals (CATAE, DTN2 and DTN3), with six metal ions: Cd^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} was evaluated. Worked with a technique in batch, using raw and purified materials, in aqueous solution at room temperature, at three pH values 3.5, 6.5 and 9.5 and at varying ionic strengths. The desorption process was performed with solutions of HCl and HNO_3 (0.1%) by simple extraction and in successive stages. In all cases, the quantification of the metal ion remaining in solution was determined by atomic emission spectrometry (ICP-AES).

The mineralogical study showed that claystones (from tailings) contain varying proportions of montmorillonite (82-87%) and illite (5-9%), while the regional bentonite is mainly composed of smectite (97%) and accompanying minerals are $CaCO_3$ (calcite) and amorphous oxides or hydroxides of Fe.

For equal contact time the bentonite (CATAE) adsorbed significantly higher concentrations of metal ionic species than common clays (DTN2 and DTN3). The adsorption of each metal ion was higher when the clay minerals were free of accompanying impurities, showing the Cu^{2+} inverse behavior. The retention rates achieved were: 100% for ionic species of Cr and Pb, 96% for ionic species of Cd, 93% for ionic species of Zn and 90% for ionic species of Ni. The Cu^{2+} ion is adsorbed almost

entirely on natural mineral and only 55% when bentonite is free of oxides and hydroxides of Fe and carbonates.

For each metal ion the adsorption was slower when ions compete for the same active sites of the adsorbent, since the slope in the initial stage of the isotherms attenuated. While affinities sequence remained with the multicationic solutions tested (Cr^{3+}> Cd^{2+}> Pb^{2+}) and (Zn^{2+}> Ni^{2+}> Cu^{2+}), retention capacity decreased to divalent ions. To the solution containing Zn^{2+}, Ni^{2+} and Cu^{2+}, the adsorption process was modified. While Cu^{2+} was adsorbed gradually from the first minutes of contact with the clay, Ni^{2+} and Zn^{2+} reacted later.

Desorption in three successive stages was more effective than simple desorption, in some cases three times the amount of metal ion was removed from the surface. The solution of HNO_3 (0.1%) was more effective than the HCl (0.1%) solution in the removal of most metal ions. For common clays the differences between the two acid solutions were not significant, although it should be noted that the metal ions were more readily desorbed from common clays than bentonite. The desorption process changed when an inert electrolyte salt was added to the multicationic solution. Thus, for a solution containing 0.1 M KNO_3 both acid solutions removed 100% of Cd^{2+}, Ni^{2+} and Zn^{2+} immobilized by clay. Only 2% of retained Cr^{3+} was desorbed, while for Cu^{2+} and Pb^{2+} percentages achieved were 68% and 78% respectively.

Regarding the mechanical properties of the minerals studied and according to the existing international regulations for the manufacture of geotextiles membranes (GCLs) for sealing a disposal site for hazardous waste, only the regional bentonite (CATAE) and common clays (DTN3 and DTN2) meet specifications for use in the manufacture of GCLs.

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