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SYNTHESIS, ION EXCHANGE PROPERTIES OF NEW POLYACRYLONITRILE/VERMICULITE COMPOSITE

ЯНГИ ПОЛИАКРИЛОНИТРИЛ / ВЕРМИКУЛИТ ТАРКИБИДА СИНТЕЗ, ИОН АЛМАШИНУВИНИНГ ХУСУСИЯТЛАРИ

СИНТЕЗ, ИОНООБМЕННЫЕ СВОЙСТВА НОВОГО КОМПОЗИТА ПОЛИАКРИЛОНИТРИЛ / ВЕРМИКУЛИТ

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Аннотация

Вермикулитга кислота билан ишлов берилди. Янги адсорбент, полиакрилонитрил/вермикулит композицияси синтез қилинди. Олинган сорбент хром (VI), мис (II) ва никел (II) сувли эритмаларида адсорбсияси ўрганилди.

Аннотация

Произведена обработка вермикулита кислотой. Синтезирован новый адсорбент - композиция полиакрилонитрил / вермикулит. Изучена адсорбция полученного сорбента в водных растворах хрома (VI), меди (II) и никеля (II).

Annotation

A vermiculite was treated with acid. The new adsorbent, a polyacrylonitrile / vermiculite composition, was synthesized. Adsorption of the obtained sorbent in aqueous solutions of chromium (VI), copper (II) and nickel (II) was studied.

Таянч сўз ва иборалар: *адсорбция, полиакрилонитрил, вермикулит, малеин ангидрид, композит, полиамидоксим, статистик алмашинув сиғими.*

Ключевые слова и выражения: *адсорбция, полиакрилонитрил, вермикулит, малеиновый ангидрид, композит, полиамидоксим, статическая обменная емкость.*

Keywords and expressions: *Adsorption, polyacrylonitrile, vermiculite, maleic anhydrid, composite, polyamidoxime, static exchange capacity.*

Today ion exchange materials have found extensive application in analytical and industrial chemistry in view of their good elegant characteristics such as insoluble matrix, stiochiometric exchange, good selectivity, specificity and applicability to column operation. Meeting the stringent coolant purity requirement of the nuclear industry is solely attributable to ion exchangers [1]. The wide using of sorption methods in hydrometallurgy for concentration of some metallic ions and also for utilization of wastes, containing some harmful components such as ions of heavy metals, is connected with construction of assortment of ion exchanging and complex formation polymers and materials on their base. For decision of this problem in many countries there is a necessary arsenal of ion exchanging resins, having the high specific surface[2-3]. Molecular combination between organic polymer as supporting materials and inorganic precipitates of polyvalent metal acid salts as ion exchanger has been of great interest.The organic and inorganic composites have attracted great attention in the field of analytical as well as material science because of their unique property to combine the significant features of organic polymers with those of inorganic materials[4-5].

The mica-type silicate of VMT possesses a layered structure. Each layer of VMT consists of octahedrally coordinated cations (typically Mg, Al, and Fe) sandwiched by tetrahedrally coordinated cations (typically Si and Al). Adjoining layers are held together by a combination of electrostatic and van der Waals forces[6]

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Figure 1.

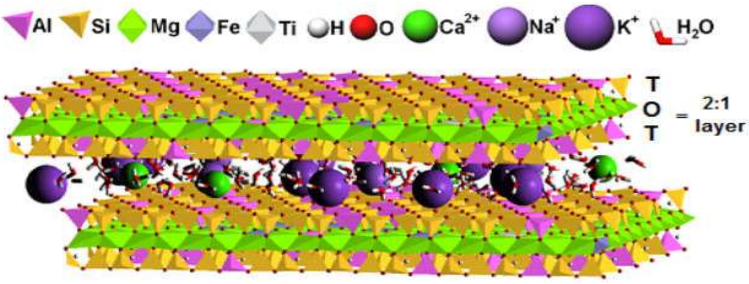


Figure 1. Model of the structure of vermiculite from Brazil; (with courtesy of dr. Jonáš Tokarský).

The general chemical formula for VMT is $(Mg, Fe, Al)_3[(Al, Si)_4O_{10}](OH)_2 M_x\ nH_2O$, where *M* is an exchangeable cation and *x* is the number of equivalents of exchangeable cations present. For layered VMT, various methods have been used to delaminate the layered structure[2-6].

The cation exchange capacity (CEC) of clay minerals is defined as “the quantity of cations available for exchange at a given pH expressed in meq/100 g which is equivalent to cmol/kg [7]. The CEC varies between the 120 and 200 cmol/kg (air dried vermiculites) or 140 and 240 cmol/kg (dehydrated vermiculites) [8]. Water molecules associated with internal surfaces evokes hydration of interlayer cations. The total amount of alkylammonium ions bound by 2:1 clay minerals is often slightly higher than the total CEC determined by other methods [11].

Owing to specifically particularities of the nitril groups the polyacrylonitril (PAN) capable to interact with different modified reagents with formation of numerous aniono- and cationogenic exchanging polymers [9].

Organo-Vermiculite Preparation. The crude vermiculite was introduced into 1 L of a 2 M HCl solution in a beaker at room temperature. The resulting slurry was magnetically stirred for 8 h. The pH of the slurry was adjusted to 3.0-4.0. The vermiculite was then separated by filtering and washed thoroughly with distilled water several times until the filtrate had a pH value of 7.0. Following washing, the obtained solid material was dried at 120 °C overnight. The acid-delaminated vermiculite was then further treated with Maleic Anhydrid (MA). To beaker were charged of MA, acid-treated vermiculite, and water. The slurry was magnetically stirred for 12 h. The resulting slurry was dried in an oven at 70 °C for 24 h under vacuum. The final MA-pretreated vermiculite was kept in a dryer.

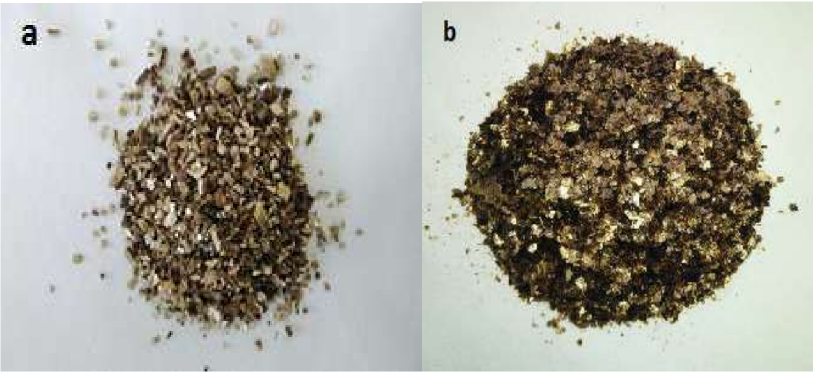


Figure 2. Normal vermiculite (a) and vermiculite treated in acid (b)

MA has a flat molecular structure in which the greatest length is about 5.126 Å, as depicted in Figure 1. This figure also reveals that the incorporation of excess MA into acid-treated vermiculite extends its gallery spacing [11]

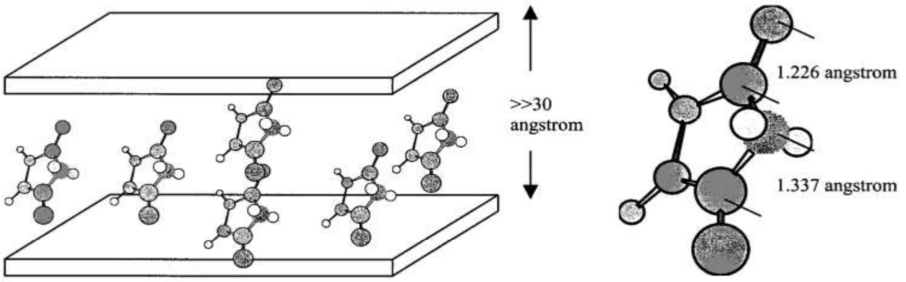


Figure 3. Structures for energy-minimized maleic anhydride and MAV

Composite preparation. MA-pretreated vermiculite (MAV) was mixed with acrylonitrile monomer dissolved in water and the resulting suspension was mixed in the 3-neck reactor by stirring, and the temperature was kept constant. $K_2S_2O_8$ and $NaHSO_3$ were dissolved in water and was then dropped into the reactor to initiate polymerization. The mixture was stirred for 10 h at 70 °C. After terminated reaction, we obtained the particles of PAN- MAV(Polyacrilonitrle - Maleic Anhydrid Vermiculite) by washing, filtering, drying, milling, and sieving, subsequently.

A model of this structure is depicted in Figure 4. It can be seen during acrylonitrile polymerization, a copolymer with MAV-containing malein [12].

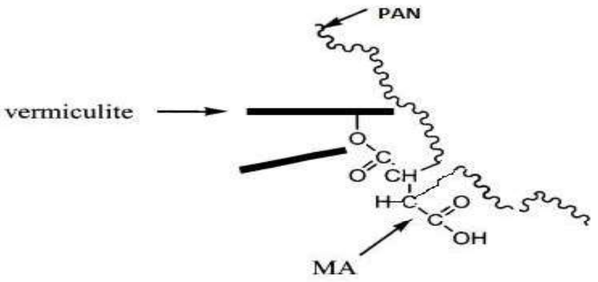
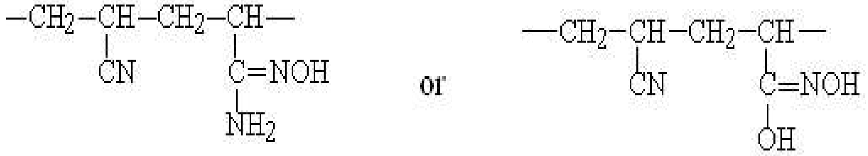


Figure 4. Ternary vermiculite/MA/PAN molecular structure.

The PAN/MAV composite was reacted with hydroxylamine to convert the nitrile group into amidoxime (AO) groups. After treatment at 90 °C for 4 h, the product PAO amidoxime (AO) / MAV was filtered, washed with water and dried under a vacuum. The modified composite with hydroxyl amine had a static exchange capacity (SEC) of 3,24 mg-eq / g according to HCl.

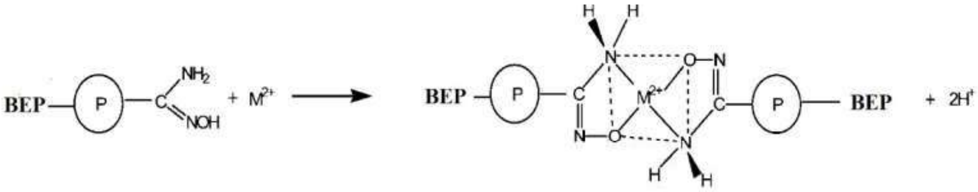
It was shown that at action on polyacrylonitrile of hydroxylamine (HA) the polyacrylamidoximic or polymeric hydroacid links have been formed [8-13]:Scheme 1



$$-CH_2-\underset{CN}{CH}-CH_2-\underset{\underset{NH_2}{C=NOH}}{CH}- \quad \text{or} \quad -CH_2-\underset{CN}{CH}-CH_2-\underset{\underset{OH}{C=NOH}}{CH}-$$

Batch adsorption studies. Batch adsorption studies were performed using different concentrations of potassium dichromate, copper sulphate and nickel chloride. The extent of metal ion removal was investigated separately by changing the adsorbent dose, pH of the solution and time of shaking of the adsorbent metal solution mixture. Stock solutions of copper(II) ion was prepared by dissolving $CuSO_4*5H_2O$, that of nickel(II) ion was prepared by dissolving $NiCl_2$ and that of chromium(VI) ion was prepared by dissolving $K_2Cr_2O_7$ in distilled water. The concentration of metal ion solution was 200 mg/l in all three cases. Batch adsorption experiments were conducted by treating 0,5 g of cross linked Polyacrylonitrile-Maleic Anhydrid-Vermiculite (PAN/MAV) copolymer with 100 ml of potassium dichromate, copper sulphate and nickel chloride solutions taken in a 250 ml stoppered bottles separately. After attaining the equilibrium adsorbent aqueous phase concentration of metal was determined with UV/VIS spectrophotometer. A similar procedure was carried out at different time intervals, adsorbent doses and pH. The pH of each solution was adjusted to different values using either NaOH or HCl.

The obtained sorbent has the properties of cationite and anionite due to the presence of both -OH and $-NH_2$ groups. Since amidoximes act as bidentate ligand, it is supposed that two amidoxime groups may be used for chelate formation with metal ions [13]. Scheme 2



The effect of adsorbent dose on the removal of Cr^{6+}, Ni^{2+} and Cu^{2+} ion was presented in Fig.5. The dependence of various metal ion removal on adsorbent dose was investigated by varying the amount of (PAN/MAV) copolymer from 1 to 6 g separately, while keeping other parameters (pH, and time) as constant. Fig. 5 shows that the removal percentage increases with increasing adsorbent dose. The increase in metal ion removal percentage with increase in adsorbent dose may be due to greater availability of extra adsorption sites for metal ions. However, the uptake capacity of metal ion per unit mass of sorbent (mg/g) decreases with increase in dose of adsorbent, which may be due to lower utilization of adsorption sites of the sorbent at higher dosage [14]. The maximum % removal of Cr(VI) was about 84% at the dosage of 6 g, while for Ni(II) and Cu(II) it was 81% and 86% at the dosage of 5 g and 6 g.

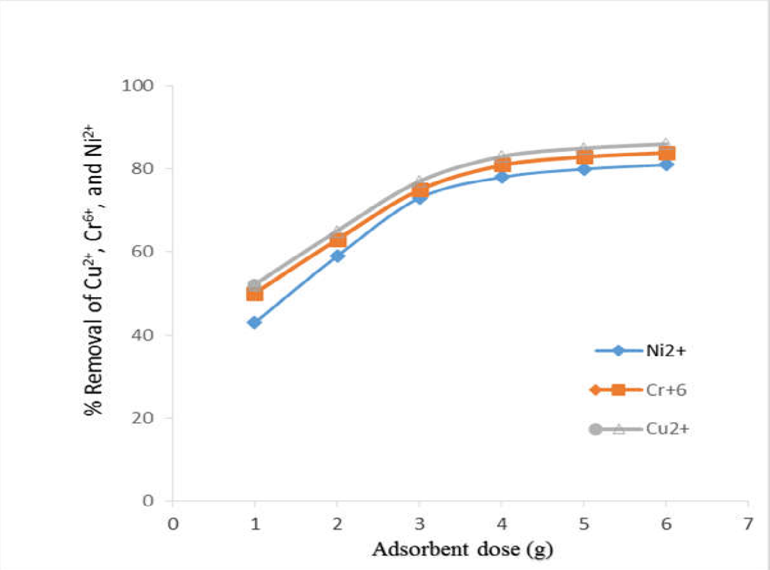


Figure 5. Effect of adsorbent dose on the removal of Cu^{2+}, Cr^{6+} and Ni^{2+}

Thus, a new PAO / MAV composite compound was synthesized. Modification with hydroxyl amine was studied. The sorption properties of Cr^{6+}, Ni^{2+} and Cu^{2+} ions were studied depending on the pH value. Repeated studies of adsorption-desorption have shown that PAO/MAV can be used as an effective and inexpensive adsorbent for the removal of heavy metals from aqueous solutions and industrial wastewater.

References:

1. Bekchanov D. J., Sagdiev N. J., Mukhamediev M. G. American Journal of Polymer Science. Vol 6, Issue 2, 46-49 (2016).
2. Marcos, C., Rodríguez, I., de Rennó, L.C., Paredes, J.I., 2004b. Vermiculite surface structure imaged by contact mode AFM. European Journal of Mineralogy 16, 597–607.
3. Simha Martynková G., Barabaszová K, Valášková M (2007) Effect of Size and Preparation Method of Particles on Intercalation Ability of Vermiculite. Acta metall. slovaca 6: 275–279.
4. Zhang K, Xu J, Wang KY, Cheng V, Wang V, Liu V (2009) Preparation and Characterization of Chitosan Nanocomposites with Vermiculite of Different Modification. Polym. degrad. stabil. 94: 2121–2127.
5. Da Silva DC, Skeff Neto K, Coaquira JAH, Araujo PP, Cintra DOS, Lima ECD, Guilherme LR, Mosiniewicz-Szablewska E, Morais PC (2010) Magnetic Characterization of Vermiculite-based Magnetic Nanocomposites. J.non-cryst. solids 356: 2574–2577.
6. Du XS, Xiao M, Meng YZ, Hung TF, Rajulu AV, Tjong SC (2003) Synthesis of Poly(arylene disulfide)-Vermiculite Nanocomposites via in situ Ring-Opening Reaction of Cyclic Oligomers. Eur. polym. j. 39: 1735-1739.
7. Tjong SC, Meng YZ (2003). Impact-Modified Polypropylene/Vermiculite Nanocomposites. J. polym. sci. pt. b-polym. phys. 41: 2332–2341.
8. Shao W, Wang Q, Chen Y, Gu Y (2006) Preparation and Properties of Polypropylene/ Vermiculite Nanocomposite through Solid-State Shear Compounding Method using Pan-Mill Equipment. Mater. manuf. process. 21: 173–179.
9. Gafurova D.A., Khakimzhanov B.Sh., Mukhamediev M.G., Musaev U.N. Sorption of Cr(VI) on the Anion-Exchange Fibrous Material Based on Nitron. Russian Journal of Applied Chemistry. Vol. 75, Issue 1, 71-74 (2002).
10. Ikramova M.E., Mukhamediev M.G., Musaev U.N. Complexation of iodine with anion-exchange polyacrylonitrile materials. Plasticheskiyi massi. Moscow. Issue 12, 17-18 (2000).
11. Xu J, Li RKY, Xu Y, Li L, Meng YZ (2005) Preparation of Poly(propylene carbonate)/Organo-Vermiculite Nanocomposites via Direct Melt Intercalation. Eur. polym. j. 41: 881–888
12. Dhamodharan R, Jeyaprakash JD, Samuel V, Rajeswari MK (2001) Intercalative Redox Polymerization and Characterization of Poly(4-vinylpyridine)–Vermiculite Nanocomposite. J. appl. polym. sci. 82: 555-561.
13. Kavakli, P. A.; Guven, O. Removal of Concentrated Heavy Metal ions from Aqueous Solutions using Polymers with Enriched Amidoxime Groups. *J. Appl. Polym. Sci.* 2004, *93*, 1705–1710