A new granulated sorbent based on acrylonitrile: synthesis and physico-chemical properties

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Abstract. It was common practice in water treatment procedures to employ functional polymers to sorb metallic species from the water. Due to the wide spectrum of potential functional groups on polymeric backbones, these sorbents had the potential to separate a huge range of metals. The characteristics of the cationic metallic ions and the functional groups were closely related to the selectivity and sorption efficiency via complexation or ion exchange interactions. Another crucial factor that needed to be taken into account was the physical makeup of the materials. Major variations in sorption characteristics were found in the sorption kinetics, which were contingent on the cross-linking density, polymer solubility and polymeric architecture. An anion-exchange and complexing property-rich novel granular sorbent was created by the chemical reaction of a cross-linked copolymer of acrylonitrile with hexahydro-1,3,5-triacrylyltriazine when subjected to hydroxylamine. Modern techniques have been used to examine the physico-chemical characteristics of the final sorbent and demonstrate the characteristics of its structural morphology.

1 Introduction

Industrial activity has caused a dramatic rise in the quantity and variety of heavy metal contamination in aqueous effluent during the past few decades. The environment has suffered greatly as a result of this expansion. Most of the time, heavy metals are hazardous and do not break down. They therefore build up in living things and pose a health danger to people. For example, heavy metals can cause renal and neurological problems and are carcinogens, such as cadmium, nickel, lead or copper. The Environmental Protection Agency's (EPA) report on Drinking Water Standards and Health Advisories lists heavy metals, whose presence in drinking water must be strictly regulated. Common water treatment facilities only remove a portion of these contaminants [1-6]. To create polymers with the necessary qualities, the structural design of polymers has drawn more attention recently. Similar polymer processes using cross-linked copolymers with a regulated

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structure and active functional groups that may interact chemically with low-molecular-weight modifying agents are still relevant in this context. These copolymers function as efficient matrices to produce complex formation processes with d-metal ions and sorbents that can exchange ions [7-9]. In this sense, the Republic of Uzbekistan produces granular sorbent based on acrylonitrile on an industrial scale, which is the subject of this study.

2 Materials and methods

Preparation of granular sorbent. The synthesis of a new granular sorbent was carried out by a chemical reaction between a cross-linked copolymer of hexahydro-1,3,5 triacrylyltriazine (HTT) and acrylonitrile (AN) (Figure 1), previously synthesized by us [10]. The chemical reaction of the AN-HTT copolymer was carried out under mild conditions, in which the probability of destruction of the bridge-forming molecule (BBT) was minimized. A polymer-analogous transformation was carried out in a slightly acidic environment - not completely neutralized with sodium carbonate with an aqueous solution of hydroxylamine at 369-371 K for 5 hours.

2.1 Potentiometric titration of anion exchanger

To carry out potentiometric titration, a series of 0.25 g samples of anion exchanger in the OH form were placed in 50 ml volumetric flasks and examined with different amounts of 0.1 N acid solution. To maintain the ionic strength of the solution, a certain amount of 0.1 N NaCl solution was added while keeping the constant volume of the mixture. The mass ratio of ion exchange resin: solution was 200. After equilibrium was established (3 days), the solution pH was determined and a potentiometric titration curve was plotted in coordinates pH - the amount of titrant (in mg - equivalent per 1 g of anion exchanger) [11-13].

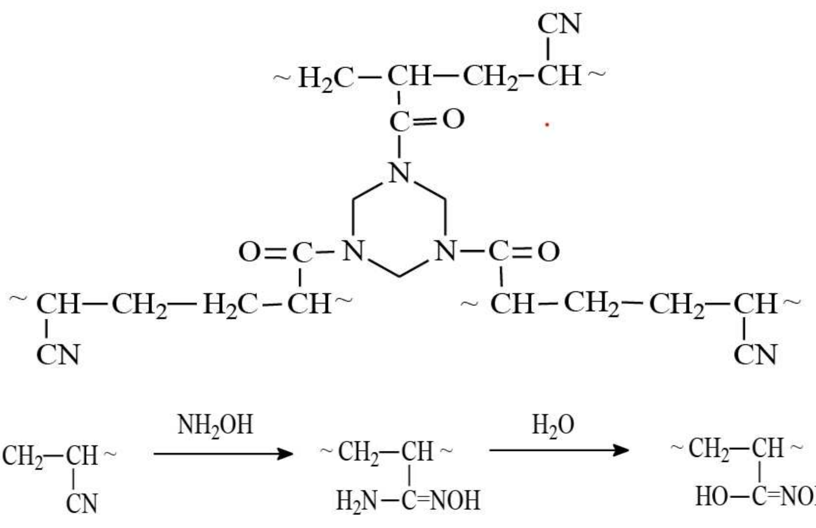


Fig. 1. Schematic representation of the structure of the AN-HTT copolymer.

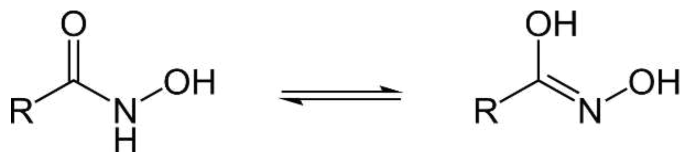
To carry out partial swelling of the granules, 5% dimethylformamide (DMF) was added to the reaction medium. IR spectra were recorded on a Nicolet iS50 Fourier transform IR spectrometer (Thermo Scientific, USA). Samples of the starting materials and ion exchanger were used in the form of pressed tablets with KBr.

The structural morphology and elemental composition of the sorbent were examined using an EVO MA 10 scanning electron microscope (Carle Zeiss, Germany) equipped with an INCA Energy 300 microanalytical equipment for energy-dispersive X-ray (EDX) microanalysis (Oxford Instruments, UK) [14-15].

3 Results and Discussion

To obtain a granular sorbent with ion-exchange and complex-forming properties, chemical modification of the cross-linked copolymer AN-HTT was carried out under the influence of hydroxylamine (HA) according to the following scheme:

As can be seen from the presented diagram, during chemical modification, i.e. aminolysis with hydroxylamine, the functional nitrile groups of the cross-linked copolymer AN-HTT form amidoxime groups, then transform into (poly)hydroxamic acids, which, due to the phenomenon of tautomerism, also have a hydroxylamine form:



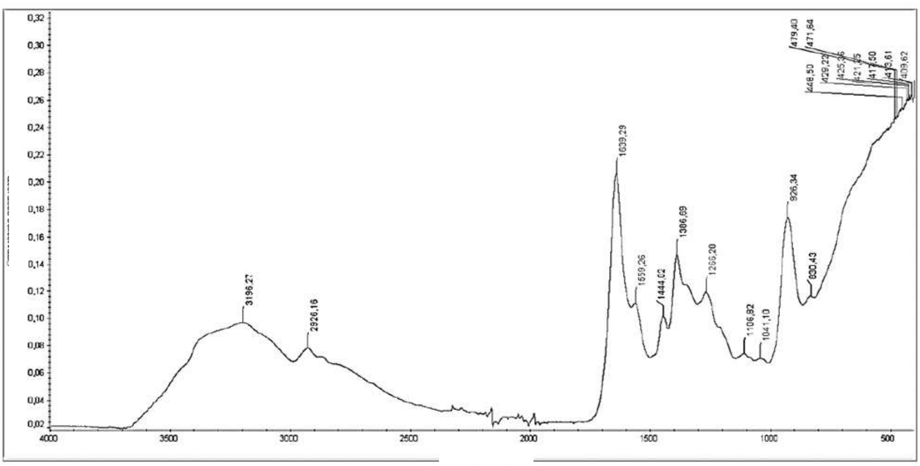


Fig. 2. Fourier transform IR spectrum of granular sorbent AN–HTT-HA.

The Infra-red spectrum derived from the modified polymer, the disappearance of the absorption frequency in the region of 2242.57 cm^{-1}, ascribed to stretch vibrations of the acrylonitrile units' nitrile group (-CN) in the first copolymer, as noted; bands are detected: absorption vibrations of the stretching vibrations of N–H groups (-N–H) at 3196.27 cm^{-1}; stretching vibrations of the amide II group (-N–C=O), which is part of the fragment, due to the bridge-forming agent. Absorption bands associated with oxime groups appear: stretching vibrations of the -C=N group (C=N) at 1639.29 cm^{-1}; stretching vibrations at 2926.16 cm^{-1} (-O=H) and bending vibrations at 1451.54 cm^{-1} (-O–H) of the O–H group. The resulting new granular sorbent/anion exchanger (AN-HTT-HA) is a spherical granule with a particle size of 0.6-1.6 mm (class A) and high (98%) mechanical strength. The morphology of the surface and cross-section of the AN-HTT-HA granule was studied by scanning electron microscopy [16-19]

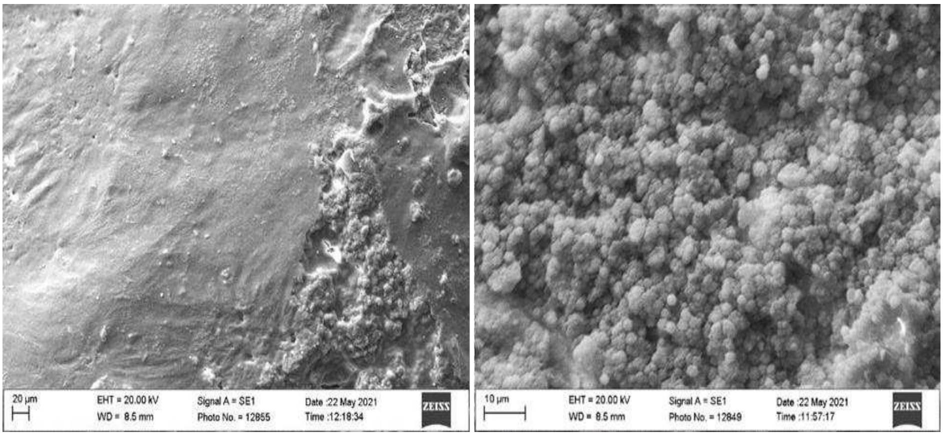


Fig. 3. Morphology of the surface and cross-section of the AN-HTT-HA anion exchanger granule.

As can be seen from the micrographs presented in Figure 3, the surface structure of the synthesized anion exchanger granule is heterogeneous with many aggregates penetrating the entire surface of the sorbent. When studying the structural morphology of a cut of an anion exchanger granule, the architecture is revealed in more detail. At 1000x magnification, it is observed that the anion exchanger granules consist of interconnected micro-sized globular particles.

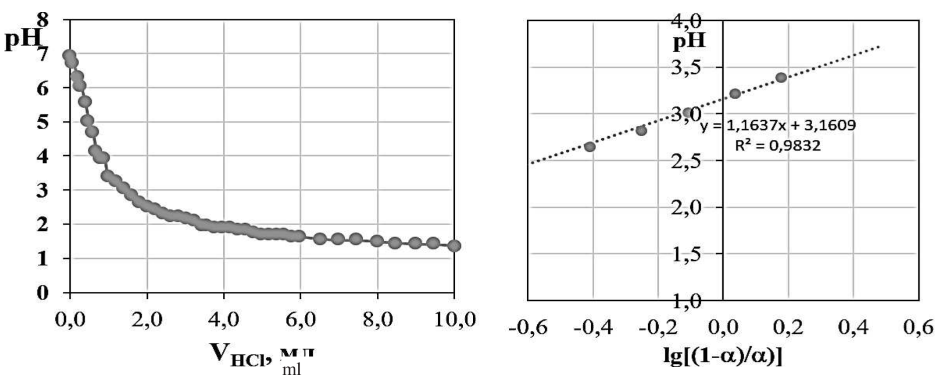


Fig. 4. The titration curve of the AN-HTT-HA anion exchanger at a constant ionic strength of a solution of 0.1 M, presented as the dependence pH = f(VHCl) (a) and Gregor coordinates (b).

The static exchange capacity of the new anion exchanger was determined based on potentiometric titration data at the constant ionic strength of the solution (Figure 4), which is 2.6 mEq/g for 0.1 N HCl. The apparent pK constant of the anion exchanger is 3.16, which can be classified as an anion exchanger of medium basicity. It should be noted that to obtain more reliable data, potentiometric titration of the anion exchanger must be carried out in non-aqueous media, therefore the found pK value should be considered approximate.

4 Conclusion

Over the past several years, treating wastewater that contains metallic cations has grown to be a significant environmental problem. Different procedures were therefore created utilizing various kinds of materials. Because of their benefits, research on the application of functional polymers in particular was growing. Several functional groups could absorb metallic cations that were documented in the literature. More specifically, because of the pair on the O or N atom, the O- or N-donor significantly produced intriguing findings. These functional groups have a very pH-dependent character. Conversely, the kind of acidic groups carried by polymeric adsorbents changed according to pH, enabling effective sorption of metallic cations as well as simple material renewal. Thus, polymers containing phosphonic, sulfonic, and carboxylic acids were widely used for the sorption of various cations, including radionuclides, rare earth elements and heavy metals. The cross-linked AN-GTT copolymer's aminolysis process allowed for the creation of a novel granular sorbent with ion exchange and complex-forming capabilities. IR spectroscopy, potentiometric titration, and scanning electron microscopy were used to analyze the novel anion exchanger's composition and structural characteristics. Therefore, one significant task will be to continue developing such granular sorbents so that they may be used to selectively extract rich metals, such as precious metals or rare-earth elements, for example.

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