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Review

A review on acrylic based hydrogels and their applications in wastewater treatment

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ABSTRACT

The acrylic based hydrogels have attracted the attention of many researchers in the field of pollutants adsorption such as dyes and metal cations due to their high swelling and adsorption capacities. This review introduces acrylic based hydrogels and focuses on their adsorption properties. We first described the methods for synthesizing hydrogels. Usual methods of characterization of acrylic based hydrogels such as swelling, adsorption capacity and desorption efficiency of the pollutants have been investigated. In addition, the adsorption isotherm and kinetic models which determine the mechanism of pollutants' adsorption by hydrogels have been introduced and relations that determine the values of thermodynamic parameters which define accomplishment of adsorption process have been investigated. In the following sections, a perfect insight has been provided on natural and synthetic acrylic based hydrogels. The effective parameters of swelling and adsorption by acrylic based hydrogels have been reviewed and the mechanism of pollutant's adsorption by acrylic based hydrogels has been discussed.

Contents

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1. Introduction

The rapid growth of industrial activities has caused environmental contaminants. Heavy metals and industrial dyes are the main pollutants of water resources in many parts of the world. Unlike organic pollutants, inorganic pollutants are not biodegradable. These contaminants cause genetic and physiologic problems in living organisms even at low concentrations. For example, Pb^{2+} damages nervous system, hematopoietic system, and kidneys or Ni^{2+} damages lung and skin. Methods such as chemical deposition, ion exchange, electrochemical removing, adsorption, coagulation, flocculation, membrane separation have been proposed to overcome these contaminants (Jang et al., 2008; Fu and Wang, 2011). Among these methods, adsorption due to its low cost, the simplicity of design and high efficiency is better than other methods (Liu et al., 2015). The use of polymeric materials as adsorbents has received the attention of many researchers. In this regard, hydrogels are the newest adsorbents that are used in the adsorption of water pollutants. Their unique properties are good mechanical properties, easy to use and reusability. Hydrogels are three-dimensional, porous, hydrophilic, physical and chemical crosslinking networks that swell thousands time of their dry weight in the vicinity of water or biological fluids (Hoffman, 2002). These materials can respond to specific changes in their environment such as temperature, pH, magnetic field, and the electric field which determines their application in the fields of medicine, tissue engineering (Pensalfini et al., 2017), wound dressing (Rakhshaei and Namazi, 2017), biosensors (Jonášová and Stokke, 2016), pharmaceutical (Treenate and Monvisade, 2017), agriculture (Guilherme et al., 2015) and adsorption (Khan and Lo, 2017). Recently, hydrogels have found a special place in the field of wastewater treatments. Factors affecting heavy metals and dyes adsorption of hydrogels are the structure and composition of them, the type of pollutant, initial concentration of pollutants in the feed solution, treatment time, temperature and pH of pollutant solution so the effect of these parameters on adsorption properties of hydrogels should be studied (Abd El-Mohdy et al., 2013). Common functional groups that are used in synthesizing hydrogels include carboxylic acids, amides, amines, hydroxyl and sulfonic acid. Super-absorbent hydrogels swell because of water penetration at pre-existing or dynamically formed distances between polymer chains (Zheng et al., 2011). Due to ionization of hydrogel's functional groups, certain charges in the polymer's chains and free counter ions in the gel phase are created that these free counter ions can't go out of the hydrogel network. The existence of charge in the network of this hydrogel which is called polyelectrolyte leads to the osmotic pressure difference between the gel and the aqueous phase. The osmotic pressure difference acts as the driving force that leads to the penetration of water until the pressure difference gets zero. As a result, whatever free counter ions concentration increases, the pressure difference will be enhanced so this leads to high swelling of the gel. It should be noted that by increasing the functional groups of hydrogels, free ions are increased. On the other hand, electrostatic repulsion between the ions along the chains causes swelling increment (Bao et al., 2012). In polyelectrolyte hydrogels, the osmotic pressure is calculated by equation (1):

$$\pi = RT\sum_i \left(c_i^g - c_i^s\right) \tag{1}$$

where R is the gas constant, T is the absolute temperature, c_i is the molar concentration of mobile i ion and sigma is the sum of all moving ions present in the gel phase and the surrounding solution, specified by subscripts g and s, respectively (Su and Okay, 2017). External solution properties such as charge capacity and salt concentration affect the swelling of hydrogels. Swelling of hydrogels, especially ionic hydrogels, in salt solutions is less than distilled water. The type of salt and its concentration can be expressed in terms of ionic strength. Thus, according to the Flory equation (Eq. (2)), the rate of swelling decreases with increasing ionic strength.

$$Q^{\frac{5}{2}} \approx \frac{\left(i \big/ 2V_u S^{\frac{1}{2}}\right) + \left(\frac{1}{2} - \chi_1\right)/V_1}{\frac{V_E}{V_0}} \tag{2}$$

where Q is the degree of swelling, $\frac{i}{V_u}$ is the polymer charge density, S is the ionic strength of the solution, $\left(\frac{1}{2} - \chi_1\right) \big/ V_1$ is the affinity of the polymer and solvent and $\frac{V_E}{V_0}$ is the crosslinking density. The diffusion process in hydrogels depends on the solvent diffusion rate and the relaxation of the polymer chains so it is categorized into three types:

1) Fickian diffusion: solvent diffusion rate is less than the rate of chain relaxation ($R_{diff} < R_{relax}$).
2) Non-Fickian diffusion: the solvent diffusion rate is greater than the rate of the chain relaxation ($R_{relax} < R_{diff}$).
3) Anomalous diffusion: the solvent diffusion rate is approximately equal to the rate of chain relaxation.

To determine the type of diffusion process, the following relation is used:

$$F = Kt^n \tag{3}$$

where F is fractional uptake at time t, k is the polymer network constant and n is diffusion power which determines the type of diffusion process. If $0.45 < n < 0.5$, then diffusion type is Fickian and if $0.5 < n < 1$, then there is a Non-Fickian diffusion (Thakur et al., 2016). Acrylic acid and methacrylic acid, as shown their structure in Fig. 1, are common monomers in the synthesis of superabsorbent hydrogels (Ferfera-Harrar et al., 2015). In the structure of these