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Adsorption and desorption behavior of silver ions onto valonia tannin resin

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Abstract: Valonia tannin (VT) was gelated through polymerization with formaldehyde to prepare an adsorbent, which was found effective to remove Ag^+ from aqueous solution. The adsorption–desorption behaviors of valonia tannin resin (VTR) were investigated under various initial Ag^+ concentrations, solution temperatures, pH values etc. The applicability of empirical kinetic models was also studied. The pseudo-second-order model studies revealed the Ag^+ sorption was very rapid. VT and VTR were characterized using FTIR and SEM before and after adsorption. The Ag^+ biosorption on VTR increased with a rise in initial concentration of Ag^+ and with a decrease in temperature. Desorption experiments were conducted at low pH values and the solutions of H_2SO_4, HNO_3 and HCl were used for desorption. The VTR shows high adsorption capacity to Ag^+ in a wide pH range of 2.0−7.0, and a maximum adsorption capacity of 97.08 mg/g was obtained at pH 5.0 and 296 K when the initial concentration of Ag^+ was 100.0 mg/L. Ag^+ ion desorption could reach 99.6% using 1 mol/L HCl+1% thiourea (NH_2CSNH_2) solution. By utilizing such characteristics of VTR, it is expected that it can be applied to recovering Ag^+ efficiently and simply with low cost.

Key words: biosorption; desorption; kinetics; silver; Ag^+ ions; absorbent; valonia tannin; resin

1 Introduction

Silver has the highest electrical and thermal conductivity among metals. It exhibits superior corrosion and oxidation resistance. Silver is a nonessential trace metal. The monovalent silver ion is more toxical for fish than copper or mercury, and it is an extremely effective bactericide [1]. Silver is not a dietary requirement for organisms. Antimicrobial agents such as silver are used in commercial textiles and they damage the cell wall or alter cell membrane permeability, denature proteins, inhibit enzyme activity or inhibit lipid synthesis, all of which are essential for cell survival [2]. The presence of pathogen microorganism in water and environment is one of the perennial problems. Recently, nano-silver-containing composite materials have been used in studies to remove bacteria, fungus, viruses and odor from water and environment [3−6]. The experimental studies showed that the dope loaded nano-silver particles have high practicality. In view of these notable properties, the industrial and technical usage of silver in photographic materials, electrical and electronic products, brazing alloys, batteries, silver painted bearings of aircraft, diesel locomotives and gas turbine engines, mirrors and in dental amalgams has exceeded its applications as a decorative and ornamental metal [7].

In literature, many natural organic and inorganic materials have been used as adsorbents. HANZLIK et al [8] studied the removal of Ag(I), Cd(II) and Cu(II) ions by adsorption by "natural carbonaceous materials (spruce wood, pine bark, cork, peat, fusinite, lignite, oxidised lignite, bituminous coal and anthracite)" [8]. Since metal ions have toxic effects on the environment, many researchers suggested cost-effective organic biosorbents such as living [9] and non-living biomass [10,11] for removing dissolved metals from wastewaters.

Recently, various sorbents have been used in studies to remove Ag ions and the heavy metals from water and waste water by sorption. Several studies have been proposed in the literature about the use of new sorbents, in relation with silver ions sorption from water solutions. These materials have some comparative advantages in contrast to common sorbent materials. In the last decade, researches have prepared new Ag sorbents using various materials by miscellaneous methods. Some remarkable studies can be seen in Table 1.

As seen in Table 1, there are researches all over the world, on the understanding of the mechanisms of removing Ag ions through new sorbents. Tannin adsorbents are used for metal sorption as powder or granules in direct use [24], and some studies have used

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Table 1 Silver sorption studies

Sorption material	pH	*T*/K	Ag^+ sorption capacity	Reference
717 anion-exchange resin	2−3		0.58 mol/g	[12]
Calcium alginate beads	4	295	52 mg/g	[13]
Chelamine	6	295	1.2 mmol/g	[14]
Polyurethane foam (PUF)	5	298	65.4 μmol/g	[7]
Carbon adsorbents	6	−	1.06 mmol/L	[15]
Shenfu3^{-1} coal	4.5	353	116.414 mg/g	[16]
Acrylic copolymers functionalized resin (As 14P)	4	298	100 mg/g	[17]
Poly(*o*-phenylenediamine) microparticles	5	303	533 mg/g	[18]
Chemically modified melamine resins	7.2	318	1.140 mmol/g	[19]
Amino/thiol-bearing resin (RIV)	6.5	301	2.86 mmol/g	[20]
6-mercaptopurinylazo resin	6	−	0.52 mmol/g	[21]
3-amino-1,2,4-triazole-5-thiol chelating polymers	6.7	328	2.43 mmol/g	[22]
Thiourea-modified chitosan resin	4	298	3.77 mmol/g	[23]
Valonia Tannin resin (VTR)	5	295	97.087 mg/g	This study

them fixed onto a constant membrane. In many studies, developed tannin resins were used for uptake platinum(IV), palladium(II) [25], and bismuth(III) [26] ions as adsorbent on their own and in others adsorbent mechanisms are studied on tannins immobilized collagen fiber membrane.

For removal of many elements such as Hg^{2+}, Zn^{2+}, Pb^{2+}, Cr^{2+}, Cd^{2+}, Ni^{2+}, Bi^{3+}, Th^{4+}, V, U and precious metals such as Au^{3+}, Pt^{4+}, Pd^{2+}, tannin sorbents have been employed in literature [27]. However, no studies on Ag^+ removal with the tannin biosorbents were found. Recovery of silver as a precious metal from industrial wastewater is important from economical and environmental perspectives. The aim of the present work was to study the detailed sorption isotherms and kinetics of less-researched Ag(I) metal from aqueous solutions by tanin resins and the desorption behavior. Experiments were performed as a function of adsorption time, initial Ag^+ concentration in the solution, and the temperature. Our objectives were (i) to determine and compare the isotherms of Ag^+ adsorption on VTR with various physico-chemical properties, (ii) to determine and compare the sorption kinetics and mechanism of Ag^+ adsorption on VTR, and (iii) to investigate the sorption–desorption hysteresis phenomena and its possible mechanism.

2 Materials and methods

2.1 Preparation of VTR

Valonia tannin was selected as the raw material to synthesize the resin. Tannin was provided from the Tuzla Organized Leather Industry (Turkey). A certain amount of tannin powder was dissolved in ammonia solution at room temperature. Then, tannin was gelated through polymerization with formaldehyde (37%) at 343 K. After gelation at 343 K for 14 h, the obtained tannin resin was crushed and sieved to produce particles of 38−53 μm in diameter. They were washed successively with distilled water and HNO_3 solution (0.5 mol/L) to remove unreacted substances, and finally rinsed with distilled water again.

2.2 Batch equilibrium studies

The concentration of the silver solution was determined by an atomic absorption spectrophotometer (Shimadzu, AA-6200 type). The adsorbed Ag^+ concentrations were obtained from the difference between total initial Ag^+ concentration and finally detected Ag^+ concentration. The maximum adsorption capacity (Q_m) was calculated from isotherm data. The amount of Ag^+ ion sorption onto VTR can be calculated by [28]

$$q_e = \frac{C_i - C_e}{m} V \quad (1)$$

where q_e is the silver ion adsorbed onto the VTR (mg/g); C_i is the initial silver ion concentration (mg/L); C_e is the final silver ion concentration in the solution (mg/L), V is the volume of the solution (L); m is the mass of used VTR adsorbent (g). Batch adsorption studies were conducted to determine the relationship between adsorbent and adsorbate, varying the amounts of adsorbate. In the study, VTR particle size of 38−53 μm was used. Agitation rate on the Ag uptake was studied by using 350 r/min stirring speed. All experiments were repeated three times and the results given here are the average of there values.

In the all batch experiments, contact time was 180 min. Parameters such as temperature and pH are quite important on adsorption. The pH of the solution was adjusted to desired values with 0.1 mol/L HNO_3 and 0.1