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Metal sericin complexation and ultrafiltration of heavy metals from aqueous solution

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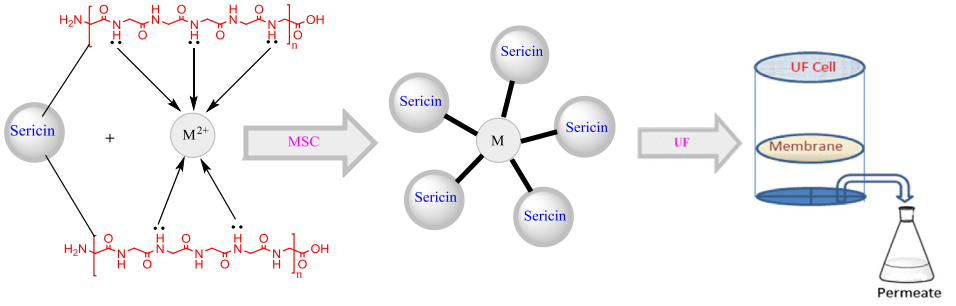
HIGHLIGHTS

- Metal-sericin complexation in ultrafiltration study was discussed.
- Effect of metal concentration and sericin dose on *R*% and *J* was evaluated.
- Role of anions in ultrafiltration study of metal ions of salt pairs was elaborated.
- Kinetic and pH study of metal removal from aqueous solution was made.

GRAPHICAL ABSTRACT



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ABSTRACT

This work exclusively confers theoretical insight into ultrafiltration of heavy metal ions (Pb^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) from aqueous solution using sericin biopolymer. Sericin is a water soluble bio-macromolecule and has potential to show chemical interaction with metal ions due to protein units containing several amino acids. The functional groups of sericin such as amine (NH_2—), disulfide linkage (—S—S—) and carboxylic acid (—COOH) assign it role of poly dentate ligand (PDL). Provision of negatively charged surface with lone pair of electrons facilitates metal-sericin complexation owing to d-electron deficient metal ions. Sericin-chelated metal ions are retained by pores of membrane when the aqueous solution is subjected to pass through membrane on account of their enhanced size. Metal trapping efficiency of sericin was measured by determining rejection percentage (*R*%) and permeate flux (*J*) at three different transmembrane pressures (TMP) during ultrafiltration study. More importantly, effect of anions was evaluated by comparing two different salts of same metal ion. High formula weight and greater solubility of salts leave significant impact on *R*% and *J*. Greater contact time between metals and sericin enhanced *R*% followed by reciprocal trend of *J* in batch experiment. In addition, basic pH helps to increase *R*% values of metal ions in sericin supported ultrafiltration study.

1. Introduction

Discharge of toxic organic compounds and metallic ions into sewage systems may damage the operational process of biological treatment plants [1]. The environmental and ecological requirements include low energy, cheap labor and small capital costs, but the conventional water treatment techniques are incapable to remove the metal ions from aqueous effluents up to the minimum desirable concentration. Secondly, technologies involving process of ion exchange, activated carbon adsorption, electrolytic removal are prohibitively expensive [2]. Application of pressure

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driven membranes is very common in order to segregate metal ions or organic dyes from industrial wastes or natural waters [2–4]. Of many separation techniques membrane driven technique is effective and compatible to other techniques regarding technical and economic feasibility [5]. Membrane separation process for instance, microfiltration, nanofiltration and ultrafiltration are only limited to retain the molecules of higher masses and unable to remove all the contaminants [6]. Removal of metallic ions can be accomplished by either reverse osmosis (RO) or at least nanofiltration on account of smaller size of target metal ions. Nonetheless, use of dense polymeric membranes in such techniques significantly enhances the capital and operating costs [7,8]. Likewise, micellar enhanced ultrafiltration (MEUF) technique has been executed to eliminate ions and soluble organic solutes from aqueous environment using electrostatic attractive forces and hydrophobic–hydrophobic interactions [9–12]. The negative aspect of MEUF is the transfer of monomeric surfactant molecules through the membrane to the aqueous stream namely permeate [13]. The idea of enhanced ultrafiltration (UF) works on the principle of metal–polymer binding to make macromolecular complexes that are hampered by the small pores of membrane on one side while the non-complexed metal ions pass through other side of employed membrane. The major concern is to find the suitable polymer for effective complexation with target metal ions [14,15]. Over the past many years, variety of polymers have been used to remove metal ions from water for instance; polyelectrolytes, poly (ethylenimine) and poly (diallyl dimethyl ammonium chloride) [16]. Since water treatment technologies require benign and safe polymers, eventually researchers have drawn their attention to natural materials for example; clay materials, agricultural wastes, biomass, marine organism and biopolymer chitosan for the removal of heavy metal ions from aqueous solutions [16,17]. The silkworm cocoons contain two major proteins, fibroin and gummy substance sericin that constitute 20–30% silk fiber and is water soluble glycoprotein [18]. In addition, sericin is specifically synthesized in the middle silk gland of the silkworm [19]. Sericin extracted from *Bombyx mori,* comprises a group of polypeptides with molecular mass of 20–400 kDa and has particularly rich serine content [20,21]. Presence of high percentage of water-soluble amino acids (serine and threonine) in sericin makes it moisturizing agent in cosmetic industry [22]. We exclusively used this biopolymer (sericin) to entrap heavy metal ions by keeping in view its water solubility and remarkable property of chelation in our study as shown in Fig 1 [23]. A metal-sericin complex (MSC) of considerable size is formed on mixing in water. Sericin-enhanced metal ions were subjected to pass through the ultrafiltration membrane. On account of larger size MSC, trapped metal ions are hampered by the smaller pores of UF membrane. The pure stream of water on the other side of membrane is taken out as permeate. In this study we discussed in detail theatrical or physical behavior of metal-sericin complexation in ultrafiltration.

2. Theory

2.1. Metal-sericin complex (MSC) formation and pH effect

To discuss theoretically, we ignore other functional groups in sericin polymer and only consider role of most effective NH_2— functional group with lone pair of electrons for chelation. A complex formation reaction between divalent metal ions (M) and amino (NH_2—) group of PDL sericin (S) can be written as:

$$M + mS \leftrightarrow MS_m \tag{1}$$

where M, are free metal ions in aqueous solution and S is repeating unit of PDL sericin. Charges have been ignored for understanding.

The amine (NH_2—) and carboxyl (—COOH) group which are responsible for sericin solubility in water plus its potential role for metal chelation phenomenon. The higher ratio of serine and threonine amino acids impart acidic characteristics to solution when sericin is dissolved in water [24]. Thus, sericin units experience competitive reaction of protonation into SH.

$$S + H \leftrightarrow SH \tag{2}$$

The quantities of SH and S in sericin-water solution without metal ions are related to pH value with help of Henderson–zHasselbalch equation:

$$pH = pK_a - n \cdot \frac{log(1-\alpha)}{\alpha} \tag{3}$$

where "pK_a" is the dissociation constant of "SH", n is constant which depends on interaction caused by each neighboring polyelectrolyte and α is the degree of protonation of PDL sericin and expressed as:

$$\alpha = \frac{[S]}{[S]_0} \tag{4}$$

$[S]_0$ is the initial concentration of PDL sericin in solution.

Using Eqs. (3) and (4), concentration of [SH] and [S] as a function of pH can be achieved:

$$[S] = [S]_0 \left[1 + 10^{\frac{pK_a - pH}{n}}\right]^{-1} \tag{5}$$

$$[SH] = [S]_0 \left[1 - 10^{\frac{pK_a - pH}{n}}\right] \tag{6}$$

It was experimentally found by Von Zelewsky et al. that such polymers give pK_a and n values equivalent to 7.7 and 7 respectively if the degree of protonation is higher than 0.3 [25]. Conversely, pK_a

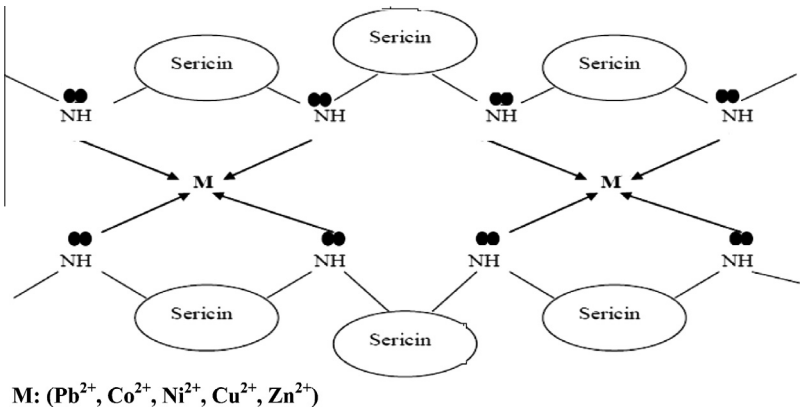

Fig. 1. Metal-sericin complexation during the process of chelation of metal ions with active amino groups of sericin.