

Potential Use of Modified Derivative of Chitin and Chitosan on Precious Metal Recovery: A Review

ABSTRACT

Recovery of metals serves as an attractive approach to gain precious and rarely available metals on earth which are important in industries. For years many methods have been practiced for this recovery such as adsorption, liquid-liquid extraction, or membrane processes. Adsorption provides a beneficial offer compared to others due to its cheap, easy maintenance, and high efficiency. Lately, the focus of adsorption has shifted to the use of biosorbent derived from a natural resource, including chitin and chitosan. Chitin and chitosan, which mainly produced from crab and shrimp shell, have been explored for any kind of precious metal recoveries such as platinum, palladium, gold, silver, and others. Various modifications to its structure also have been employed in order to gain more efficient performance. Here we are going to discuss chitin and chitosan along with its engineered and modified form recent advances on precious metal recovery as well as its potential of future research opportunities.

Keywords: Adsorbent, Chitin, Chitosan, Precious metals

1. INTRODUCTION

Natural polysaccharides have been explored in multi-application fields due to its versatile properties, environmental consideration, relatively low-cost manufacturing process, and excelled in sustainability. Compared to a synthetic one, natural polysaccharides offered easy regeneration via renewable resources, thus enabling massive production on an industrial scale. One of the most well-known natural polysaccharides in the world is chitin, derived mainly from crab and shrimp shell. Its production accounted for 100 billion tons annually making it the second most abundant polysaccharides in the world after cellulose [1]. Chitin and its derivative, chitosan, have been applied in numerous fields including aquaculture, environmental, food technology, material science, chemical engineering, soft matter and interfaces, electronics and optics, adsorbent, tissue engineering, biochemistry and biotechnology, energy, drug delivery as well as biomaterial [2-15]. Its application in other fields is still wide open for further exploration.

Chitin and chitosan also well explored as adsorbent materials for environmental remediation addressing pollution of mainly heavy metals [16]. It is proven to have a superior capacity for various types of heavy metals, make it utilization versatile and beneficial. Along with toxic heavy metals, it is also capable to recover precious metals found in nature or sourcing from a secondary source, such as gold, silver, titanium, palladium, etc [17,18]. This captures the interest of scientists and engineers to optimize the use of chitin and chitosan to

create green mining processes, especially for precious metals recovery. The fact that these biopolymers are relatively cheap and easily regenerate, gives them a special advantage that benefits both the environment and the industries in terms of the economical aspect.

The structure of chitin and chitosan which comprise an N-acetylglucosamine functional group allowed us to modify it using a relatively simple biochemical approach thus enhanced its activity [19]. Its ease of regeneration into nanofibrous form and nanoparticle form also adds more advantageous properties to chitin and chitosan [20]. Numerous researches on its structural modification has been reported and published for years, specifically on surface functionalization and composite fabrication [21]. In this review study, we will discuss more on recent developments of chitin as well as its derivative on precious metals recovery and its future prospect of research to be addressed in the fields.

2. CHITIN AND CHITOSAN

Chitin is a linear polymer composed mostly of units of 2-(acetylamino)-2-deoxy-D-glucose which form a covalent β -(1 \rightarrow 4)-linkages, resembling linkages in cellulose [22]. Chitin is widely distributed in the biosphere environment such as crustaceans (crabs, shrimps, and lobsters), jellyfish, external structural components of insects, fungal cell walls (22-40%), algae, nematodes or plants [23]. Chitin chains are related to one another by a very strong hydrogen bond between the NH group of one chain and the C = O group of another adjacent chain. This hydrogen bonding causes chitin to not dissolve in water and form fibers (fibrils) [24].

Chitin is an amorphous or crystalline solid, white in color, and biologically degradable. Due to its presence of inter and intramolecular hydrogen bonds, chitin is unable to be dissolved in water and others common organic solvents. However, it is possible to dissolve in concentrated acids such as phosphoric acid, nitric acid, sulfuric acid and anhydrous formic acid. The acetyl group in chitin can be degenerated in concentrated thus releasing its monomer [25]. When the degree of acetylation (defined as the average number of units of N-acetyl-D-glucosamine per 100 monomers written as a percentage) is somewhere around 50% or less, chitin can dissolve in acidic solutions, thus forming its derivative called chitosan [26].

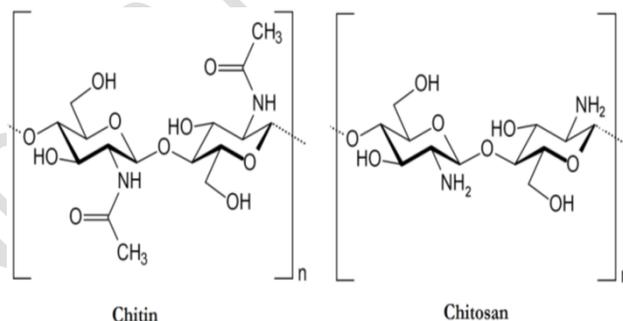


Fig. 1. Chitin and Chitosan Chemical Structure

Chitosan is a natural polymer compound derived from chitin which is isolated from fishery waste, such as skin. Chitosan is a product of chitin deacetylation through a chemical process using the sodium hydroxide base or an enzymatic process using the enzyme chitin deacetylase. This fiber is not digested and is not absorbed by the body. The prominent characteristic of chitosan is the ability to absorb fat up to 4-5 times its weight [28]. Commercial chitosan has an average molecular weight of between 3,800 and 500,000 g / mol and degrees of deacetylation of 2% to 40% [29]. The more acetyl groups lost from chitosan biopolymers, the stronger the interaction between ions and hydrogen bonds from

chitosan [30]. Chitosan is non-toxic and easily biodegrade in nature. Same with chitin, chitosan is insoluble in water as well as in strong base solutions, Chitosan dissolves well in weak acids such as formic acid and acetic acid but slightly soluble in hydrochloric acid and nitric acid [31].

Chitosan is the most useful chitin derivative. This is due to the high molecular weight, the nature of polyelectrolytes, the presence of functional groups, the ability to form a gel, and the ability to adsorb. Furthermore, chitosan can be modified chemically and enzymatically and is biodegradable and biocompatible with human cells and tissues. For its utilization, molecular weight and deacetylation rate are very important, because these two parameters affect solubility, physicochemical properties, and biocompatibility and immunity activities. The capacity to absorb chitin and chitosan increases with the increase in the content of free amino groups [32].

3. APPLICATION IN PRECIOUS METAL RECOVERY

3.1. Gold Recovery

Gold has been long known for its valuable properties that can be used in many applications. Besides being used in jewelry, it is also used widely in electronic and computers [33]. Its inert characteristic and biocompatible properties make its application prolonged to biomedical and health-related fields [34]. Furthermore, their ability to form a nanoparticle structure enhanced its utilization in green chemistry, environmental science, and catalysis [35-36]. Because of these extraordinary properties that gold possess, the efforts to recover it are rising tremendously for the past years.

Gold can be recovered from a primary source such as leaching solutions as well as a secondary source like electronic waste, computer scrap, and electroplating waste [37]. One of many ways to perform the recovery is through adsorption using strong biosorbent, including Chitin and Chitosan. It has been proposed that biosorbents are efficient approach on gold recovery from primary or secondary sources with minimum financial cost. Chitin and chitosan have been widely reported to have this strong ability to recover gold effectively.

Modifications of chitin and chitosan structure to gain more gold recovery capacity have been reported widely. A dithiocarbamate-chitin composite reported to able adsorb 12.6 mg/g gold in low pH and eluted easily in 1 M Nitric acid containing 5% of Thiourea [38]. Chitosan bead conjugated with chicken eggshell membrane also has been reported to effectively adsorbing gold up to 19 mg/g [39]. Unmodified chitosan also reported being able to adsorb gold at 30.95 mg/g capacity and the N-Carboxymethyl Chitosan slightly increase its capacity to 33.90 mg/g [40]. Dwivedi et. al [41] demonstrated a biomimetic adsorbent by conjugating gallic acid to the chitin nanofibrous network. The adsorbent possesses a superior capacity up to 503 mg/g surpassing many commercial adsorbents in the market like granulated and powdered activated carbon.

Chitin and chitosan can be viewed as microporous-structured biopolymers; along these lines, pores are sufficiently large to let gold ions through. The system of particle adsorption on permeable adsorbents may include three steps. First, dissemination of the particles to the outer surface of adsorbent; followed by dispersion of particles into the pores of adsorbent and lastly, adsorption of the particles on the inside surface of the adsorbent. The initial step of adsorption might be influenced by metal particle fixation and disturbance period. The last advance of the adsorption is considered as a rate-limiting step and as a generally fast process [42].

3.2 Silver Recovery

Silver is one of the most widely used precious metals especially in surface coating and also photo film. Beside its photosensitive properties, it also exhibits a good antibacterial property [43]. Silver is additionally delegated as a perilous substance [44], and in California,

its release is restricted to as low as 5 ppm [45]. Silver also is known to have serious health effects on humans and many aquatic organisms. Thusly, the recovery of silver as well as its removal from environmental systems is a priority concern to gain a safe environmental condition. Several methods have been employed for this including electrolysis, metallic substitution, and precipitation. Nevertheless, these aforementioned methods are not suitable for the recuperation of silver at less than 100 ppm [46]. Furthermore, metallic substitution and precipitation produce other problems that require further treatment. The particle trade strategy can recover silver at relatively low concentration, but it is quite expensive and high maintenance processes [47]. Chitin and chitosan derivative used as adsorbent has been explored for silver recovery and showing some good sign of performances.

Chitin has been reported to have a strong ability to chelate metal including silver. This is supported by the fact that chitin is generally more stable in an acid condition, compared to chitosan. Songkroah *et. al* [48] reported that the highest adsorption capacity for both chitin powder and flake was 4.37 and 3.61 mg/g, respectively. A thiourea-modified chitosan resin was also reported to be able to chelate silver ion for 3.77 mmol/g maximum capacity at acidic pH [49]. Various silver complexes with ammonia, thiocyanate, thiosulfate cyanide as well as free hydrated silver ion were also reported to be removed from solution using chitosan in a stirred-batch and column methods. The maximum capacity resulting in the column method peaked around 42 mg/g [50].

According to published research, mechanisms involved in silver adsorption to chitin or chitosan include in two steps. The first is an electrostatic association between protonated chitin and anionic silver as motioned by the solid pH and brief timeframe to balance. Second is coordination between electron group of nitrogen and additionally oxygen in acetyl moiety, acting as a Lewis base, and silver [51]. Wang *et. al* [49] also proposed that the main adsorption mechanism of silver adsorption onto modified chitosan might be chemisorption and comprise of the outer surface adsorption and the gradual adsorption stage. In a steady adsorption stage, intra-particle diffusion is a rate-limiting step, thus governing the adsorption mechanism.

3.3 Platinum Recovery

Platinum is one of the most commonly utilized metal among respectable metals, because of its uses in reactant forms. It is broadly utilized in numerous fields including reactant operators, electrical enterprises, medication, and gems [52,53]. However, Platinum are available at exceptionally low concentration in the world as well as in the ocean or stream waters [54]. Because of their less accessibility in nature and their developing interest in different ventures, the expense of these metals is quickly expanding. In the most recent decades, a few procedures have been utilized and completed to recoup and isolate platinum from manufactured or mechanical effluents, for example, sorption [55], fluid extraction, or layer forms [56]. Due to its economically important use of Platinum, a suitable and cost effective means to recover Platinum, particularly from wastewater generated by industries or in nature where very low concentration of it exist, ought to be required for minimizing the overall environment and economic budget. Adsorption gives off an impression of being a progressively green and successful procedure with high efficiency. Various adsorbents along these lines have been created and used to recoup PGMs from watery arrangements including chitin and chitosan.

Monocarboxymethylated chitosan (MCM-Chitosan), N,N-dicarboxymethylated (IDA-chitosan), diethylene-triamine-penta-acetic acid type of chitosan (DTPA-Chitosan) and crosslinked chitosan have been investigated for Platinum recovery. The maximum adsorption capacity of each adsorbent for platinum was topped by DTPA-chitosan, followed by MCM-chitosan and IDA-chitosan and finally cross-linked chitosan, although the capacity is relatively low which were around 2.1 mol/kg, 1.6 mol/kg, 1.6 mol/kg and 1.1 mol/kg, respectively [57]. Furthermore, a hybrid cationic Chitosan/E. coli fiber biosorbent was also

reported for platinum recovery thermodynamically up to 290.98 mg/g [58]. Thiourea Derivative of Chitosan was also reported to enhance chitosan sorption capacity. The sorption capacity for thiourea derivative of chitosan with glutaraldehyde crosslinkers was up to 386.9 mg/g in the sulfuric acid system and 346.2 mg/g in the hydrochloric acid system, indicating that pH controlling the mechanism [59]. Polyethyleneimine (PEI)-loaded core-shell chitosan hollow beads were reported to have an exceptional sorption capacity for platinum which was calculated to be 815.2 ± 72.6 mg/g [60].

Mechanisms of platinum sorption onto engineered chitosan sorbents have also reported and differed specifically to the modification. On account of glutaraldehyde-crosslinked sorbents, adsorption happens through particle trade responses, while on account of thiourea subordinates, sorption results from the blend of particle trade and complexation responses [59]. These adjustments in structure and component clarify the less delicate conduct of the new subordinate to pH and contender particle impacts. Chemisorption was also proposed as the mechanism that governs the adsorption of platinum [58]. Some also postulated that high sorption capacity was obtained because the sorption mechanism is mainly based on the electrostatic attraction between functional groups and metal species where Pt complexes were attracted by the positively charged chitosan.

3.4 Palladium Recovery

Palladium is one of the most expensive metals. Due to its extraordinary properties in reactant forms, it is generally utilized in industries. The low concentration of palladium in the earth-crust and the low accessibility of this metal, making its generation limited so that numerous procedures to recover it both from primary or secondary sources have to be performed [61]. Together with platinum (Pt), rhodium (Rh), ruthenium (Ru), osmium (Os), and iridium (Ir), palladium is categorized as Platinum Group Metals or PGM. Those rare and precious metals were currently the main concern in mining industries.

In the process of green and cost, an efficient search of adsorbent, chitin and chitosan derivative was also taken part in the exploration. Many reported the capacity of the biopolymer on palladium sorption. Glutaraldehyde-crosslinked chitosan was reported to be able to adsorb palladium up to 204.7 mg/g on the sulfuric acid system and 162.6 mg/g on the hydrochloric acid system [62]. An ion-imprinted chitosan fiber was also successfully synthesized and reported to have a maximum capacity of around 324.6–326.4 mg/g for palladium sorption [63]. Thiocarbamoyl chitosan also reported having a maximum capacity of 3.43 mmol/g for palladium [64]. Mincke et al [65] prepared three new derivatives of chitosan which were phenanthroline-dicarbaldehyde cross-linked chitosan (Ch-PDC), bipyridine-dicarbaldehyde cross-linked chitosan (Ch-BPDC) and glutaraldehyde cross-linked chitosan grafted with hydroxyquinoline-carbaldehyde (Ch-GA-HQC). For all derivatives, the adsorption was facile and saturation reached within a half-hour. The Langmuir isotherms indicated a maximum sorption capacity for palladium of 119.5 mg/g for Ch-PDC, 98.3 mg/g for Ch-BPDC, and 203.9 mg/g for Ch-GA-HQC.

Metal particle sorption, including palladium, on chitosan is postulated to happen through a few single or blended systems including (i) coordination on amino group in a pendant manner or mix with neighboring hydroxyl group, (ii) electrostatic interaction (in acidic media), (iii) particle exchange with protonated amine moiety through proton or anion exchange, the counter particle being traded with the metal anion [65]. Adsorption can happen through electrostatic interaction between contrarily charged metal species and decidedly charged amine moiety or through coordination of the amine and hydroxyl group with the metal species. By expanding the pH, a slight increment of the adsorption limit with regards to Pd can be credited to a marginally better coordination collaboration contrasted with electrostatic attractions. The administering speciation of the metal species additionally influences the adsorption. The sort of speciation is exceptionally controlled by the pH of the

arrangement and centralization of chloride particles present during adsorption. Speciation displaying is frequently utilized in writing to examine the kind of speciation of the metal species.

4. CHITIN AND CHITOSAN BASED ADSORBENT FOR PRECIOUS METALS

Metals, including toxic heavy metals, have been a major focus for both scientists and engineering [66-68]. Significant improvements have been made for the sorption capacity, embarking the potential use of chitin based adsorbent [69]. The utilization of benign and simple chemistry to modify the structure of the biopolymers was a primary focus on several works published recently. The Langmuir isotherm is an important evaluation characteristic to get the information of its maximum capacity, along with other modeling studies such as kinetic, thermodynamic, and intraparticle diffusion. As it stated before, numerous studies have been done from recent year regarding use of chitin and chitosan in this field. List of various modifications made to the chitin and chitosan in recent years are presented in table 1 followed by its maximum capacity.

Table 1. List of Chitin Chitosan Based Adsorbent for Precious Metal

Adsorbent	Precious Metal	Capacity
Chitin flake [48]	Silver	3.61 mg/g
Chicken eggshell membrane-conjugated chitosan beads [39]	Gold	19 mg/g
N-Carboxymethyl Chitosan [40]	Gold	33.90 mg/g
Chitosan (Unmodified) [40]	Gold	30.95 mg/g
Chitin Powder [48]	Silver	4.37 mg/g
dithiocarbamate-chitin [38]	Gold	12.6 mg/g
gallic acid-chitin nanofiber [41]	Gold	503 mg/g
	Gold	3.81 mmol/g
Thiocarbamoyl chitosan [64]	Platinum	3.43 mmol/g
	Palladium	1.24 mmol/g
	Gold	70.34 mg/g
l-lysine modified crosslinked chitosan resin [70]	Platinum	129.26 mg/g
	Palladium	109.47 mg/g
	Gold	198.5 mg/g
Chitosan hydrogel with 2,5-dimercapto-1,3,4-thiodiazole (CTS-DMTD) [71]	Platinum	16.2 mg/g
	Palladium	13.8 mg/g
	Gold	169.98 mg/g
glycine modified crosslinked chitosan resin [72]	Platinum	122.47 mg/g
	Palladium	120.39 mg/g
Chitin nanofibrous membrane [73]	Gold	243.2 mg/g
PEI-modified chitosan fiber [74]	Gold	251.7 mg/g
Aminophenylthiomethyl Chitosan Derivative [75]	Platinum	2.96 mmol/g
	Platinum	129.9 mg/g
thiourea-modified chitosan microspheres [76]	Palladium	112.4 mg/g
	Platinum	386.9 mg/g
Thiourea derivative of chitosan [76]	Gold	571.2 mg/g
	Platinum	304.1 mg/g
Glutaraldehyde cross-linked chitosan [59,62,77]	Palladium	180 mg/g
	Palladium	287.4 mg/g
Chitosan (Rubeanic acid derivative) [78]	Palladium	352 mg/g
	Platinum	530 mg/g
Chitosan Gel Beads [79]	Palladium	360 mg/g

Chitosan cross-linked with 1,10-phenanthroline-2,9-dicarbaldehyde [65]	Platinum	119.5 mg/g
	Palladium	262.6 mg/g
Chitosan cross-linked with 2,2-bipyridine-5,5-dicarbaldehyde [65]	Platinum	98.3 mg/g
	Palladium	154.7 mg/g
glutaraldehyde cross-linked chitosan grafted with 8-hydroxyquinoline-2-carbaldehyde [65]	Platinum	203.9 mg/g
	Palladium	340.3 mg/g
Chitosan Microspheres Anchored with 1,2-Ethylenedisulfide Moiety [80]	Palladium	2.41 mol/kg
Dialdehyde carboxymethyl cellulose cross-linked chitosan [81]	Palladium	89.38 mg/g
	Platinum	80.83 mg/g
poly(ethyleneimine) grafting (PEI) Chitosan [82]	Platinum	580 mg/g
	Palladium	400 mg/g

5. CONCLUSION

Chitin and chitosan along with its modified and engineered form have been studied for years in precious metal recovery. Significant advancements have been made but a possible new modification to further enhance its performance is still on-going. The challenges lie in how to maximize the capacity of metal sorption, reusability study, and leveling up on the industrial scale. Noting that many researchers are still focusing on batch or column studies, a scaling-up study in a bigger hierarchy is our research agenda. Furthermore, its sustainability for raw materials preparation will add more benefits to the use of chitin and chitosan for this purpose, making it a green and environmentally wise approach.

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