

Regeneration of Chitosan-Based Adsorbents Used in Heavy Metal Adsorption

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Abstract: Adsorption of heavy metal ions on chitosan-based adsorbents has been extensively investigated. However, few studies explored the feasibility of desorbing and regenerating chitosan. Adsorbents used after adsorption of heavy metals are discarded, and this practice exacerbates the solid treatment problem. Regeneration and reuse of exhausted adsorbents should be considered to operate environment-friendly and cost-effective adsorption. This review was performed to summarize the desorption of heavy metal ions and possible regeneration of chitosan-based adsorbents using various desorption agents such as acids, alkalis, salts, and chelating agents. It was found that the highest desorption efficiencies were obtained by acidic eluents. The percentage use of desorption agents for desorbing followed the order of acids (49.3%) > chelators (26.9%) > alkalis (14.9%) > salts (8.9%). Moreover, the proper desorption time was estimated to be 0.84 by 1.37 h. The beneficial information is provided for the regeneration and recovery of chitosan adsorbents.

Keywords: Chitosan, adsorption, heavy metal, environmental.

1. Introduction

Water is an essential and valuable resource for humans' living and development. Water resources are increasingly decreasing and need to be preserved. In recent years, industrialization, agricultural activities, rapid population growth and urbanization have contributed negatively to clean water resources [1]. Different pollutants such as pharmaceuticals, pesticides, dyes and heavy metals have contaminated the water resources. Presence of these contaminants in aqueous environments is environmentally hazardous for human beings and animals [2].

Among these pollutants, heavy metal is one of the most hazardous species, due to their toxic nature. Heavy metals such as cobalt, mercury, copper, zinc, chromium, cadmium, lead, nickel, arsenic, etc. can enter to the water bodies (directly or indirectly) through various industries (fertilizer, mining, painting, batteries, tanneries, metal plating industries, etc.) [3, 4]. Heavy metals are toxic, non-biodegradable and

exist in different oxidation states for long period in the environment. Therefore, it is essential to eliminate heavy metal ions from contaminated wastewater before discharging to environment [5].

Adsorption is often the most effective and economically viable method to remove pollutants from wastewater [6]. It is particularly suitable when the target pollutant is non-degradable, like in the case of heavy metals, so that destruction technologies are not efficacious [7, 8]. Adsorption can be also economically advantageous compared to other technologies if it is possible to find adsorbents that maximize the elimination of pollutants per unit adsorbent mass [9]. In this case, the adsorbing material shows a favorable adsorption behavior, that is, the amount of the pollutant on its surface at equilibrium is remarkably greater than the residual amount in the (waste-) water [10, 11]. However, if such condition is satisfied, it means that the counter-process, i.e., desorption, is unfavorable. An ineffective or slow desorption/regeneration of the adsorbents might be a serious issue for novel sorbents and their applicability on wastewater treatment.

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Currently, adsorption has a limit that hinders a wider use of such technology: the lack of adequate regeneration methods to recycle the adsorbent. In fact, without regeneration, pollutants may be released into environment by disposal or storage of spent adsorbents. Moreover, storage and dumping of spent adsorbents may lead to explosions, fires, and stinks [12]. Therefore, the spent adsorbent should be stabilized before disposal. The recycling process is performed by repeating the adsorption and desorption cycles and provides substantial economic and environmental benefits [13]. Indeed, researchers are more inclined toward regeneration and reuse of adsorbents because of the high cost of production, stabilization, and disposal.

Desorption still remains challenging despite the simplicity of adsorption of pollutants from the aqueous solutions because of the high affinity of the adsorbates to the surface of adsorbents. Desorption is primarily performed to remove the reversible adsorbate molecules on the adsorbent and to regenerate the adsorbents [14]. Regeneration is one of the significant characteristics of an appropriate adsorbent for practical applications. In addition, the cost of adsorbent preparation enhances the importance of regeneration. An adsorbent can be applied industrially if it can be used in several regeneration processes (adsorption-desorption cycle). Regeneration of adsorbent generally leads to the recovery of adsorbate molecules, reuse of adsorbent in the adsorption process, reduced secondary waste and cost of adsorption process, and also helps to better understand the adsorption process mechanism [15, 16].

Chitosan is the second most abundant naturally available polymer. This polymer has high affinity to adsorb different pollutants from aqueous solution. Chitosan is advantageous because of the following characteristics: low price and abundance, antibacterial property, nontoxicity, biocompatibility, biodegradability, macromolecular structure, hydrophilicity, cationicity, active sites, and high adsorption capability [17]. Chitosan-based adsorbents have been extensively and

successfully applied, but the adsorbed pollutants may be leached to the environment after adsorption. Chitosan-based adsorbents eventually become saturated, toxic, and hardly biodegradable after adsorption [18]. Therefore, spent chitosan adsorbents should be recovered completely prior to disposal and release back into the environment. In addition, its good affinity with many inorganic and organic pollutants suggests a slow regeneration process. Hence, regeneration of spent chitosan adsorbents is not only important for an effective and environment-friendly elimination of pollutants from the aqueous media, but also necessary for its economic utilization on a largescale [19, 20].

Numerous studies have focused on the elimination of heavy metals from aqueous solutions using chitosan-based adsorbents. However, few studies have reported on the recycling, regeneration, or disposal of spent chitosan adsorbents after adsorption. Hence, this issue should be investigated properly to explore for an appropriate solution to chitosan disposal. Thus, a review is needed to summarize the research findings in the desorption, regeneration, and recovery of spent chitosan-based adsorbents for heavy metal removal. The main objective of present study is to review the reports on the regeneration of chitosan and its derivatives to recover adsorbents after heavy metal adsorption. Appropriate information is collected and discussed in relation to the efficiencies of different desorption agents and spent adsorbents after regeneration. Furthermore, some of the results about adsorption performance of chitosan and its derivatives have been compared and discussed accordingly in this review paper. This review is mainly composed of following aspects: (a) adsorption of heavy metal on chitosan-based adsorbents, (b) a highlight on regeneration of saturated chitosan adsorbents, (c) a structured review on the use of various eluents for regeneration of chitosan and its derivatives for removal of heavy metal ions, and (d) a review on the mechanism of desorption of heavy metal ions from

saturated adsorbents and parameters affecting desorption.

2. Regeneration of Chitosan-Based Adsorbents

From environmental, economic and practical points of view, regenerability is an important parameter in evaluating the efficiency of an adsorbent. Regeneration is defined as the rapid recycling or recovery of spent adsorbents using technically and economically feasible methods. For the preparation of new adsorbents, cost is considered as one of the crucial factors. Therefore, the regeneration of spent adsorbents has immense importance for removal of contaminants from aqueous solutions. In the literature, different methods have been adopted for regeneration of saturated adsorbents which are classified into three major groups: biological, thermal and chemical. Some important advantages, disadvantages and affecting factors of these methods are summarized in Table 1.

Selecting an appropriate method for regeneration of adsorbents is dependent on type and nature of adsorbent and adsorbate as well as the cost and processing conditions. Therefore, the adopted method for regeneration of spent adsorbent should be eco-friendly, easy to operate, cost effective, efficient, and give the ability to reuse the spent adsorbent in water treatment. Low mechanical stability, low chemical stability and biodegradability of chitosan are some factors affecting regenerability of chitosan-based adsorbents. Besides all disadvantages of thermal and biological methods, some drawbacks of chitosan can hinder the use of these methods for regeneration of chitosan-based adsorbents. Chitosan shows a high sensitivity to high temperature. Thermal analysis of chitosan shows that this polymer is not able to withstand high temperatures [21]. In addition, presence of oxidizable or hydrolysable bonds in the backbone of chitosan and their accessibility for microorganisms lead to biodegradation of this polymer [22]. Thus, from practical and economical viewpoints, regeneration of saturated chitosan-based

adsorbents by chemical treatment method (washing with a suitable desorption agent or eluent) is preferred over other options due to its simplicity, convenience, effectiveness and low cost. In chemical regeneration method, different specific chemicals are applied as desorption agents for desorption of particular species from spent adsorbents [23, 24].

Desorption of adsorbed metal ions from chitosan-based adsorbents is one of the most important advantages of applying these adsorbents during adsorption. Nevertheless, chitosan may not be used in continuous recycling, if the regeneration experiment is performed under unsuitable conditions, because of its biodegradability and dissolution tendency under acidic environment. However, a proper strategy can be designed to achieve an effective desorption and regeneration.

Chitosan is a deacetylated form of chitin and composed of D-glucosamine and N-acetyl-D-glucosamine units, with two hydroxyl groups and one amino group in the repeating glucosidic residue. The abundant reactive functional groups on the chitosan structure lead to its high adsorption capability. Interaction of chitosan with metal ions could be the result of chelation interaction, electrostatic attraction, or ion exchange mechanism, in which pH plays a vital role [28]. Chitosan contains high amount of nitrogen in the form of amine groups, which are responsible for the chelation and binding with metal ions. The lone pair of electrons on the amino groups serves as the active adsorption site with high affinity for adsorption [18]. In addition, chitosan is a polymer with high cationicity (pKa 6.2-7) such that in acidic media, chitosan is protonated and exhibits electrostatic characteristics and adsorption capacity through anion exchange mechanisms [29, 30].

Chitosan-based adsorbents could be regenerated by desorption [31]. Adsorption of cationic and anionic heavy metal compounds is feasible in solutions at low and high pH levels, respectively. Thus, changing the

Table 1 General classification of regeneration methods of adsorbents.

Regeneration method	Advantages	Disadvantages	Affecting factors	Ref.
Biological	Complete recovery of adsorption capacity by biodegradation of adsorbed organic compounds on the adsorbents through conversion into small ionic toxicants	<ul style="list-style-type: none"> • Suitable for biodegradable contaminants • Toxicity of some contaminants to microorganisms • Fouling the pores on the adsorbents by microbial activity 	<ul style="list-style-type: none"> • Nature and type of microorganism and adsorbents • Adsorbent concentration • Microbial growth condition • Molecular structure of organic pollutants 	[25]
Thermal	<ul style="list-style-type: none"> • Most widely used • Suitable for industrial scale 	<ul style="list-style-type: none"> • Slow regeneration rate • Needs high temperature • Not cost effective • Not carried out <i>in situ</i> • Release of harmful gases • Weight and adsorption capacity losses • Incapable of completely regenerating 	<ul style="list-style-type: none"> • Heating time and temperature. • Type of adsorbate and adsorbent 	[26, 27]
Chemical	<ul style="list-style-type: none"> • Cost effective • Fast regeneration • Very short process time 	<ul style="list-style-type: none"> • Effect on the surface properties of adsorbents • Production of oxidized sludge/wastage • Needs further purification of the solvent • Incomplete recovery of adsorption capacity 	<ul style="list-style-type: none"> • Solvent concentration • Adsorbates solubility • Adsorbents properties • Solution pH 	[23]

pH in adsorption solutions leads to reverse reaction and desorption of the adsorbed ions from the saturated adsorbents. Therefore, after adsorption, regeneration of chitosan might be accomplished by eluting the spent adsorbents with a suitable eluent.

A suitable desorption agent for regenerating chitosan-based adsorbent might be able to effectively recover the adsorbent for reuse in adsorption process [32, 33]. In addition, this agent should not be expensive, harmful to the environment, nor destructive to the chitosan-based adsorbents, and can restore close to the original state of the physical and adsorption properties of chitosan [34, 35]. Therefore, choosing a suitable eluent with proper desorption properties facilitates a successful desorption and regeneration of spent adsorbents. Various desorption agents, including acids, alkalis, salts, and chelating agents, have been applied to regenerate chitosan adsorbents after adsorption of heavy metals. The capabilities of different desorption agents for desorbing heavy metals and regenerating chitosan-based adsorbents are described as follows. Table 2 is representing a summary of acid, chelator, alkali and salt desorbing

agents for recovering heavy metals from chitosan adsorbents.

2.1 Desorption Mechanism

Adsorption and desorption processes are determined by several physico-chemical factors. Since chitosan can bind metal ions by forming chemical bonds, the chemical parameters play major role in such process mechanism. The pH level of a solution effectively facilitates the adsorption process. The optimum pH for adsorption depends on the types of adsorbate and adsorbent. The free electron pair of nitrogen on amine groups is responsible for the adsorption of adsorbates on chitosan adsorbents. Decreased pH (acidic media) results in the protonation of amine groups and enhances the cationicity potential of chitosan, thereby, improving the adsorption process [18]. By contrast, the deprotonation of protonated amine groups in basic solutions may affect the adsorption behavior of chitosan adsorbents and reduce adsorption capacity [36, 37]. The adsorption and binding of adsorbate with adsorbent is favored at a specific pH. Thus, changing the pH value might reverse

Table 2 Summary of the acid, chelator, alkali and salt desorbing agents for recovering heavy metals from chitosan adsorbents.

Adsorbent	Adsorbate	Regeneration			Ref.
		Eluent	Adsorption (%)	Desorption (%)	
Chitosan/iron oxide nanocomposites	As(III)	0.1 N HCl	87	99	[38]
GLA crosslinked chitosan/polyaniline	Cd(II)	0.5M HCl	-	98.94	[39]
	Pb(II)		-	97.5	
Magnetic chitosan/butyl acrylate				97.5	
Magnetic chitosan/butyl methacrylate	Ni(II)	0.1M HCl	-	73.8	[40]
Magnetic chitosan/hexyl acrylate				100	
ECH/triphosphate crosslinked chitosan	Cu(II)	1.0M HNO ₃	-	88.7	[41]
		0.1M HNO ₃	-	87.9	
TPP crosslinked chitosan/montmorillonite beads	Cu(II)	0.005 M EDTA	-	86	[42]
Magnetic/2-aminopyridine glyoxal Schiff's	Cu(II)	0.01EDTA	-	97.2	[43]
Chitosan/perlite beads	Cu(II)	0.01M EDTA	-	96	[44]
Phosphated chitosan/ethyl hexadecyl dimethyl ammonium bromide	Cr(VI)	5% NH ₄ OH	-	70	[45]
Ferric hydroxide chitosan beads	As(III)	0.1M NaOH	88.9	100	[46]
		1.0M NaOH	79.8	100	
		0.1M NaOH	72.5	82.4	
		1.0M NaOH	43.9	100	
GLA crosslinked chitosan/aminoguanidyl	Ag(II)	2.0M KNO ₃	-	95	[47]
Chitosan/bentonite	Cu(II)	0.1M NaCl	-	36	[48]
	Ni(II)		-	47	

the reaction. Furthermore, the variation in pH level is crucial in the adsorption/desorption of adsorbed ions in chitosan-based adsorbents. Filipkowska [49] and Ha et al. [50] analyzed the desorption performance of chitosan adsorbents and found that adjusting the pH value enhanced the adsorption and desorption performances of adsorbents. The highest adsorption and desorption efficiencies were observed at pH levels of 5 and 11, respectively. Temperature increase may also intensify the positive charge of heavy metal (Me) compounds and consequently break down the binding of adsorbate and adsorbent [51, 52]. At high temperature, the breakdown of adsorbate and adsorbent binding also increases the release of adsorbed ions and improves desorption performance.

With regard to the mass transfer phenomena from the solid phase (i.e., adsorbate) to the liquid one that determine the regeneration kinetics, it is a complex process that involves several diffusion mechanisms. In general, metal desorption from a porous adsorbent may be limited by intra- and extra-particle diffusion.

The intra-particle diffusion includes metal transfer to liquid-filled macro-pores (with a diameter larger than 50 nm); solid diffusion in micro-pores (> 2 nm), where interactions between pore walls and the adsorbate are stronger than those of large-pores; and the reaction kinetics of the chemisorption processes. The extra-particle diffusion is limited by the external mass transfer between the surface of particles and the liquid phase; and the fluid phase mixing, or the lack of it. Some studies identified the intraparticle diffusion in small pores as the main rate-limiting step of the adsorption-desorption process [53, 54]. Nonetheless, the weight of the extra-particle diffusion may become relevant under non-optimal conditions, like employment of unfavorable desorption agent [55].

Concerning regeneration effectiveness, the majority of chitosan-based adsorbents used in adsorption presented an acceptable desorption performance when an efficient and effective desorption agent is applied. Desorption by acidic eluents is more effective than that of other eluents. In acidic environments, the high

number of H^+ ions in the solution desorbs adsorbed ions. Compared with heavy metal ions, H^+ ions have stronger affinity to adsorb on chitosan functional groups and higher diffusivity coefficient because of their smaller radii [56, 57]. Consequently, the cationic exchange between H^+ and adsorbates, the protonation



Among the alkali solutions, NaOH and NH_4OH solutions are the most effective and frequently used to desorb heavy metal ions from adsorbents. Desorption mechanism by basic treatments involves deprotonation and negatively charged adsorption sites in adsorbents. These characteristics weaken the existing electrostatic



The desorption mechanism using salt eluents and chelating agents may be the deprotonation of functional groups of adsorbents, which releases heavy metal ions. Moreover, the strong electronic supply capability of these desorption agents easily desorbs



During electrolysis desorption, ions move toward the electrode of the opposite charge. The electrolysis of chitosan adsorbents saturated with



3. Conclusion

Regeneration is an important factor determining the reusability and effectiveness of adsorbents. This factor also contributes to the economic feasibility and efficiency of the adsorption technology. Elution by an eluent is the most common approach in the literature to regenerate chitosan-based adsorbents. The percentage application of eluents followed the order of salts < alkalis < chelators < acids. The HCl, EDTA,

of adsorption sites, and the replacement of H^+ ions with heavy metal ions in adsorbent-adsorbate complexes release adsorbed ions into the desorption solution and reduce the heavy metal ions that bind on adsorbents [58, 59]. This reaction is shown in the following equation (Eq. (1)):

interactions between chitosan adsorbent functional groups and heavy metal ions and the subsequent separation of adsorbed ions from adsorption sites [60, 61]. The reaction responsible for the desorption process by NaOH, which is the most frequently applied basic eluent, is given as follows (Eq. (2)):

adsorbed metal ions and forms a steady complex with desorption agents [62,63]. The desorption mechanism in NaCl and EDTA solutions could be explained through the following equations (Eqs. (3) and (4)):

adsorbates converts amide groups of chitosan into amine groups and deposits adsorbates onto the electrode with the opposite charge (Eq. (5)) [64, 65].

NaOH, and then NaCl solutions are the most commonly used desorption agents. Increase in regeneration cycle decreases adsorption and desorption efficiencies. The increase of eluent concentrations enhances desorption efficiency. However, high concentration of eluents may affect adsorbent structure and decrease desorption efficiency. At high temperature, the breakdown of adsorbate and adsorbent molecules binding also increases the release of adsorbed ions and improves the desorption performance.

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