NTU Journal of Pure Sciences (2025) 4 (2) : **51-68**
DOI: https://doi.org/10.56286/ntujps.v1i3

IRAQI Academic Scientific Journals

ISSN: 2789-1089 EISSN: 2789-1097
NTU Journal of Pure Sciences
Available online at: https://journals.ntu.edu.iq/index.php/NTU-JPS/index

A Comparative Study on the Removal of Heavy Metal Ions from Wastewater with Adsorption Technique by Red Mud-Chitosan Composite: A Review

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Article Informations

Received: 1-6- 2024,
Accepted: 28-11-2024,
Published online: 30-6-2025

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Key Words:
Adsorption, Red mud, Chitosan, Heavy metals, Pollution.

A B S T R A C T

The problem of water pollution persists to this day. To reduce water pollution, which includes water produced from industrial units and wastewater, it had to be treated using several methods. This review focused on the use of adsorption technology, considered the most common method due to its ease of design and efficiency in removing pollutants. Recently, studies have shown that modifying red mud with chitosan can produce a new composite, RM/CS, as its efficiency in removing pollutants is good. This review summarizes previous studies conducted on the adsorption of heavy metal ions from aqueous solutions using the RM/CS component, comparing the maximum adsorption capacity qmax and removal with red mud activated by acidic or heat treatment, or both, and comparing it with the removal efficiency mediated by chitosan alone, studying the effect of the PH ,adsorption time apprised, and applying the Langmuir and Freundlich of the reaction isotherm to evaluate the efficiency of red mud modified with chitosan.

Introduction

Water is essential to all living things and serves as their foundation. For millions of people worldwide, however, it is becoming a more scarce and degraded natural resource. One of the main issues in recent years has been finding enough water, which is required for a population that is expanding quickly for a variety of purposes. [1]. types of pollutants that are there. The characteristics of the industrial area primarily influence wastewater. Nonetheless, a few of the frequent contaminants are often It may be found as liquid waste in the form of metal ions, such as lead (pb), chromium (Cr), copper (Cu), cadmium (Cd), and nickel (Ni), as well as a variety of compounds, dyes, phenols, insecticides, and detergents. Aromatics [2,3]. There are many techniques to remove pollutants from water, such as coagulation, filtration, electrocoagulation, precipitation, floatation, electrodialysis, membrane, adsorption, ion exchange, reverse osmosis, and advanced oxidation processes. Among the technologies available for water treatment, the adsorption process is considered one of the most efficient methods for treating and removing organic pollutants in wastewater treatment. The reason for this is the simplicity of design and operation, insensitivity to toxic pollutants, high removal efficiency, availability of various adsorbent types, etc. [4,5,6].

The most crucial component of adsorption technology is the adsorbent, as it directly influences both the cost and adsorption capability of pollutants to be treated. There are different types of adsorbents that may be organic, inorganic, hybrid, or biological materials. It gives acceptable results for wastewater disinfection. There are some important examples of high-performance adsorbents, including activated carbon, [7,8] zeolites (active and natural), [9], red mud [10] Modifier: red mud [11], chitosan [12], natural clay minerals, [13] modifiers Clay (bentonite) minerals, [14] Clay-polymer compounds, [15] Silica nanoparticles, [16] Ceramics, [17] Agricultural Waste, [18] Biochar, [19] Biomass, [20], clay-polymer composites [21]. The development of adsorbents with high efficiency and low cost has received great research interest in the field of pollution [22]. Many adsorbents have been proposed in the literature to remove various pollutants from wastewater. In recent years, the search for low-cost adsorbents with the ability to adsorb contaminants has been demonstrated. The main goal of adsorption in recent times has been the use of low-cost materials. Red mud (RM), which has been shown to be used in its original form or after modification processes to remove heavy metals, radionuclides, organic materials, and inorganic materials from aqueous solutions [23,24]. For the last 20 years, chitosan has attracted a lot of attention. Adsorbents are advantageous. Their remarkable intrinsic benefits, which include their cheap cost, simple processing, biodegradability, natural abundance, and environmental friendliness, are responsible for the latter. Numerous investigations have been carried out to confirm the propensity of biopolymer-based adsorbents to adsorb various contaminants, such as heavy metals and medications [25].

This review presents each of these adsorbents individually and their application in the removal of the above-mentioned heavy metals, as well as studies that used red mud-modified chitosan to remove heavy metals from waste water.

1. Heavy metal pollution

Minerals are heavy metals with a density of 5g/cm ^{3}. They are commonplace in nature and harm both the environment and living things [26]. Local activities govern and influence the amount and composition of heavy metals [27, 28], whereas metal characteristics and other environmental parameters are used to monitor those suspended in the air [29]. Many surfaces and groundwater in most countries in the world are affected to some extent by heavy metal pollution, but the severity of pollution varies greatly from one region to another and is controlled mainly through local activities. Heavy metals have a significant impact in many areas of Europe [30]. In Asia, including the countries of India, Pakistan, and Bangladesh, there is severe surface water pollution due to untreated liquid waste flowing directly into surface drains by small industrial units and from the use of raw sewage in vegetable production near major cities, all of which flows into surface water through surface runoff and groundwater through filtration processes [31]. Local activities govern and influence the amount and composition of heavy metals [27, 28], whereas metal characteristics and other environmental parameters are used to monitor those suspended in the air [29]. Heavy metal pollution has been reported in many are of africa in cluding (mostly lead, cadmium, mercury, copper, cobalt, zinc, chromium, nickel, manganese, iron, mercury, and oreand) are North, East, South, and West Africa. The water exceeds recommended limits, contaminating surface water in the area [32]. Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms, and many heavy metal ions are known to be toxic or carcinogenic [33]. In addition, some elements, such as Zn, Cu, Fe, etc., benefit humans and animals, but within acceptable concentrations. They then become toxic if the concentrations of the mentioned elements rise above the required limit. Table 1 below shows common heavy metals, their harmful effects on humans, and permissible limits.

Table 1. The most important metal and their effect on human health and their permissible limits.

Toxic elements	Effect of toxic elements on human health	Permissible limits (ppm)	Ref.
Cd	Cadmium causes kidney and liver damage, anemia, carcinogenic in inhalation, retard growth and also causes renal arterial hypertension.	0.003	[34]
Cr	Chromium is a carcinogenic substance Lung cancer by inhalation.	0.05	[35]
Ni	Nickel compounds cause skin inflammation and are carcinogenic to humans.	0.07	[36]
Cu	High copper concentration can cause taste problems Liver damage and other problems in the body.	2	[37]
As	Arsenic toxicity causes various diseases.	0.01	[38]
Pb	Anemia, nephropathy, heart disease, nervous system disease	0.01	[39]

3.Industrial Generation of Red Mud

Three industrial procedures are primarily used to extract alumina from bauxite: the Bayer process, the sintering process, and the Bayer-combined sintering process . Because it uses less energy and has an easy-to-understand production process, the Bayer process generates almost 95% of the alumina used worldwide ,varied production methods result in varied compositions of red mud. [40] In comparison to red mud from the other two procedures, Bayer red mud, for instance, has a lower CaO content and a higher Fe_2O_3 and Al_2O_3 content. In contrast, the RM created by the Bayer-combined sintering method contains significantly more SiO_2 than the RM created by the Bayer technique. Nevertheless, the SiO_2 content generated by the Bayer-combined sintering procedure was less than that generated by the Bayer technique [41].

RM has been used as an absorbent to remove various types of pollutants from water and wastewater. Red mud is the result of solid waste residues formed after the caustic digestion of bauxite ores during alumina production. Every year, we produce about 90 million tons of red mud globally [42]. RM is composed of fine particles containing aluminum and iron. Silicon, titanium oxides, and hydroxides.The red color of red mud is due to presence of oxidation iron .Due to the strong alkalinity of RM, the pH value of the red mud leaching solution is usually between 11-13, so it cannot occupy a large space for storage [43,44]. However, RM is an inexpensive material to prepare adsorbents with high surface area, fine particle size, and strong adsorption [45]. These industrial wastes are highly alkaline, so it cannot be added directly to water. Therefore, before using red mud for removal, it must be neutralized. It depends on the chemical and physical properties of red mud, mainly on bauxite minerals and quality, and, to a lesser extent, on the operating conditions of the Bayer process. In addition, the name of the mud varies but rather depends on the proportions of oxides included in its composition. [46] However, there are some common characteristics of red mud from different manufacturing processes, such as small particle size, complex phase composition, and high alkalinity. [47]

The main components of RM are Fe_2O_3, Al_2O_3, SiO_2, CaO, Na_2O, and TiO_2, which account for approximately 85% of RM [48]. The composition of red mud can vary greatly depending on its location. As in the Table 2 below:

Table 2. Chemical composition of red mud in different regions (wt %).

Area	Al_2O_3 %	Na_2O %	CaO %	TiO_2 %	Fe_2O_3 %	SiO_2 %	Ref.
Korea/ Yeongam	28.4	20.1	27.6	6.0	3.3	13.0	[49]
Iraq/ Sulaymaniyah	17.0	56.0	5.3	___	5.0	3.0	[50]
India /Odisha	13.0	7.0	54.0	3.5	___	8.0	[51]
China/ Corporation	6.93	19.14	12.76	3.43	2.37	46.02	[52]
Turkey /Konya	23.29	12.08	35.73	4.08	2.81	7.40	[53]
Italy/ Eurallumina alumina plant	17.19	9.58	30.45	8.61	7.77	12.06	[54]
Iran /Jajarm	17.25	19.29	28.41	7.36	21.35	1.79	[55]
Brazil/Balcarena	15.10	15.60	45.60	4.29	1.16	7.50	[56]
Australia/ Queensland Alumina Ltd	25.45	17.06	34.05	4.90	3.69	2.74	[57]
Greece /Agios Nikolaos	23.6	10.2	44.6	5.7	11.2	2.5	[58]
France/European alumina manufacturer.	13.9	4.19	52.7	7.4	4.1	2.1	[59]
Russia/ Kamensk-Uralsky	11.8	8.71	36.9	3.54	23.8	0.27	[60]

3.1 Modification of red mud

Red mud remediation has drawn attention as a feasible reuse technique for heavy metal removal . As was already noted, red clay is rich in metal oxides and can be employed in engineering and environmental systems as an adsorbent for heavy metals. In addition to mitigating the risks provided by heavy metal pollution in soil and water, reusing red mud for heavy metal removal reduces the problems connected with red clay disposal.Due to its porous structure, high alkalinity, and high iron oxide concentration, red mud is a useful adsorbent with a high adsorption capacity. The alkalinity of red mud is high. This elevated alkalinity has an impact on the reaction environment's pH. Because of their high alkalinity, RM materials have a surface covered in negative charges, which facilitates RM's ability to adsorb charges from cationic pollutants. [61] Nevertheless, the adsorption capacity of using raw RM directly as an adsorbent is limited. Thus, the major purpose of treatment techniques such heat treatment, alkali activation, and acid activation is to increase its adsorption capability [62].

The physical and chemical properties of red mud can be improved by processing it. In several ways, including acid treatment, neutralization, heat treatment, organic modification, composite material synthesis, etc., it is reported that these modifications improved the adsorption efficiency for heavy metal ions. [63] Table 3 Acidification treat ment increase the surface ara and porosity of red mud ,which imporoves its ability to remove water containations. This increases the surface area and generates new cavities. However, there is a disadvantage related to acid treatment, which has been found to dissolve a type of compound responsible for the adsorption sites within the red clay composition. Concentrated hydrochloric acids, diluted hydrogen chloride, and nitric acids are among the acids utilized in this process. [64,65,66,67,68]. For example, the heat treatment of red mud is able to decompose unstable compounds and organic materials, which improves their physical and chemical properties and leads to increased absorption capacity. In addition, red mud may also be made less alkaline by using a saltwater neutralization procedure without sacrificing its capacity to neutralize acids. Also, red mud thermally activated with seawater removes at least twice the concentration of anionic species compared to thermally activated red mud alone. [69][70].

Table 3. Type of modification of Red Mud.

Type of treatment	Method	Red Mud	Ref.
Acid treatment	Heat treatment (200, 400, 600, 800ºC); acid treatment (0.25-2 M)	Konya, Turkey	[71]
	Soaked in a 1 M HNO_3 solution with red mud and nitric acid (w/v) at a 1:2 ratio; activated for 4 hours at 150ºC	LamDong province, Vietnam	[72]
	Acid treated with 31% HCl at a red mud/HCl	Bauxite mill, Iran	[73]
	Red mud, was boiled in 200 mL of 2.25M HCl concentration for 20 minutes, dried at 40 °C	Vedanta Aluminum Industries, Langigarh, Odisha, India	[74]
Heat treatment	Heat treatment at 800ºC and acid treatment with 1 M HNO_3	Minim-Martap bauxite	[75]
	Heat treatment at 700°C / 2h , 1 M HCl for 24 hours at a liquid/solid ratio of 20	Worsley Alumina, Australia	[76]

mL/g, followed by two hours of air heating at 700°C to treat the resultant sample	Hindustan Aluminium Company (HINDALCO), Renukoot, India	
The samples were heated in a furnace for 3 hours at 400°C, 500°C,600°C and 800°C	the National Aluminium Company Ltd., Damanjodi, .Orissa, India	[77]
The alkaline red mud was suspended in distilled water with a weight-based liquid-to-solid ratio of 2/1, and it was stirred until the pH reached an equilibrium of 8.0–8.5 before the red mud dried.	Alumínio City, São Paulo State (Brazil).	[78]
Neutralization by CO_2 gas sequestration and 500ºC calcination of the neutralized sample	Seydis¸ehir Aluminium Plant Konya, Turkey	[79]
Blender RM, maize straw, and bentonite at mass ratio of 2:1:0.5, dried at 105°C for 24 h, furnace at 900°C with the heating rate of 10°C for 60 min.	R & D Laboratory of NALCO, Damanjodi, Orissa, India	[80]
The polymeric Al/Fe modifiers were prepared, involved the mixing of the given amount of clays with the polymeric metal species for 4 h at 55 ◦C	Shandong Aluminum Industry Co. Ltd. (Zibo, China).	[81]
Cleaned for 24 hours using 2.0% H_2O_2. To activate, add 50.0 g of red mud to 500 mL of 0.5 M $Fe(NO_3)_3 \cdot 9H_2O$ in a 1.0 L container and shake magnetically for 10 hours at 70 °C.	Sigma-Aldrich Chemicals Corporation UK.	[82]
Red mud (15 g), fly ash (2 g), sodium carbonate (1 g), sodium silicate (1.2 g), and powdered quicklime (0.8 g) were combined and roasted for 2 hours at 400 ºC, then calcined for 0.5 hours at 900 ºC.	Bharat Aluminum Company Limited 66 (BALCO), Korba-India	[83]
In a beaker, 200 mL of double-distilled water was combined with 7.8241g of $ZrOCl_2$ and 10 g of RM to create a combination that had a Zr-to-RM mass ratio of 0.4	Shandong Aluminum Company. Ltd., China	[84]
Three distinct ratios of RM to fly ash (4:1, 1:1, and 1:4) were combined to create three modified composite materials (C4R1, C1R1, and C1R4) with silicon-alumina ratios of 0.95, 0.78, and 0.62.	Local Aluminum Corporation, China	[85]
Combining starch, bentonite, and dewatered red mud in mass ratios 95:5:5.	A company in Guangxi City.	[86]
1.0 mL of 5% (m/v) sodium dodecyl sulfate (SDS) surfactant was added, and the mixture was agitated for one hour after adding 0.1 g RM to 50 mL of distilled water for two hours.	Shandong Aluminum Company. Ltd., China.	[87]

Rm-Chitosan composite	After adding 2 g of red mud to the 1% chitosan solution and vigorously stirring it for two hours, the mixture of chitosan - red mud was dripped into a 7% ammonia solution (v/v) using a syringe.	Vedanta Aluminum Industries,Langigarh, Odisha, India.	[88]
	In 100 ml of chitosan solution with 2.0 g of chitosan dissolved in 2% acetic acid solution, 10.0 g of red mud was added. The mixture then underwent a 24-hour DI water wash, a 24-hour drying period at 100 °C, and a 24-hour agitation period at 1000 rpm to complete the alteration.	National Aluminium Company Pvt. Ltd., Orissa, India	[89]
	Made by dissolving 38 g of NaOH in 32 mL of DW with the addition of 8 g of red mud. 8 g of colloidal silica and 2 g of NaOH were combined at 100°C, and 0.24 g of aluminum powder was added.	The waste of the Saigon underground water plant, Ho Chi Minh City, Vietnam. C	[90]

1.1 Acid -Heat treatment of red mud to remove some heavy metal from aqueous solution

Recent research has shown that red mud's enormous surface area (between 11.65 and 30.72 m2/g), strong basicity (pH between 9.2 and 12.8), and inexpensive cost make it an efficient treatment for heavy metals in wastewater [91,92].Heavy metals such as As (III), As (V), 4 Cd (II), Cr (V), Cu (II), Ni (II), Pb (II), and Zn (II) in wastewater were adsorbed by red mud. Given that it may be used to clean wastewater; red mud is regarded as an ecologically friendly substance.Acid tratment ,heat tratment,or combining red mud with other materals can improve its ability to remove heavy metals from water [93]. Various treatment approaches have been documented in the literature; this review discusses a few of them. The following table shows studies that dealt with treating red mud with acid, heat, or both, listing the optimal conditions of the adsorption process for the purpose of removing heavy metal ions from aqueous solutions.

Table 4. Treatment of red mud to remove some heavy metal

Type red mud	Methods	Pollutant	Optimal condition	%Removal adsorption	Ref.
China	0.5 M HCl solution for 2 h at 80˚C	Cr^{+6}	PH= 2 Temp=30 C˚ t = 120 min dose = 0.5mg adsorbate (0.08 mg.L^{-1})	97.31%	**[91]**
Konya, Turkey	red mud was washed with distilled water, acid pretreatment and boiling .	Cu^{+2}	PH = 5.5 Temp = 30± 1 °C t = 60 min dose = 0.5mg adsorbate (1g/ml)	--------	**[92]**
China	red mud heat-treated at 200, 400, 800, 900 °C	Cd(II)	PH=6 Temp = 20-25 C˚ t = 24h dose = 0.5mg Adsorbate (200mg/L)	-------	**[93]**
Vietnam	acid (H_2SO_4)(1.18M) concentration, activating temperature and activating time were 300 – 900°C,	As(V)	Temp = 80 C˚ t = 3h adsorbate (2 mg/L)	------	**[94]**

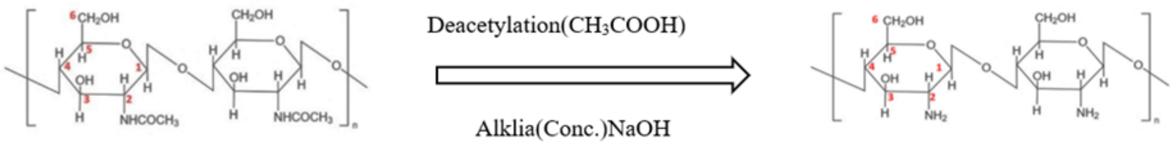
Australia	neutralizing treatment with seawater	As(V) Mn^{+2}	PH= 5.2 PH= 8.1 t = 5 min dose 10mg/L adsorbate (10PPb,2 ppm)	99.66% 95.25%	**[95]**
Konya, Turkey	Heat treatment (200, 400, 600, 800ºC); acid treatment (0.25-2 M);	As(III) As(V)	PH =7.2 PH = 3.5 Temp = 25 C° T = 60 min Dose = 20 g/L Adsorbate (10mg/L)	87.54% 96.52%	**[96]**
Paulo State, Brazil	Heat treatment 400ºC ,Acid treatment (0.05 mol L^{-1} HCl)	Cu(II)	PH= 5-5.5 dose = 1g adsorbate = 0.5–1.0 mmol	79.4%	**[97]**
north of China	Heat treatment at 500 °C	Cd	PH=6 Temp = 20C° t = 24h dose = 0.5mg Adsorbate (200mg/L)	----	**[98]**
Lanjigarh, India.	Acid treatment with 31wt %(0.2-mol L−1) of HCl,	Cd(II)	PH=6 Temp = 20C° t = 0.7h dose = 0.5mg Adsorbate (100mg/L	91.29	**[99]**
Shandong, China	Acid treatment with 0.1 mol L^{-1} HCl	Cd(II)	PH=6.5 Temp = 25C° t = 48h dose = 25g/L Adsorbate (1124mg/L	80%	**[100]**

Generation of Chitosan

Chitosan (2-acetamido-2-deoxy-β-D-glucose) is a partially deacetylated polymer of chitin. It is usually made from chitin by using a strong alkaline solution to deacetylate it. As in the following equation. After cellulose, chitin is the second-most common biopolymer found in nature. It is mostly taken out of the shells of marine crustaceans and insects. Chitin modified into chitosan has high potential as an adsorbent. [103,104] In addition to being biodegradable and inexpensive, chitosan has great absorption properties due to its high-performance amine and hydroxyl groups in its backbone, which act as active sites for the adsorption of metal ions [105,106]. However, chitosan cannot be used directly as an adsorbent due to its high crystallinity, low mechanical strength, and instability in acidic media. Therefore, chitosan needs to be modified to transform it into a suitable compound for adsorption [107].

Chitosan from different sources is used for many things, such as removing metal ions, removing organic matter, transferring genes, implanting bones, giving medications, immobilizing enzymes, and working with lipids. limiting and encouraging the development of plants, healing wounds, preserving food, and producing and storing energy., etc. is due to the two effective functional groups on its chains, which are the (-NH2) group and the hydroxyl groups (-OH). These groups are changed for manufacturing chitosan derivatives with improved biodegradability, biocompatibility, non-toxicity, and antimicrobial activity[108,109,110].

The greatest sorption capability for several metal ions is found in chitosan [111]. Due to its modest solubility at low pH, chitosan presents challenges for creating commercial applications. It also has a propensity to gel in an aqueous solution and has a soft shape. Furthermore, it takes time for chitosan to be absorbed. Transfer of metals In process design, contaminants at binding sites are crucial. Chitosan chelates five to six times the amount of minerals in chitin. This is attributed to the presence of free amino groups in chitosan due to deacetylation of chitin [112]. Many studies have been conducted on chitosan for the purpose of improving adsorption properties, which have been successful in many cases [113].



Chitin Chitosan

4.1. Remove heavy metal by Chitosan

Metal ions may attach chemically or physically to a variety of functional groups found in biopolymers, such as hydroxyl and amines, which are the case with chitosan. Adsorption in Physical Form Chitosan has been shown in earlier research to be effective in the removal of certain rare metals from wastewater, such as Cu(II), Pb(II), U(VI), Cr(III), Cr(VI), Ni(II), Cd(II), Zn(II), Co(II), Fe(II), Mn(II), Pt(IV), Ir(III), Pd(II), V(V), and V(IV). Chitosan was employed in this review in a number of forms, including flakes, powder, and beads. [114, 115, 116, 117, and 118]. This indicates that in A Neutral pH: More mineral ions are absorbed by chitosan. According to [119], Chitosan chelates with metal ions wher by it donates in pair electrons from its functional groups to form coodirate covalentt bond with metal ions . Therefore, the absorption of heavy metal ions by chitosan is strongly dependent on the pH from the solution. pH affects properties Adsorbents are absorbed and thus change the capacity removal of heavy metals ions from aqueous solutions, Various modifications have been made to chitosan with the aim of improving adsorption properties has been successful in many cases. In this review, the adsorption capacity of chitosan alone was discussed and compared with chitosan mixed with red clay, highlighting the optimal conditions for conducting the adsorption process [120].

Below is a Table 5: showing the use of different forms of chitosan to remove heavy metals mentioning the optimal conditions for the adsorption process. It was mentioned that the maximum removal of (Cd, Cr, Pb and Cu ions) from its solutions by chitosan at pH (2-6), and optimum temperature was at 25±5 C◦.

Table 5. Use chitosan to remove some heavy metal from aqueous solution.

Type Chitosan	Pollutant	Optimal condition	%Removal adsorption	Ref.
Chitosan flakes (85% deacetylated) was purchased from Sigma Chemicals	Cr (VI)	Dose = 0.1 g pH = 3.0, Temp =30 C◦ Time = 16 h, Adsorbate (50mg/L)	--------	[119]
chitosan" was synthesized using locally available fish shells	Cu (II)	PH = 5.7 Time= 2h Temp =30 C◦ Dose =50mg Adsorbate (3,5,8 ppm)	-----	[120]
chitosan was obtained from Sigma–Aldrich	Cu(II) Cr(VI)	PH = 6 PH = 4 Time= 24h Temp =25 C◦ Dose =0.05 Adsorbate (100mg/L)	-----	[121]

Pure chitosan	Pb(II) Cd(II)	PH = 7 PH = 6.8 Time= 120 Time= 180 Temp =25 C° Dose =0.5 Adsorbate (40mg/L , 80mg/L)	77%	[122]
porous chitosan beads	Cd(II)	PH = 2.1 Time= 51h Temp =25 C° Dose =0.5 Adsorbate (200 mg/L)	-------	[123]
Chitosan crosslinked	Pb^{2+} Hg^{2+}	PH = 4 PH = 6 Time= 24h Temp =25 C° Dose = 25mg Adsorbate (10ppm)	94%	[124]
Chitosan was procured from Sigma-Aldrich Corporation, Bangalore, India.	Pd(II)	PH = 8 Time= 300min Temp =25 C° Dose = 0.6 Adsorbate (50mg/L)	---------	[125]
Chitosan was purchased from Fluka	Cu(II)	PH = 6 Time= 60 Dose = 0.01 Adsorbate (100ppm)	65.44 %	[126]
Chitosan (Aldrich Chemical) Company, South Africa)	Cu (II) Cr (VI)	PH = 5 Time = 2.8 h Temp =25 ±1 C° Dose = 1g Adsorbate (200ppm)	-------	[127]
Chitosan from crustacean shells (Aber Tech, Plouvien, France) As a Flakes	Cr(VI)	PH = 4 Time= 96h Temp =25 C° Dose = 30mg Adsorbate (20mg/L)	-----	[128]

Raw Chitosan was purchased from Sigma (USA), Natural chitosan	Cr(VI)	PH = 6 Time= 24h Temp =25 C° Dose = 0.3g Adsorbate (250mg/L)	---------	[129]
Chitosan prepared from fresh water crab shells	Cr(VI)	PH = 3 Time=12h Temp =25 C° 500 mg/L Adsorbate (5mg/L)	-------	[130]
chitosan flakes, a substance of practical quality that is derived from crab shells and has a minimum of 85% deacetylation.	As(V)	PH = 3.5 Time= 30min Temp =24 ± 2 C° Dose = 0.0250 g Adsorbate (3000mg/L)	90%	[131]

4.2. Remove heavy metal by modified red mud / chitosan

After presenting the literature in which red mud was used as an absorbent material to remove pollutants such as heavy metal ions, However, its adsorption capacity is not high. This is because the properties of red mud and the proportions of its components depend greatly on its origin and location [134]. Various methods have been performed to modify red mud, such as the acid treatment and heat treatment mentioned above. Previously, modification was done by synthetic polymers [135]. However, there have been a number of studies on modifying red mud with natural polymers that are environmentally friendly, benign, and low-cost. Recently, RM/CS, a new material, was successfully synthesized by modifying red mud with chitosan. This material was used as a novel adsorbent to efficiently remove heavy metal ions from aqueous solutions [91]. On the other hand, chitosan is one of the adsorbent materials that is of great importance to people. In the past few years, however, the adsorption capacity and selectivity of chitosan can be improved by modifying it with several materials through different processes and methods [136]. One of these methods is to modify it with red mud. Despite the limited study of RM/CS, as mentioned previously, Table 6 presents the optimum conditions for previous studies to conduct the adsorption process to remove heavy metal ions by chitosan modification (red mud, bentonite, and kaolin). The surface morphologies of CS, RM, and RM/CS were studied using an assay scanning electron microscope (SEM) at different magnifications. The SEM images in Figure 1 indicate that CS shows a smooth surface, while RM has a porous structure containing aggregates of molecules to form a bulk. After modification with CS to produce the RM/CS composite, the new material retains the porosity of the red mud, but the particles are distributed more evenly. This indicates This indicates improved removal efficiency of heavy metal ions from aqueous solutions by the RM/CS composite, as shown in the figure below.

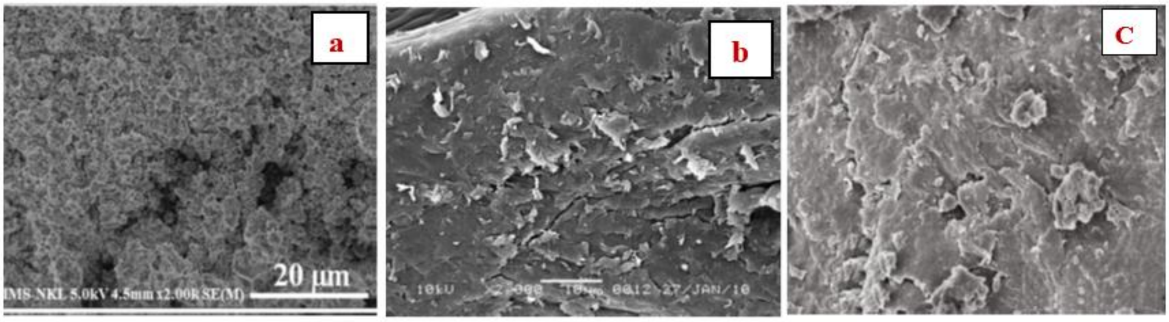


Figure 1. (a) SEM image of RM [137]. (b) SEM image SEM image of Chitosan [126]. (c) SEM image of RM/CS [138].

Table 6. Modified red mud / chitosan to remove heavy metal ions from aqueous solution.

Type red mud	Type of Chitosan	pollutant	Optimal condition	% Removal adsorption	Ref.
Red mud (bentonite, clay)	chitosan (medium molecular	Cr (VI)	PH=2 T=60 min, Temp= 25 C° Dose=0.1 Adsorbate =58ppm	99.84%	[138]
Iran	France	Cd (II)	PH=6.5 T=15, Temp = 25 C° Dose=0.5 Adsorbate =100ppm	--------	[139]
Vietnam	Chitosan (flake form, yellow color), Vietnam	Ni (II)	PH=6 T=180 min , Temp= 50 C° Dose=0.25 mg	81.33%	[140]
Bijoypur clay	Chitosan was extracted from this waste prawn shell	Cr (VI)	PH=4 T= 30-180 min Temp= 25 C° Dose=0.1mg Adsorbate =60ppm	-------	[141]
China	Shanghai Macklin Biochemical Co., Ltd., China	Cr (VI)	PH=3 T=90 min , Temp= 25 C° Dose= 20 mg Adsorbate = 400ppm	87.61	[142]
Vietnam	CS (yellow color), from the shrimp shells	Pb (II)	PH=5.5 T=180 min, Temp= 30 C° Dose=0.1 Adsorbate =500mg/g	-------	[143]
USA	chitosan flakes with high molecular weight	Cr (VI)	PH=2 T=60, Temp= Dose=1.5 Adsorbate = --	76	[144]
Bijoypur Clay	Extraction of Chitosan from Waste Prawn Shell	Cr (VI) Pb (II)	PH=6 T=120 min, Temp= 27 C° Dose=0.05 Adsorbate =25ppm	39.50 50.90	[145]
United Arab Emirates	Chitosan (448877ALDRICH)	Cd Cr Pb Cu Ni	PH=6 T=120 min, Temp= 27 C° Dose=0.05 Adsorbate =25ppm	--------	[146]

clay (sodium montmorillonite)	Chitosan solution	Cu (II)	PH=6 T=180 min , Temp= 25 C° Dose=0.02 Adsorbate =11,24,5.5, 15, 7mg L^{-1}	----	[147]
Nano clay	Crosslinking chitosan	Pb (II)	PH=7 T=60 min, Temp= 25 C° Dose=0.3 Adsorbate =55 mg L^{-1}	94.9	[148]
Clay from Aldrich	Chitosan deacetylation degree	Pb (II)	PH=4.5 T=80 min, Temp= 25 C° Dose=0.5 Adsorbate =4mg L^{-1}	----	[149]
bentonite from Henan , China.	chitosan from Jinan Haidebei Marine	Ni (II)	PH=5.5 T=2880-7200, Temp= --- Dose=--- Adsorbate = 100 mgL^{-1}	94.8%	[150]
Bentonite from Shanghai Aladdin	chitosan from Shanghai Aladdin.	Cr (VI) Cu (II)	PH=3.5 T=2880-7200, Temp=--- Dose= --- Adsorbate = 100 mgL^{-1}	84.59 60.1	[151]
bentonite, USA	chitosan (75–85% deacetylation),).	As(V)	PH=---- T=2 h, Temp= 50 C° Dose=1: 0.01 Adsorbate = 15 mg L^{-1}	----	[152]
bentonite	Chitosan commercial	Pb (II) Cd (II) Hg (II)	PH= 3 T= 120, Temp=25 C° Dose=0.5 g Adsorbate =50 ppm	-----	[153]

Conclusion

Red mud and chitosan composite RM/CS have become good alternatives to overcome the problem of natural adsorbents. Chitosan has been used over the past decades to remove a wide range of pollutants, including heavy metal ions, from aqueous solutions. Its use was, however, limited by a number of factors, including its chemical makeup, which prevented it from absorbing large amounts of pollutants, and its heat sensitivity in contrast to red mud, which is thermally stable across a wide temperature range. Therefore, modifying red mud with chitosan in ideal doses gave promising results in the removal process. On the other hand, RM/CS composites show benefits, including the availability of raw materials, high efficiency in the removal process, simple manufacturing method, low cost, and method of formation, which is considered sustainable green manufacturing. However, comparing all these studies and presenting the optimal conditions for them is almost impossible due to the difference in parameters and quality of adsorbent materials. We suggest intensifying studies on this subject with replacement raw materials and efficiency evaluations.

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