Adsorbents for Heavy Metal Decontamination

Subjects: Materials Science, Composites

Contributor: SONAL CHOUDHARY

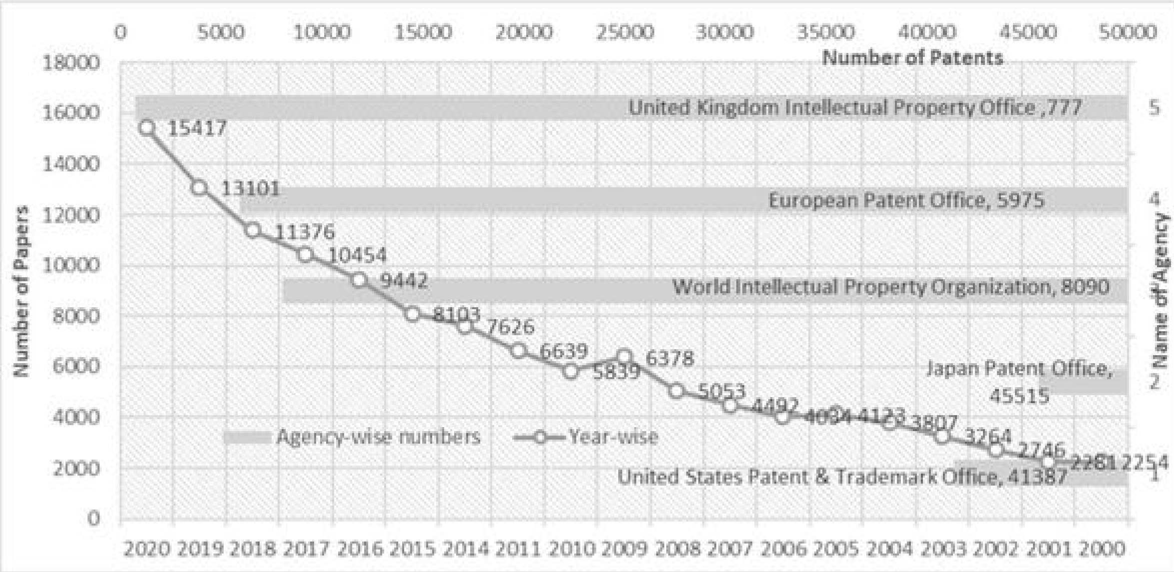
The adsorption isotherm model is a valuable method for determining the theoretical optimal adsorption power as well as the potential interactions between adsorbents and adsorbate. Sorption isotherms are mathematical models that illustrate the allocation of metals in between adsorbate and adsorbent. The distribution of metals in between adsorbate and adsorbent depends upon the nature of the adsorbent whether it is homogeneous or heterogeneous, the type of exposure, and the bonding between adsorbent and adsorbate.

heavy metal | adsorption | polymeric adsorbents | bioadsorbent | wastewater

1. Introduction

Many pollutants are entering water bodies due to the continuous increase in the number of global inhabitants, manufacturing units, unplanned urbanization, cultivation ventures, and the use of chemicals [1]. In today's scenario, researchers are working on the effective removal of various pollutants such as heavy metals, synthetic colors, sediments, chemicals, radioactive, pharmaceuticals, and other waste material from the natural cycles [2]. Among all the contaminants, heavy metals are the most prevalent contaminant found in water. Heavy metals are described as elements with a particular density greater than 5 g/cm 3 [3]. This classification covers critical elements for trace concentrations (for example iron, vanadium, cobalt and copper, manganese, zinc, strontium, and molybdenum). If the threshold amount is surpassed, however, multiple damages in living systems may be found [4]. Heavy metals are found in the atmosphere from both natural (e.g., soil erosion, weathering of the earth's crust, volcanic eruptions) and anthropogenic sources (e.g., mining and mineral beneficiation, industrial effluents from cement, food, fiber, paper, electronic operations, chemical formulations for plague control, and so on) sources [5]. Since heavy metals do not decay in the atmosphere, their accumulation in environmental compartments (such as air, soil, and waters) could contribute to their migration into food and water intended for human consumption in the long run [6]. This is a significant environmental issue, prompting scientists to focus on new technologies that will enable heavy metals to be removed from polluted environmental supplies. Heavy metals act as a poison to metabolic activities and enzyme inhibitors [7]. These toxic metals are not degraded biologically and tend to accumulate in living beings, resulting in different illnesses and disorders. Heavy metals leak into nature by various modes like combustion of coal, sewage waste-water, and emission of toxic gases by automobiles, battery manufacturing industries, activities related to extraction of minerals, leather industries, alloy industries, and the consumption of non-renewable energy resources [8]. Various methods like filtration, precipitation through chemical methods, neutralization, ion exchange, and adsorption are used to bind heavy metal ions from the wastewater discharged from many industries [9][10][11][12]. To date, a large number of published papers on wastewater treatment have increased progressively since 2000 (**Figure 1**).

Figure 1. Number of research papers and patents available on the use of various materials for wastewater treatment per year from 2000 to 2020 from Scopus with the keywords “wastewater treatment”.



The removal of heavy metal ions has always been a challenge for scientists as effective adsorbents are required for their elimination. Adsorbents have many benefits over traditional chemical sorbents in water treatment systems: biodegradability in natural/environmental settings, high abundance in nature, high surface-area, a greater tendency to adsorb such metal ions, appropriate pore dimension and volume, more mechanical strength, compatibility, they are easily available, they are easily renewable, they have a cheap cost, their eco-friendliness, they have easy manufacturing methods, and they are more specific in nature [13]. These structures have a high surface area to volume ratio and multiple active binding sites on their surface, enabling heavy metals to be maintained effectively under some conditions (e.g., –COOH, –NH 2, –OH, –SH groups) [14]. Adsorption is generally dependent on the association of hydroxyl, amino, and carboxylic groups on the adsorbent’s surface with metal ions such as Cu 2 +, Pb 2+, and Cr 3+ cations [15][16].

In the past two decades, the adsorption of heavy metals with environment-friendly and economical materials like agricultural, industrial, or urban residues has come up with a promising technology in the removal of pollutants from aqueous discharge [17]. Hence, a lot of research has been reported by many authors using economical adsorbents such as lignin, bark, chitosan, clay, zeolite, activated carbons, synthetic polymeric adsorbents, and so on [18]. The present review focuses on the use of various types of adsorbents for the removal of heavy metal ions. There are not many research papers that use multiple types of adsorbents in a single frame to eliminate them. The classification of various types of adsorbents like natural, synthetic, and modified adsorbents have been covered in this review which otherwise was not included in any of the reviews published before [19][20][21][22][23].

Adsorption is a commonly proposed technique since it is highly effective in the extraction process and is easy to apply; adsorbents are available in different ranges and are cheaper in cost [24]. Several chelating resins were synthesized by the polymerization of traditional chelating monomers i.e., methacrylic acid, acrylamide, vinyl pyridine, and vinyl imidazole [25][26]. Researchers synthesized a polymer by reacting this with ligands having a low molecular weight which resulted in a new polymer with some functionality or new group in the modified polymer [27]

[28]. Additionally, the functionalization of the polymer matrix results in the formation of new chelating resin [29]. Because of the existence of reactive hydroxyl and amino moieties, chitosan is a natural biopolymer that is abundant in nature and has the ability to adsorb a considerable amount of metals. Furthermore, modification of chitosan through physical and chemical techniques were able to increase its sorption abilities for metal ions like As 3+ or As 5+ [30][31][32], Cr 6+ [33][34][35], Pb 2+ [36][37], Cu 2+ [38][39][40], Hg 2+ [41][42][43], Cd 2+ [44][45][46], Ni 2+ [47][48][49], Zn 2+ [50][51], Ag + [52][53], Co 2+ [54], Mn 2+ [55], U 6+ [56][57], V (3+,4+ and 5+) [58], and Pt 4+ [59]. Similarly, Jiang et al., synthesized polystyrene-supported chitosan beads cross-linked with glutaraldehyde for rapid extraction of copper ions [38]. Yan et al. (2010) studied whether the coagulation procedure was useful in the removal of arsenic (As), and found that Al and Fe salts were effective coagulants for extraction. Furthermore, since 2000, the amount of data available on adsorption in water treatment has steadily risen (**Figure 1**), suggesting a rise in research interest in this area [60].

2. Adsorption Mechanism

The adsorption process is the most efficient and admirable process for the treatment of toxic metals present in wastewater. In this process, toxic material is shifted by physical or chemical means onto the available surface of the adsorbent (**Figure 2**) [61]. The adsorption process is a cheap method and has a very low operating cost, and causes less contamination during the extraction process of toxic metal in comparison to conventional methods. In the adsorption methods, sorbents can be regenerated as well as reused several times for effective removal, and hence are considered to be an environmentally friendly method [62]. The major characteristics required for the choice of adsorbents are price effectiveness, large surface area, pore size distribution, presence of functional moiety, and polar characteristics of the sorbent which determines the efficiency of adsorption methods [63]. It is, therefore essential to understand the adsorption process. Adsorption is a mass transport method of solute present in the solution and accumulated onto the surface of the adsorbent which is generally a solid substance [64]. There are two kinds of force i.e., physical and chemical interactions that exist between adsorbent and adsorbate. Physical forces are weak and adsorbed molecules can be attached to adsorbents anywhere, meaning physical forces are non-specific in nature. Chemical adsorption is specific in nature and adsorbate binds to adsorbents through the covalent or electrostatic bonds. In the case of physical adsorption, forces are Van der Waals, dispersion interactions, and hydrogen bonding.

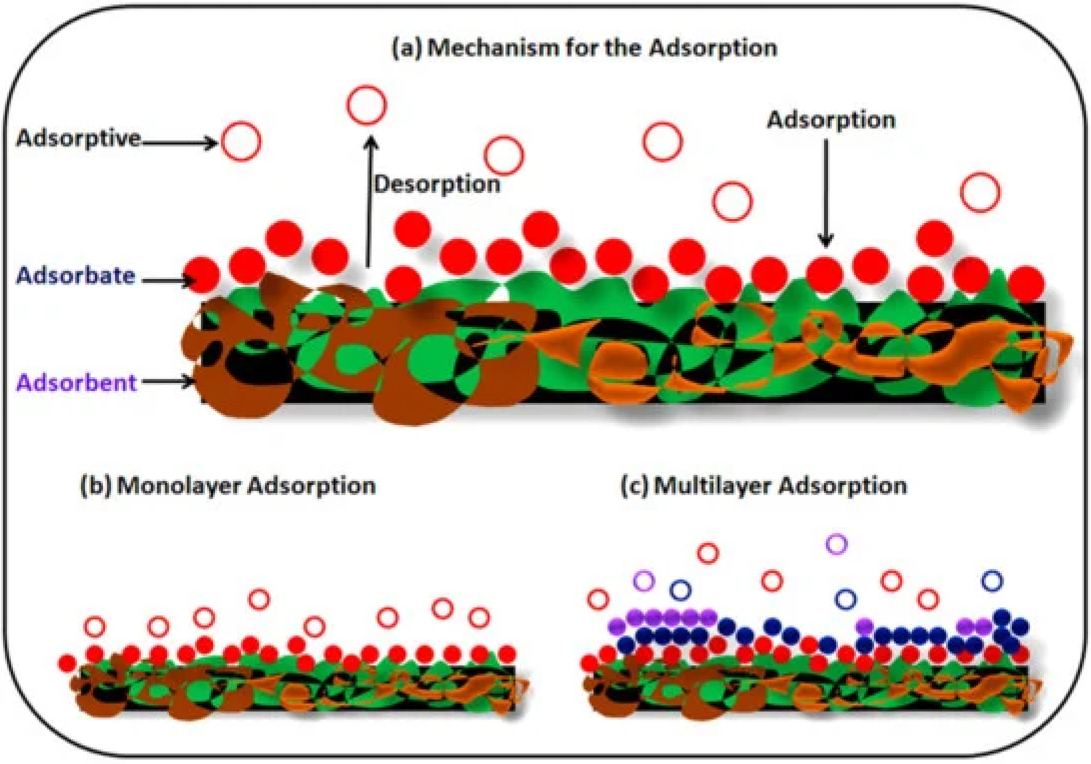


Figure 2. (**a**) General mechanism for the adsorption, (**b**) monolayer adsorption, and (**c**) multilayer adsorption.

3. Adsorption Modeling

Adsorption kinetics data are expected to create an efficient and reliable design model for the removal of pollutants from aqueous media. Kinetic models explain the sorption process and method used. It also explains the speed with which adsorption sites of adsorbent are occupied and the number of unoccupied sites. The adsorption kinetic is commonly used to predict the various adsorbent's sorption ability. Kinetic modeling actually gives information about adsorption mechanisms and possible rate-controlling steps such as mass transport or chemical reaction processes. Kinetic models help us to find out the metal extraction rate which finds the time to attain the equilibrium. The rate of the removal of solute depends upon the physical or chemical properties of the sorbent and also on the various parameters that affect the rate of adsorption. Usually, the rate of sorption of toxic ions becomes better with time until the equilibrium was achieved between the amounts of adsorbates in the solid phase and the amounts of adsorbates present in the liquid. Mostly, the rate of adsorption is fast at the start and steadily slows down as equilibrium is reached. The time to obtain equilibrium varies with the adsorbates, adsorbent, initial concentration, and the various parameters that affect the solution. There are different kinds of models used by researchers to study the sorption process such as Lagergren's pseudo-first-order (PFO), pseudo-second-order, Elovich kinetic equation, and parabolic diffusion model. Among the entire models, the rate of sorption was generally studied through the Lagergren pseudo-first-order model. At present, the pseudo-second-order (PSO) model has been generally used for the sorption process because of its excellent illustration of the practical facts for all sorbent sorbate systems. For this, PFO and PSO kinetic models will be utilized to describe the adsorption kinetics of heavy metal ions onto adsorbent, which was defined as follows.

The pseudo-first-order kinetic model has been mostly used to speculate the rate of sorption of metal which is described as: dq/dt = k 1 (q e − q) (1)

The term q is the quantity of metal sorbed in a particular time (mg/g), q e is the quantity of metal sorbed at equilibrium time (mg/g), k 1 is pseudo-first-order rate constant (g mg −1 min −1). We integrate Equation (1) by using boundary conditions q = 0 at t = 0 and q = q at t = t, then solve Equation (1) as below: In (q e /q e − q) = K 1 T (2)

The sorption kinetics can also be studied by the pseudo-second-order model. PSO model assumes that the rate of adsorption of solute is proportional to the available sites on the adsorbent. Equation (3) shows the linear form of PSO. dq t /dt = k 2 (q e − q t) 2(3) where K 2 (g mg −1 min −1) is the equilibrium rate constant of pseudo-second-order adsorption. On integrating (3) and noting that, q = 0 at t = 0, the following equation is obtained. t/q t = 1/ k 2 qe 2 + 1/q e t (4)

4. Adsorption Isotherm

The above equation is a straight-line having intercept log K f and slope equal to 1/n.

For metal ion sorption, the temperature is important as far as thermodynamic adsorption is concerned. Usually, endothermal and exothermic sorption processes are the two general types that exist. These are determined by the increase or decrease of the temperature throughout the adsorption process. Thermodynamic functions such as entropy, enthalpy, and free changes in energy can be determined using the Van’t Hoff equation during the adsorption process as given below: d(lnKeq)/dT = ΔH/RT 2 (9) where Keq = qe/C. Keq is the equilibrium constant. The change in free energy could be evaluated with the help of Equation (10): ΔG 0 = ΔH 0 − TΔS 0 (10)

The change in enthalpy and entropy of the adsorption process could be evaluated from the slope and intercept of a line obtained by plotting ln Keq vs. 1/T.

Gibb’s free energy, enthalpy, and entropy changes are important design factors for assessing the performance and predicting the mechanism of an adsorption separation process, as well as one of the fundamental needs for characterization and optimization **Table 1** show typical values for thermodynamic parameters for adsorption of heavy metal ions on adsorbents [65].

References

1. Vakili, M.; Rafatullah, M.; Salamatinia, B.; Abdullah, A.Z.; Ibrahim, M.H.; Tan, K.B.; Gholami, Z.; Amouzgar, P. Application of chitosan and its derivatives as adsorbents for dye removal from water and wastewater: A review. Carbohydr. Polym. 2014, 113, 115–130.

2. Reddy, D.H.K.; Lee, S.M. Application of magnetic chitosan composites for the removal of toxic metal and dyes from aqueous solutions. Adv. Colloid Interface Sci. 2013, 201, 68–93.
3. Jaishankar, M.; Tseten, T.; Anbalagan, N.; Mathew, B.B.; Beeregowda, K.N. Toxicity, mechanism and health effects of some heavy metals. Interdiscip. Toxicol. 2014, 7, 60.
4. Luo, C.; Liu, C.; Wang, Y.; Liu, X.; Li, F.; Zhang, G.; Li, X. Heavy metal contamination in soils and vegetables near an e-waste processing site, south China. J. Hazard. Mater. 2011, 186, 481–490.
5. Morais, S.; Costa, F.G.; Pereira, M.D.L. Heavy metals and human health. Environ. Health Emerg. Issues Pract. 2012, 10, 227–245.
6. Escudero, L.B.; Quintas, P.Y.; Wuilloud, R.G.; Dotto, G.L. Biosorption of metals and metalloids. In Green Adsorbents for Pollutant Removal; Springer: Cham, Switzerland, 2018; pp. 35–86.
7. Jan, A.; Azam, M.; Siddiqui, K.; Ali, A.; Choi, I.; Haq, Q. Heavy Metals and Human Health: Mechanistic Insight into Toxicity and Counter Defense System of Antioxidants. Int. J. Mol. Sci. 2015, 16, 29592–29630.
8. Bratjer, K.; Dabek-Zlotorzynska, E. Separation of Metal Ions on a Modified Aluminum Oxide. Talanta 1990, 37, 613.
9. Beauvais, R.A.; Alexandratos, S.D. Polymer-supported reagents for the selective complexation of metal ions: An overview. React. Funct. Polym. 1998, 36, 113–123.
10. Cassidy, H.G. Adsorption and Chromatography; Interscience Publishers: New York, NY, USA, 1951.
11. Kantipuly, C.; Katragadda, S.; Chow, A.; Gesser, H.D. Chelating polymers and related supports for separation and preconcentration of trace metals. Talanta 1990, 37, 491–517.
12. Reed, B.E.; Lin, W.; Matsumoto, M.R.; Jensen, J.N. Physicochemical processes. Water Environ. Res. 1997, 69, 444–462.
13. Markovic, S.; Stankovic, A.; Lopicic, Z.; Lazarevic, S.; Stojanovic, M.; Uskokovic, D. Application of raw peach shell particles for removal of methylene blue. J. Environ. Chem. Eng. 2015, 3, 716–724.
14. He, J.; Lu, Y.; Luo, G. Ca (II) imprinted chitosan microspheres: An effective and green adsorbent for the removal of Cu (II), Cd (II) and Pb (II) from aqueous solutions. Chem. Eng. J. 2014, 244, 202–208.
15. Reddy, N.A.; Lakshmipathy, R.; Sarada, N.C. Application of Citrullus lanatus rind as biosorbent for removal of trivalent chromium from aqueous solution. Alex. Eng. J. 2014, 53, 969–975.
16. Akkaya, G.; Güzel, F. Bio removal and recovery of Cu (II) and Pb (II) from aqueous solution by a novel biosorbent watermelon (Citrullus lanatus) seed hulls: Kinetic study, equilibrium isotherm,

SEM and FTIR analysis. Desalin. Water Treat. 2013, 51, 7311–7322.

17. Kumar, B.; Smita, K.; Sánchez, E.; Stael, C.; Cumbal, L. Andean Sacha inchi (Plukenetia volubilis L.) shell biomass as new biosorbents for Pb 2+ and Cu 2+ ions. Ecol. Eng. 2016, 93, 152–158.
18. Bailey, S.E.; Olin, T.J.; Bricka, R.M.; Adrian, D.D. A review of potentially low-cost sorbents for heavy metals. Water Res. 1999, 33, 2469–2479.
19. Agarwal, M.; Singh, K. Heavy metal removal from wastewater using various adsorbents: A review. J. Water Reuse Desalin. 2017, 7, 387–419.
20. Atkovska, K.; Lisichkov, K.; Ruseska, G.; Dimitrov, A.T.; Grozdanov, A. Removal of heavy metal ions from wastewater using conventional and nanosorbents: A review. J. Chem. Technol. Metall. 2018, 53, 202–219.
21. Vardhan, K.H.; Kumar, P.S.; Panda, R.C. A review on heavy metal pollution, toxicity and remedial measures: Current trends and future perspectives. J. Mol. Liq. 2019, 290, 111197.
22. Sheth, Y.; Dharaskar, S.; Khalid, M.; Sonawane, S. An environment friendly approach for heavy metal removal from industrial wastewater using chitosan based biosorbent: A review. Sustain. Energy Technol. Assess. 2021, 43, 100951.
23. Hasanpour, M.; Hatami, M. Application of three-dimensional porous aerogels as adsorbent for removal of heavy metal ions from water/wastewater: A review study. Adv. Colloid Interface Sci. 2020, 284, 102247.
24. Alinnor, I.J. Adsorption of heavy metal ions from aqueous solution by fly ash. Fuel 2007, 86, 853–857.
25. Duran, A.; Soylak, M.; Tuncel, S.A. Poly(vinyl pyridine-poly ethylene glycol methacrylate-ethylene glycol dimethacrylate) beads for heavy metal removal. J. Hazard. Mater. 2008, 155, 114–120.
26. Kara, A. Poly (ethylene glycol dimethacrylate-n-vinyl imidazole) beads for heavy metal removal. J. Hazard. Mater. 2004, 106, 93–99.
27. Şenkal, B.F.; Biçak, N. Glycidyl methacrylate-based polymer resins with diethylene triamine tetra acetic acid functions for efficient removal of Ca (II) and Mg (II). React. Funct. Polym. 2001, 49, 151–157.
28. Coutinho, F.M.B.; Rezende, S.M.; Barbosa, C.C.R. Influence of the morphological structure of macroreticular amidoxime resins on their complexation capacity. React. Funct. Polym. 2001, 49, 235–248.
29. Atia, A.A.; Donia, A.M.; Elwakeel, K.Z. Selective separation of mercury (II) using a synthetic resin containing amine and mercaptan as chelating groups. React. Funct. Polym. 2005, 65, 267–275.

30. Gang, D.D.; Deng, B.; Lin, L. As (III) removal using an iron-impregnated chitosan sorbent. J. Hazard. Mater. 2010, 182, 156–161.
31. Gupta, A.; Yunus, M.; Sankararamakrishnan, N. Chitosan- and Iron–Chitosan-Coated Sand Filters: A Cost-Effective Approach for Enhanced Arsenic Removal. Ind. Eng. Chem. Res. 2013, 52, 2066–2072.
32. Wang, J.; Xu, W.; Chen, L.; Huang, X.; Liu, J. Preparation and evaluation of magnetic nanoparticles impregnated chitosan beads for arsenic removal from water. Chem. Eng. J. 2014, 251, 25–34.
33. Liu, C.; Li, Y.; Hou, Y. Preparation of a Novel Lignin Nanosphere Adsorbent for Enhancing Adsorption of Lead. Molecules 2019, 24, 2704.
34. Kumar, A.S.K.; Kumar, C.U.; Rajesh, V.; Rajesh, N. Microwave assisted preparation of n-butylacrylate grafted chitosan and its application for Cr (VI) adsorption. Int. J. Biol. Macromol. 2014, 66, 135–143.
35. Shen, C.; Chen, H.; Wu, S.; Wen, Y.; Li, L.; Jiang, Z.; Li, M.; Liu, W. Highly efficient detoxification of Cr (VI) by chitosan–Fe (III) complex: Process and mechanism studies. J. Hazard. Mater. 2013, 244, 689–697.
36. Liu, B.; Lv, X.; Meng, X.; Yu, G.; Wang, D. Removal of Pb (II) from aqueous solution using dithiocarbamate modified chitosan beads with Pb(II) as imprinted ions. Chem. Eng. J. 2013, 220, 412–419.
37. Lu, Y.; He, J.; Luo, G. An improved synthesis of chitosan bead for Pb(II) adsorption. Chem. Eng. J. 2013, 226, 271–278.
38. Jiang, W.; Chen, X.; Pan, B.; Zhang, Q.; Teng, L.; Chen, Y.; Liu, L. Spherical polystyrene-supported chitosan thin film of fast kinetics and high capacity for copper removal. J. Hazard. Mater. 2014, 276, 295–301.
39. Negm, N.A.; El Sheikh, R.; El-Farargy, A.F.; Hefni, H.H.H.; Bekhit, M. Treatment of industrial wastewater containing copper and cobalt ions using modified chitosan. J. Ind. Eng. Chem. 2015, 21, 526–534.
40. Sikder, M.T.; Mihara, Y.; Islam, M.S.; Saito, T.; Tanaka, S.; Kurasaki, M. Preparation and characterization of chitosan–carboxymethyl-β-cyclodextrin entrapped nanozero-valent iron composite for Cu (II) and Cr (IV) removal from wastewater. Chem. Eng. J. 2014, 236, 378–387.
41. Allouche, F.-N.; Guibal, E.; Mameri, N. Preparation of a new chitosan-based material and its application for mercury sorption. Colloids Surf. Physicochem. Eng. Asp. 2014, 446, 224–232.
42. Jaiswal, A.; Ghsoh, S.S.; Chattopadhyay, A. Quantum Dot Impregnated-Chitosan Film for Heavy Metal Ion Sensing and Removal. Langmuir 2012, 28, 15687–15696.

43. Wang, Y.; Qi, Y.; Li, Y.; Wu, J.; Ma, X.; Yu, C.; Ji, L. Preparation and characterization of a novel nano-absorbent based on multi-cyanoguanidine modified magnetic chitosan and its highly effective recovery for Hg(II) in aqueous phase. J. Hazard. Mater. 2013, 260, 9–15.
44. Liu, D.; Li, Z.; Zhu, Y.; Li, Z.; Kumar, R. Recycled chitosan nanofibril as an effective Cu (II), Pb (II) and Cd (II) ionic chelating agent: Adsorption and desorption performance. Carbohydr. Polym. 2014, 111, 469–476.
45. Kyzas, G.Z.; Siafaka, P.I.; Lambropoulou, D.A.; Lazaridis, N.K.; Bikiaris, D.N. Poly (itaconic acid)-Grafted Chitosan Adsorbents with Different Cross-Linking for Pb (II) and Cd (II) Uptake. Langmuir 2014, 30, 120–131.
46. Monier, M.; Abdel-Latif, D.A. Preparation of cross-linked magnetic chitosan-phenylthiourea resin for adsorption of Hg(II), Cd(II) and Zn(II) ions from aqueous solutions. J. Hazard. Mater. 2012, 209–210, 240–249.
47. Aliabadi, M.; Irani, M.; Ismaeili, J.; Piri, H.; Parnian, M.J. Electrospun nanofiber membrane of PEO/Chitosan for the adsorption of nickel, cadmium, lead and copper ions from aqueous solution. Chem. Eng. J. 2013, 220, 237–243.
48. Heidari, A.; Younesi, H.; Mehraban, Z.; Heikkinen, H. Selective adsorption of Pb (II), Cd (II), and Ni (II) ions from aqueous solution using chitosan–MAA nanoparticles. Int. J. Biol. Macromol. 2013, 61, 251–263.
49. Tirtom, V.N.; Dinçer, A.; Becerik, S.; Aydemir, T.; Çelik, A. Comparative adsorption of Ni (II) and Cd (II) ions on epichlorohydrin crosslinked chitosan–clay composite beads in aqueous solution. Chem. Eng. J. 2012, 197, 379–386.
50. Kyzas, G.Z.; Siafaka, P.I.; Pavlidou, E.G.; Chrissafis, K.J.; Bikiaris, D.N. Synthesis and adsorption application of succinyl-grafted chitosan for the simultaneous removal of zinc and cationic dye from binary hazardous mixtures. Chem. Eng. J. 2015, 259, 438–448.
51. Milosavljevic, N.B.; Ristic, M.Đ.; Peric-Grujic, A.A.; Filipovic, J.M.; Strbac, S.B.; Rakocevic, Z.L.; Krusic, M.T.K. Sorption of zinc by novel pH-sensitive hydrogels based on chitosan, itaconic acid and methacrylic acid. J. Hazard. Mater. 2011, 192, 846–854.
52. Song, X.; Li, C.; Xu, R.; Wang, K. Molecular-Ion-Imprinted Chitosan Hydrogels for the Selective Adsorption of Silver(I) in Aqueous Solution. Ind. Eng. Chem. Res. 2012, 51, 11261–11265.
53. Zhang, M.; Zhang, Y.; Helleur, R. Selective adsorption of Ag+ by ion-imprinted O-carboxymethyl chitosan beads grafted with thiourea–glutaraldehyde. Chem. Eng. J. 2015, 264, 56–65.
54. Aliabadi, M.; Irani, M.; Ismaeili, J.; Najafzadeh, S. Design and evaluation of chitosan/hydroxyapatite composite nanofiber membrane for the removal of heavy metal ions from aqueous solution. J. Taiwan Inst. Chem. Eng. 2014, 45, 518–526.

55. Al-Wakeel, K.Z.; Abd El Monem, H.; Khalil, M.M.H. Removal of divalent manganese from aqueous solution using glycine modified chitosan resin. J. Environ. Chem. Eng. 2015, 3, 179–186.

56. Mahfouz, M.G.; Galhoum, A.A.; Gomaa, N.A.; Abdel-Rehem, S.S.; Atia, A.A.; Vincent, T.; Guibal, E. Uranium extraction using magnetic nano-based particles of diethylenetriamine-functionalized chitosan: Equilibrium and kinetic studies. Chem. Eng. J. 2015, 262, 198–209.

57. Xu, C.; Wang, J.; Yang, T.; Chen, X.; Liu, X.; Ding, X. Adsorption of uranium by amidoximated chitosan-grafted polyacrylonitrile, using response surface methodology. Carbohydr. Polym. 2015, 121, 79–85.

58. Padilla-Rodriguez, A.; Hernandez-Viezcas, J.A.; Peralta-Videa, J.R.; Gardea-Torresdey, J.L.; Perales-Perez, O.; Roman-Velazquez, F.R. Synthesis of protonated chitosan flakes for the removal of vanadium (III, IV and V) oxyanions from aqueous solutions. Microchem. J. 2015, 118, 1–11.

59. Zhou, L.; Xu, J.; Liang, X.; Liu, Z. Adsorption of platinum (IV) and palladium (II) from aqueous solution by magnetic cross-linking chitosan nanoparticles modified with ethylenediamine. J. Hazard. Mater. 2010, 182, 518–524.

60. Yan, L.; Yin, H.; Zhang, S.; Leng, F.; Nan, W.; Li, H. Biosorption of inorganic and organic arsenic from aqueous solution by Acid thiobacillus ferrooxidans BY-3. J. Hazard. Mater. 2010, 178, 209–217.

61. Ojedokun, A.T.; Bello, O.S. Sequestering heavy metals from wastewater using cow dung. Water Resour. Ind. 2016, 13, 7–13.

62. Demirbas, A. Heavy metal adsorption onto agro-based waste materials: A review. J. Hazard. Mater. 2008, 157, 220–229.

63. Vunain, E.; Mishra, A.; Mamba, B. Dendrimers, mesoporous silicas and chitosan-based nano sorbents for the removal of heavy-metal ions: A review. Int. J. Biol. Macromol. 2016, 86, 570–586.

64. Owsik, I.A.; Kolarz, B.N.; Jermakowicz-Bartkowiak, D.; Jezierska, J. Synthesis and characterization of resins with ligands containing guanidinine derivatives. Cu (II) sorption and coordination properties. Polymer 2003, 44, 5547–5558.

65. Liu, Y. Is the free energy change of adsorption correctly calculated? J. Chem. Eng. Data 2009, 54, 1981–1985.