

## MAGNETIC NANOPARTICLES AS EFFECTIVE ADSORBENTS FOR THE REMOVAL OF HEAVY METALS FROM WATER: A REVIEW OF SURFACE MODIFICATION (2015-2022)

(Nanzarah Bermagnet Sebagai Penjerap yang Berkesan untuk Penyingkiran Logam Berat daripada Air: Tinjauan Kajian Pengubahsuaian Permukaan (2015-2022))

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### Abstract

The use of biopolymer composite materials in the usage of magnetic nanoparticles for the removal of heavy metal pollutants has received little attention, despite their remarkable physical and chemical properties that suggested their huge potential as promising adsorbents. . Therefore, various sorbents for heavy metals removal have been prepared including surface-modified magnetic nanoparticles (MNPs). MNPs are susceptible to oxidation in the air and agglomeration in solvents rendering them to lose their essential adsorbent properties. Silica coating has proven to prevent degradation of the MNP and functionalizes the surface with silanol groups. A fundamental understanding of various surface modifications would be beneficial for near future research as well as industrial applications. Thus, this article aims in reviewing the most recent advances for surface modification of MNPs materials, including biopolymer materials, focusing on the chemistry preparation, characterization, optimization, mechanisms of adsorption, isotherms and kinetic models in order to remove various metals in water.

**Keywords:** magnetic nanoparticles, functionalization, modification biopolymer, heavy metals, water environment

### Abstrak

Penggunaan komposit bioplimer sebagai nanozarah bermagnet untuk penjerapan logam berat kurang mendapat perhatian, walaupun ianya mempunyai ciri fizikal dan kimia yang luar biasa yang menjadikan komposit bioplimer sebagai penjerap berkesan. Oleh itu, pelbagai penjerap untuk penyingkiran logam berat telah disediakan termasuk permukaan nanopartikel bermagnet yang diubah suai (MNPs). MNPs mudah teroksidasi di udara dan mudah bergumpal dalam pelarut menyebabkan bahan ini kehilangan ciri-ciri

penjerapan yang penting. Salutan silika telah dibuktikan menghalang kemerosotan MNPs serta menyebabkan permukaan tersebut berfungsi dengan kumpulan silanol. Pemahaman yang baik tentang pelbagai pengubahsuaian permukaan akan memberi manfaat untuk penyelidikan masa hadapan serta aplikasi industri. Maka, artikel ini bertujuan untuk membincangkan dengan lebih mendalam kemajuan terkini dalam pengubahsuaian permukaan MNP termasuk bahan biopolimer, fokus terhadap penyediaan secara kimia, pencirian, keadaan penjerapan optimum, mekanisme penjerapan, model isoterma penjerapan dan model kinetik yang digunakan untuk penyingkiran bahan pencemar ion logam yang berbeza dalam persekitaran air.

**Kata kunci:** nanopartikel bermagnet, kefungsiannya, biopolimer pengubahsuaian, logam berat, persekitaran air

### Introduction

Pollution from heavy metals (lead, cadmium, and copper) poses a serious risk to human lives as well as the environment (water, soil, and air) across the world. Metallic elements with relative densities are greater than those of water, greater than or equal to 5 g/cm<sup>3</sup>, and the potential to be hazardous even at low concentrations are referred to as heavy metals. [1]. These heavy metals (lead, cadmium, and copper) are non-biodegradable, and therefore, tend to bioaccumulate in the biological and ecological system over a prolonged period, potentially causing damage to living organisms. The discharge of a high concentration of heavy metals into the environment could be from mining, agricultural, domestic, and industrial activities [1, 2]. The dumping of effluents into water bodies could cause harm to aquatic environments. Thus, due to health threats of the heavy metals, the industries that have the potential in polluting the water bodies should treat their effluents sufficiently before releasing them to fit into the environmental guideline standard. To prevent long-term exposure, it is essential to monitor contamination levels from their drainage source. Non-essential heavy metals such as mercury (Hg), lead (Pb), arsenic (As), cadmium (Cd), and antimony (Sb) are listed in several regulatory bodies as contaminants in various water matrices. The World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA) have stipulated regulatory limits for Pb to be 0.005 mg/L as well as 0.015 mg/L in drinking water, considering its dangerous impacts on the environment and humans [3, 4, 5]. The limits for Hg, Cd, and As in drinking water are 2, 5, and 100 µg/L, respectively [6]. Some heavy metals (i.e. zinc (Zn), copper (Cu), iron (Fe), and selenium (Se)) are essential because they are required for various biological processes and physiochemical functions in most kinds of living organisms [7]. These categories of metal elements remain safe to all living organisms as

long as their concentrations are within acceptable threshold values stipulated by regulatory bodies.

Several techniques for removing heavy metals from the water include precipitation [8], ion exchange [9], coagulation [10], and floatation [11]. However, these methods exhibited several disadvantages and limitations due to their high cost, low effectiveness, disposal of sludge, and inaptness to a wide variety of pollutants. The issue with the disposal of the resulting waste and/or sludge using these techniques makes adsorption a more promising choice due to its reusability of sorbents thus, being the more economical and easy separation method of materials because of the magnetic property of MNP full term? (MNPs). Adsorbents have been prepared from agricultural wastes [9, 12], clay [13], zeolite [14], activated carbon [15] and biopolymers [12]. A new class of material and organic-inorganic hybrid material have become more popular in creating high-performance adsorbents. Magnetic polymeric-based and/or silica-based nanoparticles showed the potential to remove metal through surface modifications. The modified hybrid materials have better properties than the original components. Thus, the surface coating of magnetic nanoparticles (MNPs) is one of the fundamental challenges that stands against researchers for the utilization of these materials for water purification. Recently, MNPs materials received greater attention due to their unique properties in terms of readiness to be modified and nontoxic properties. The MNPs were prepared and used as cores shells. Chemical co-precipitation was mostly recommended since it was considered the easiest and the fastest method with less hazardous chemical and procedure requirements. This method involved the preparation starting from the aqueous mixtures of solutions of Fe(II)/Fe(III) and salt solution by adding a base solution under an inert atmosphere at room temperature with a slight increase in temperature [14, 15].

The MNPs have a high surface area which yields a lot of active sites for various modifications, but due to the setbacks of agglomeration, the active site could be reduced, and this was a major challenge for the preparation of MNPs. The surface coating with inorganic or organic surfactants can be an alternative method to remedy the agglomeration of the MNPs. For instance, the use of certain inorganic capping agents such as silica ( $\text{SiO}_2$ ) has a unique physical and chemical property that could generally be applied during this process. Meanwhile,  $\text{SiO}_2$  is more chemically stable in acidic media, thus, suitable to be used for surface coating of the MNPs. Thus, this could curb the process of agglomeration and serve as a protection for the MNPs in acidic environments. The surface coatings are done with the use of  $\text{SiO}_2$  immediately as the next step after the preparations of MNPs. The  $\text{SiO}_2$  layer is usually coated on the MNPs surface by the application of the Stober method whereby the  $\text{SiO}_2$  were used to cover the surface of the MNPs to form the silica coated magnetite ( $\text{Fe}_3\text{O}_4/\text{SiO}_2$ ) nanoparticle core-shell system [16]. After the  $\text{SiO}_2$  coating, the next step was the functionalization of the MNPs surface. There are several techniques designed to functionalize MNPs surfaces. However, the easiest way is to graft the acid-functionalized group-containing compound with an organic mixture for example oleic acid [17] and n-octadecyl phosphonic acid [17], or it could be done directly onto the surface of MNPs dependent on Lewis acid/base interaction, which will change the MNPs into a hydrophobic adsorbent. Additionally, a silane coupling agent could be directly immobilized onto the surface of MNPs. For instance, amino-group functionalization of MNPs could be achieved through direct salinizing the MNPs with 3-aminopropyltriethoxysilane (APTES) or indirectly onto the surface of the silica-coated MNPs. This paper reviews the advancements in the synthesis of MNPs materials and surface modification with functional groups (e.g.,  $-\text{NH}_2$ ,  $-\text{COOH}$ , or  $-\text{SH}$ ). The use of biopolymer organic components containing polysaccharides obtained from sporopollenin, alginate, chitin, and chitosan used as adsorbent composites for the removal of metal ions pollution in aqueous solutions were discussed. The focus was made on the preparation chemistry, characterization, and optimization, mechanisms of adsorption, isotherms, and kinetic

models, for the removal of various metals in water.

### Chitosan-based MNPs adsorbent

Chitosan (CS) is the major derivative of chitin which could be produced by the process of the deacetylation of the chitin in basic conditions, it is known for its good and outstanding properties such as biocompatibility, biodegradability, antibacterial properties, and non-toxic properties [18,19]. The structure of CS was composed of a linear-linked polysaccharide of randomly distributed ( $\beta$ -4)-linked-D-glucosamine (deacetylated unit) and N-acetyl-D-glutamine (acetylated unit). It has several commercial and biochemical uses [20]. In addition, it is known for its exceptional ability as an effective adsorbent due to its amino ( $-\text{NH}_2$ ) and hydroxyl ( $-\text{OH}$ ) functional groups in their molecules which served as attraction sites toward metal ions. The adsorbents prepared from chitosan-based MNPs for removing metal in water are tabulated in Table 1 [21-37]. In 2018, Song et al. [21] prepared a novel magnetic thiolated/quaternized/chitosan composite ( $\text{Fe}_3\text{O}_4/\text{SH}/\text{CS}$ ) using an inverse suspension technique. The  $\text{Fe}_3\text{O}_4$  was prepared as a precursor followed by the incorporation of the CS and the SH components. The purpose of the addition of CS was to boost the adsorbent's adsorption capacity through their functional groups. All results from this characterization confirmed the presence of  $-\text{OH}$ ,  $-\text{NH}$ , and  $-\text{SH}$  in the composite, as well as the composition of the adsorbent, which revealed the synthesis process was successful. The composite showed high removal efficiency for  $\text{Hg}(\text{II})$ ,  $\text{Pb}(\text{II})$ ,  $\text{As}(\text{V})$ ,  $\text{Zn}(\text{II})$ ,  $\text{As}(\text{III})$ ,  $\text{Cu}(\text{II})$ , and  $\text{Cd}(\text{II})$  in basic conditions (pH 6 to 9).  $\text{Pb}(\text{II})$  showed the highest adsorption capacity of 235.63mg/g while the maximum adsorption capacities values for the other metal ions were 66.27, 67.69, 28.00, 33.99, 13.63 and 16.34 mg/g for  $\text{As}(\text{V})$ ,  $\text{As}(\text{III})$ ,  $\text{Cu}(\text{II})$ ,  $\text{Hg}(\text{II})$ ,  $\text{Zn}(\text{II})$  and  $\text{Cd}(\text{II})$  respectively. Additionally, the Freundlich isotherm was more fitted for all the metal ions due to the correlation coefficient ( $R^2$ ) values  $\geq 0.99$ , than the Langmuir, indicating heterogeneous adsorbate and multilayer adsorbent interaction sites. The kinetic process fitted best to pseudo-second order where the  $R^2$  values were  $\geq 0.99$ , indicating the chemisorption process. The adsorbent showed excellent reusability for  $\text{Pb}(\text{II})$  (as model ion) where the removal efficiency for the  $\text{Pb}(\text{II})$

was achieved at 93% at 5 cycles.

A new adsorbent from attapulgite (ATP), ethylenediaminetetraacetic acid (EDTA), and chitosan to form the composite adsorbent ( $\text{Fe}_3\text{O}_4/\text{ATP}/\text{EDTA}/\text{CS}$ ) was performed by Sun and co-workers [22]. The process of synthesis was done first by combining ATP and  $\text{Fe}_3\text{O}_4$ , followed by the addition of CS gel beads to the  $\text{Fe}_3\text{O}_4/\text{ATP}$  nanoparticles, where glutaraldehyde (GA) was employed as the cross-linker. Finally, gel beads- $\text{Fe}_3\text{O}_4/\text{ATP}/\text{CS}$  were modified by EDTA to form the new  $\text{Fe}_3\text{O}_4/\text{ATP}/\text{EDTA}/\text{CS}$  adsorbent via amidation reaction (i.e., formation of amide through the reaction between carboxylic acid and amine by using a coupling agent such as EDTA) to further enhance removal efficiency. The magnetic material structural formation was confirmed by FTIR with Fe-O spectrum at  $571\text{ cm}^{-1}$ ,  $1663\text{ cm}^{-1}$  (C=N) vibration that showed a reaction took place between CS and GA,  $1631\text{ cm}^{-1}$  ( $-\text{COO}^-$ ),  $1398\text{ cm}^{-1}$  (C-O) indicating a carbonyl group had been introduced to EDTA and that the synthesis of the new adsorbent was successful. The maximum adsorption ability of the fabricated  $\text{Fe}_3\text{O}_4/\text{ATP}/\text{EDTA}/\text{CS}$  adsorbent material was 368.32, 267.94, and 220.31 mg/g, onto Pb(II), Cu(II), and Ni(II) in that order. The adsorption capacities of  $\text{Fe}_3\text{O}_4/\text{ATP}/\text{CS}$  were 224.15, 144.47, and 105mg/g for Pb(II), Cu(II), and Ni(II), respectively, with lower values when compared to those of  $\text{Fe}_3\text{O}_4/\text{ATP}/\text{EDTA}/\text{CS}$ . These results demonstrated that the chelation by EDTA had greatly enhanced the adsorption capacity of the main adsorbent;  $\text{Fe}_3\text{O}_4/\text{ATP}/\text{EDTA}/\text{CS}$ . The procedure of adsorption better fitted the kinetics of pseudo-second data with  $R^2$  values 0.9998, 0.9978, and 0.9967 for Pb(II), Cu(II), and Ni(II), respectively, indicating a chemisorption process. Additionally, the authors discovered that the adsorption mechanism to be homogeneous adsorbate and monolayer active sites interaction with high  $R^2$  values 0.9995, 0.9950, 0.9958 Pb(II), Cu(II), and Ni(II), respectively, satisfying Langmuir isotherm than the Freundlich's physisorption process. Consequently, the adsorbent could still demonstrate good adsorption capacity of repetitive use (5 cycles) by retaining its potential ability > 89% for Pb(II), Cu(II), and Ni(II), thus this indicated its capability to save cost. Chen et al. [23] explored Champ cellulose (*Millettia speciosa*) as

well as chitosan to prepare magnetic hydrogels (MSCC/CS hydrogel) composite adsorbent for the removal of Cu(II). The purpose of adding CS was to enhance the adsorption process through the presence of amino-functional groups. The characterization results of functional groups involved in the synthesis process and the mechanisms of interactions demonstrated that electrostatic attraction was involved, with amino groups dominantly operating in the Cu(II) adsorption mechanism. The FTIR characterization showed the functional groups of -OH for cellulose at a broad peak at  $3421\text{ cm}^{-1}$  and subsequent adsorption peaks at  $2902\text{ cm}^{-1}$  and  $1429\text{ cm}^{-1}$  for C-H stretching vibrations in methyl and methylene, respectively. Other peaks at  $1429\text{ cm}^{-1}$  and  $1371\text{ cm}^{-1}$  for C-H bending vibration as well as - $\text{NH}_2$  from CS were observed, indicating successful synthesis. The results from the adsorption kinetic process revealed the pseudo-first order kinetic process had a better match than the pseudo-second-order kinetic process, which had an  $R^2$  value of 0.9822 for the adsorption of Cu(II). Therefore, physisorption dominated the process. The adsorption isotherm revealed that the Freundlich model had a higher  $R^2$  value of 0.9975 than the Langmuir isotherm, indicating a heterogeneous and multilayer adsorption of Cu(II) onto the adsorbent. The results of the thermodynamic analysis showed that the Cu(II) adsorption process was spontaneous and endothermic, with values for G and H of -6.04KJ/mol and +18.79KJ/mol, respectively. The  $\Delta S$  value was at +0.8KJ/mol which also implied the randomness of the process as well as endothermic. Furthermore, the increment in pH increased the adsorption capacity of MSCC/CS hydrogel due to the interaction of Cu(II) on the adsorbent's negative parts. On top of that, the authors reported that the adsorbent had reasonable reusability, with an adsorption efficiency of > 75% for 5 consecutive cycles.

Elanchezhian et al. [24] developed magnetic kaolinite (MKa) that immobilized in chitosan beads (CB) by a simple co-precipitation method (MKa/4%CB). The MKa was prepared first before CB was introduced into the mixture and applied for the removal of Cd(II) and Pb(II) from a wastewater ecosystem. The purpose of the modification with CB is to enhance the adsorption process through some amino functional group's

addition. Findings from FTIR characterization revealed the presence of Fe-O spectra between 580 and 630, a shift of spectra from 3430  $\text{cm}^{-1}$ , 1629  $\text{cm}^{-1}$ , 630  $\text{cm}^{-1}$ , to 3438  $\text{cm}^{-1}$ , 1631  $\text{cm}^{-1}$ , 636  $\text{cm}^{-1}$ , and 585  $\text{cm}^{-1}$  for magnetic kaolinite. In addition, the peaks with chitosan shifted from 3430  $\text{cm}^{-1}$ , 1639  $\text{cm}^{-1}$ , 1596  $\text{cm}^{-1}$ , and 142  $\text{cm}^{-1}$  to 3457  $\text{cm}^{-1}$ , 1655  $\text{cm}^{-1}$ , 1676  $\text{cm}^{-1}$ , and 1460  $\text{cm}^{-1}$ , respectively, for -OH, -CH, -CN and -NH<sub>2</sub> vibration stretching, thus confirming successful synthesis process. The adsorption mechanism of both metals unto MKa/4%CB was through ion-exchange and coordination bonding, due to the more active sites of -NH<sub>2</sub> and -OH functional groups contributed by CB. The optimization factors were achieved at pH 6, initial concentration of the adsorbate of 20mg/L, adsorbent dosage as 100mg, temperature 25°C, and shaking speed at 200rpm. The adsorption isotherm studies fitted with Langmuir, which indicated homogeneous and monolayer adsorption sites were available as compared to heterogeneous sites. Additionally, the calculated adsorption capabilities were 90.9 and 88.5 mg/g for Pb(II) as well as Cd(II). The adsorption kinetic data plot demonstrated that both metal ions fitted into the pseudo-second order, thus demonstrating a chemisorption process. Synthesized adsorbents could be used for 4 cycles without any substantial adsorption capacity reduction. Huang et al. [25] prepared a phosphorylated(P), CS-coated Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> NPs adsorbent (Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/CS/P) and used it to remove Pb(II). The purpose of phosphorylating the adsorbent was to enhance the Pb(II) adsorption performance of the adsorbent and also alter the selectivity of other metals' adsorption. At pH 6.0, the researchers conducted multi-ions solution competitive assays. The results revealed that Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/CS/P had a 10-fold greater ability to remove Pb(II) than other metals, with a distribution coefficient of 0.75 L/g, while Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/CS exhibited highly discriminating sorption towards Ag, according to the multi-ions solution competitive trial. The removal of Pb(II) improved when compared to the uncoated silica adsorbent due to the presence of P. The Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/CS/P could provide greater acidity protection against any probable Fe leaching after the acidity studies at pH 1. Furthermore, the XPS and FTIR spectral analyses showed that the exceptional adsorption process and the discriminatory tendency to remove Pb(II) were mostly

manipulated by coordination connecting phosphate groups on the adsorbent surface of the material. The Langmuir adsorption capacities were 151.8, 131.8, 27.7 and 25.8mg/g for Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/CS/P, Fe<sub>3</sub>O<sub>4</sub>/CS/P, Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/CS, Fe<sub>3</sub>O<sub>4</sub>/CS, with the R<sup>2</sup> values 0.999, 0.986, 0.933 and 0.945, respectively; indicating a monolayer - surface-active sites interaction with a homogeneous adsorbate. The kinetic adsorption of Pb(II) unto Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/CS/P, Fe<sub>3</sub>O<sub>4</sub>/CS/P, Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/CS, and Fe<sub>3</sub>O<sub>4</sub>/CS revealed the best fit for pseudo-second order than the -pseudo-first order with R<sup>2</sup> > 0.992, thus indicating a chemisorption process.

Liu et al. [26] synthesized magnetic anaerobic granule sludge/chitosan (M/CS/AnGS) composite adsorbent and applied it for Pb(II) and Cu(II) removal from the water solution. The purpose of the modification is to enhance the process of adsorption through the addition of some functional groups. The FTIR revealed the presence of broad band spectra for -NH<sub>2</sub> and -OH were responsible for the adsorption and confirmed the success of the synthesis process. The optimum parameters influencing the adsorption capability of the CS/AnGS were an adsorbent dosage of 16 mg, pH 6, and a short contact time of 30 min. The highest adsorption capacities were 97.97 and 83.65 mg/g for Pb(II) and Cu(II), respectively. These were higher than the works of Zhang et al. [27] with 50.4 and 57.1mg/g for Pb(II) and Cu(II) in that order. The adsorption kinetics model of Pb(II) and Cu(II) is better suited to the pseudo-second order compared to the pseudo-first order with the R<sup>2</sup> values of 0.999 and 0.993, respectively, suggesting the chemisorption adsorption process. The Langmuir isotherm showed monolayer active site adsorption with R<sup>2</sup> of 0.9801 and 0.9920 respectively, indicating homogeneous adsorbate and a monolayer active site. Zhang et al. [24] prepared magnetic cyanoethyl chitosan beads (M/CNS/CS) and applied them for Co(II) removal from wastewater. The magnetite was prepared through co-precipitations and the cyanoethyl was used for the functionalization of the composite. The adsorption capacity towards Co(II) was enhanced by the grafting of cyanoethyl groups onto the CS. The FTIR revealed the presence of broad band spectra for -NH<sub>2</sub> and -OH around 3000-3700  $\text{cm}^{-1}$  in chitosan, 1598  $\text{cm}^{-1}$  and 1132  $\text{cm}^{-1}$  for -NH<sub>2</sub>, and a new band at 2250  $\text{cm}^{-1}$  for -CN

spectrum due to the successful synthesis of M/CNS/CS. Hence, -CN, OH and -NH<sub>2</sub> were responsible for the removal of Co(II). The optimal factors were achieved at pH 6.72, contact time 4h, initial concentration of cobalt ions 500 mg/L, and temperature 308K. Additionally, the second-order model, as well as the Langmuir model data, were the best fittings with the coefficient of regression  $R^2 > 0.99$ . This indicated that the chemisorption process and a monolayer surface-active sites interaction. The adsorption capability of 17.92 mg/g was less when compared to the adsorption capacity of 34.92mg/g obtained by Lee, et al. [42]. In that study, they used the same purpose of treatment of wastewater containing Co(II) heavy metal ions. The thermodynamic factors indicated endothermic and spontaneous process with the values as  $\Delta H = +28.76\text{KJ/mol}$ ,  $\Delta S = +128.7\text{J/mol}$  and  $\Delta G = -12.22\text{KJ/molK}$ .

Zhang et al. [27] synthesized a facile magnetic-responsive CNT/chitosan aggregate adsorbent (CNT/CS) and applied it for the removal of various contaminants via a two-step approach. The purpose of the modification is to enhance the adsorption process through the addition of some active sites due to functional groups. FTIR characterization revealed the spectra of 3450-3500 cm<sup>-1</sup> for -OH stretching vibration in CNT, 1656 cm<sup>-1</sup> and 1595 cm<sup>-1</sup> due to carbonyl group of CNT, and 3480 cm<sup>-1</sup> and 3375 cm<sup>-1</sup> for -OH and -NH<sub>2</sub>, respectively, which showed the formation of CS on top of CNT, thus confirming successful synthesis process of the adsorbent. The result of adsorption capacity for heavy metals by CNT/CS aggregate observed the order of Fe(III)>Cu(II)>Pb(II)>Zn(II), with adsorption capabilities of 68.8, 57.1, 50.4, and 16.6 mg/g in that order, perhaps due to electro positivity sequence. The mechanism of interaction was mainly due pi-pi stacking, cation-pi interactions, hydrophobic effect, and chelation tendencies of the metal ions. Meanwhile, the performance of CNT/CS was better than CNT alone due to the presence of the functional groups -OH, and -NH<sub>2</sub> on the CS which enhanced the removal of the contaminants. The isotherm kinetics for the metal ions well supported the kinetic isotherm model of pseudo-second order with  $R^2 \geq 0.997$ , close to unity implying a chemisorption adsorption process. Since the adsorbent could be reused as it could retain over 78% of its original

worth, the CNT/CS material demonstrated great potential in the removal of multiple pollutants from aqueous mixtures.

The adsorbent's crosslinked CS/g/PMAM through the method of grafting CS with poly(methacrylamide (g/PMAM) was synthesized by Sutirman and co-workers. They applied for removal of Cu(II) and Cd(II) in aqueous solution [28]. The modified CS was to improve acid resistance and also enhance the adsorbent's adsorption capacity toward the removal of metal ions in aqueous solutions. FTIR characterization showed the presence of -OH and -NH<sub>2</sub> functional groups at spectral bands of 3423 cm<sup>-1</sup> and 1615 cm<sup>-1</sup> in chitosan and bands shifted to 3423 cm<sup>-1</sup> and 1623 cm<sup>-1</sup> to confirm the successful synthesis of the adsorbent CS/g/PMAM. By comparing the functional groups, C-O, C=O, -OH, -NH<sub>2</sub>, and C-NH<sub>2</sub>, the X-ray photoelectron spectroscopy (XPS) analysis revealed that adsorption of both metal ions occurred on the surfaces of the adsorbent by chelation via C-O, C=O, and C-NH<sub>2</sub> functional groups. The behaviors of crosslinked CS/g/PMAM from metals were investigated. It was revealed that the solution pH played a major role in adsorption Cu(II) and Cd(II) favored pH 4 and pH 5, respectively. Their Langmuir maximum adsorption capacities were 140.9 mg/g and 178.6 mg/g, respectively, with a better fit than the Freundlich isotherm data proposing monolayer adsorption than the Freundlich isotherm. Pseudo-second order indicated a better fit ( $R^2 = 0.999$ ) than pseudo-first order, indicating that chemisorption or electron transfer was the dominant mechanism onto the crosslinked CS/g/PMAM. Additionally, the X-ray photoelectron spectroscopy (XPS) analysis revealed that adsorption of both metal ions occurred on the surfaces of the adsorbent by chelation via C-O, C=O, and C-NH<sub>2</sub> functional groups. Pooladi et al. [29] synthesized a new adsorbent of chitosan-hydroxyapatite-MNPs (CS/HAP/Fe<sub>3</sub>O<sub>4</sub>) and applied it for the removal of Cu(II) and Zn(II) from aqueous solutions. The purpose of the modification was to introduce some new functional groups active sites for the adsorption of the metal ions. The authors used chitosan and HAP because the two materials were low-cost and easily accessible, acquired from shrimp shells as well as bone ash, respectively. The adsorbent performances of CS/HAP/Fe<sub>3</sub>O<sub>4</sub> were better than the

HAP/Fe<sub>3</sub>O<sub>4</sub> due to the surface modification with the functional groups of the CS when compared. The FTIR characterization results showed the presence of the functional groups of -OH and -NH<sub>2</sub> to confirm the success of the synthesis process. The optimized removal experiment parameters employing fundamental composite design (CCD) together with response-surface-methodology (RSM) were 65 min contact time for Cu(II), initial concentration of 2.87 mg/L, Zn(II) initial concentration of 2.61 mg/L, pH 5.5 and adsorbent dosage 0.018g. The adsorption capabilities for Cu(II) and Zn(II) were 3.659 and 6.497mg/g, respectively. The authors attributed the low adsorption capacities that resulted to the synergistic negative influence of the cation on each other's adsorption behavior and perhaps their differences in the electrochemical series. The acquired adsorption isotherm data were well fit by the Temkin and Langmuir isotherms for Cu(II) and Zn(II), respectively, with coefficients of determination R<sup>2</sup> of 0.987 and 0.987, respectively, as compared to the Freundlich isotherm with R<sup>2</sup> of 0.912. The adsorption kinetics were pseudo-second order kinetic models for Zn(II) and Cu(II) with R<sup>2</sup> ≥ 0.99 indicating that the adsorption was chemisorption and a spontaneous process.

Feng et al. [30] synthesized magnetic/chitosan/bentonite (Fe<sub>3</sub>O<sub>4</sub>/CS/BT) aggregate adsorbent using organic components materials and applied it for the remediation of acid mine drainage containing Cr(VI). The purpose of the modification was to enhance the adsorption process. FTIR characterization showed the presence of -OH and -NH<sub>2</sub> functional groups at spectral bands of 3423 cm<sup>-1</sup> and 1615 cm<sup>-1</sup> in CS and bands shifted to 3423 cm<sup>-1</sup> and 1623 cm<sup>-1</sup> to confirm the successful synthesis of Fe<sub>3</sub>O<sub>4</sub>/CS/BT. The authors discovered that the adsorbent aggregates had excellent magnetism (20.0emu/g), high stability, and good performance for the removal of Cr(VI) with the maximum adsorption capability of 62.1mg/g from the synthetic aqueous solutions. The adsorption isotherm fitted into the Langmuir isotherm proposing monolayer adsorption more than the Freundlich isotherm. Additionally, the kinetic information well fitted into the pseudo-second kinetics indicating the chemisorption process. On top of that, the thermodynamic factors demonstrated that Cr(VI)

adsorption towards Fe<sub>3</sub>O<sub>4</sub>/CS/BT was exothermic as well as spontaneous in nature. The solution pH was an important factor for adsorption and was enhanced at pH 2.0 accordingly to the law of pKa. Besides that, Fe<sub>3</sub>O<sub>4</sub>/CS/BT was discovered to possess an exceptional adsorbent quality for actual acid mine drainage remediation of metals containing Ni, Zn, Fe, Cu, Cr, Pb, and Cd, with all their percentage removal > 84%. A study by Sun et al. [31] developed biopolymer chitosan/tannin (CS/TA) as an adsorption paper material for removing Cu(II) and Cd(II) from alkaline water solutions. The purpose of the chitosan was to promote flocculation on the paper material while both chitosan and tannin played the role of cross-linking on the paper material for modification. The FT-IR characterization revealed three distinct peaks at 1688, 1600, and 1200 cm<sup>-1</sup>, which correspond to the stretching spectral vibrations of C=O, -C=C- of the benzene ring, as well as -C-O- in the tannin, correspondingly. As a result, CS could substantially encourage flocculation of tannin in the CS/TA adsorbent. The CS/TA adsorbent removal ability might have been primarily supported by a complexation formation mechanism, with the maximum adsorption capacity accomplished at pH 9. Langmuir isotherms accurately matched the adsorption data with an R<sup>2</sup> value of 0.9904, which was higher than Freundlich with an R<sup>2</sup> value of 0.984, thus indicating a favorable monolayer surface adsorption, with outstanding Cu(II) and Cd(II) adsorption capacities of 684.93 and 813.01mg/g, respectively. The adsorption of the various heavy metals unto CS/TA was preferential in the order of Cu(II) > Cd(II) and that Cu(II) competed with Cd(II) for active binding sites at concentrations more than or equivalent to 200 mg/L.

Huang et al. [32] prepared a new adsorbent sodium alginate/carboxymethyl chitosan (SA/CCS) hydrogel beads polyacrylamide (SA/CCS/P) and modified kaolin (SA/CCS/K) in which a simple polyacrylamide modification kaolin procedure was developed to enhance the adsorption performance towards the removal of Cu(II). FTIR results showed the presence of the functional groups of -OH, -NH<sub>2</sub>, and -COOH which were responsible for the adsorption of Cu(II). The Langmuir adsorption capacities of adsorbents SA/CCS, SA/CCS/K, and SA/CCS/P, were 4.306, 4.621, and

5.515mg/g, respectively, showing that the modification due to polyacrylamide successfully enhanced the adsorption process and the increase due to presence of its functional groups. The increase proved that the adsorption of SA/CCS/P was better than the other adsorbents and therefore remained a good candidate for the removal of Cu(II) ions. The trend showed a substantially low removal ability which could be due to low interaction. The maximum adsorption capacity of Cu(II) onto SA/CCS/P was 5.516mg/g. Finding from both the kinetic and isothermal studies revealed that both Langmuir isotherm and pseudo-second were fitted into the adsorption process with both  $R^2$  greater than 0.999. This indicated a homogeneous surface and monolayer as well as chemisorption process. Furthermore, adding kaolin was modified to reduce the tendency of coexisting ions interference. The adsorption capacity remained above 82% after 5 cycles of the reused adsorption-desorption experiment. Zhang et al. [33] synthesized a versatile adsorbent from EDTA and chitosan biofunctionalized magnetic bamboo biochar (E/CS/M/BB) and applied it for the removal of methyl orange (MO), Cd(II), and Zn(II). Magnetite was prepared by the co-precipitation method before the addition of the bamboo biochar, while GA served as a cross-linker between the magnetic chitosan and the bamboo biochar (BB) to form E/CS/M/BB. It was found that EDTA reacted with E/CS/M and BB via the amidation method to finally obtain the new adsorbent. By comparison of the adsorbent's adsorption performance, E/CS/M/BB was better than BB due to the electrostatic attractions pi-pi bond, and hydrogen bonding, which were enhanced via the  $-NH_2$  and  $-COO^-$  functional groups from EDTA. FTIR characterization results showed the functional groups of  $-OH$ ,  $C=O$ ,  $C=C$ ,  $C-O$ ,  $N-H$ , and  $-NH_2$  to confirm the successful synthesis process. The maximum adsorption capacity at the optimum conditions were 305.4, 63.3, and 50.8 mg/g, for MO, Cd(II), and Zn(II), respectively. Pseudo-second order was more fitted with a  $R^2$  value of 0.9895-0.9982 for MO, Cd(II) and Zn(II) than the pseudo-first order with  $R^2$  values of 0.8541-0.9156, indicating chemisorption process. Additionally, the isotherm adsorption study revealed that Langmuir isotherm data was more fitted with the coefficient of determinations ( $R^2$ ) value of 0.9981-0.9999 for MO, Cd(II) and Zn(II)

than Freundlich with  $R^2$  values of 0.7658-0.8701, indicating a homogeneous adsorbate surface interaction with a monolayer adsorbent active site. Adsorption-desorption experiment demonstrated that the efficiency of E/CS/M/BB towards MO was still retained after eight rounds but decreased for Cd(II) and Zn(II) by 16.8% and 19.5% respectively, indicating the cost efficiency of the adsorbent.

Similarly, Karimi et al. [34] prepared a magnetic-based chitosan/ $Al_2O_3/Fe_3O_4$  (M/CS) nanocomposite adsorbent via ethylenediaminetetraacetic acid (EDTA) functionalization to improve the adsorption as new adsorbent (EDTA/M/CS). FTIR results showed a 1575-1639  $cm^{-1}$  shift in peaks for EDTA/M/CS showing the presence of amino group on M-CS via the vibrational bending of the amide with  $C=O$  and  $-COO^-$  on the surface of the adsorbent, thus confirming the successful synthesis process. By comparison, the EDTA functionalized M/CS adsorbent revealed that the adsorption capacity increased by about 14.3, 5.6, and 9.1 times towards Zn(II), Cu(II), and Cd(II), respectively indicating that EDTA/M/CS performed better than M-CS adsorbent. The maximum adsorption capacity of 43.93, 109.90, and 43.12mg/g for Zn(II), Cd(II), and Cu(II), respectively at pH 5.3. Finding from the isotherm studies revealed that Langmuir isotherm was mostly fitted into the isotherm data and could adequately explain the adsorption process with  $R^2$  greater than 0.99, indicating a homogeneous adsorbate surface interaction with a monolayer adsorption active site. Additionally, the adsorption kinetics fitted the pseudo-second order with  $R^2 > 0.99$  showing a chemisorption process. Furthermore, the thermodynamic study discovered that the adsorption process was exothermic and spontaneous with the values of  $\Delta H$ ,  $\Delta G$ , and  $\Delta S$  as -22.7KJ/mol, -10186.1J/mol, and 0.0451KJ/molK, respectively for Zn(II). Besides that, the values were -33.638 KJ/mol, -9797.21 J/mol and 0.0851J/molK, respectively for Cd (II). Additionally, -52.224 KJ/mol, -9129.58 J/mol and 0.1468J/molK, respectively for Cu(II) at 288K. Nasirimoghaddam et al. [36] synthesized a new adsorbent by immobilizing CS-coated magnetite (CS/ $Fe_3O_4$ ) and applying it for the removal of Hg(II) from industrial aqueous and oily samples. The preparation of  $Fe_3O_4$  was by co-precipitation of Fe(II)



and Fe(III) salts via  $\text{NH}_3$  solution before immobilizing chitosan on its' surface to enhance the adsorption of the Hg(II). FTIR characterization results revealed the Fe-O bonds and the -OH and  $-\text{NH}_2$  functional groups to confirm the successful synthesis process. The optimized parameters were temperature 289K, pH 6, adsorbent dose 10mg/ml, and 50mg/L initial concentration of adsorbates. The isotherm study revealed that the Langmuir isotherm was more fitted than the Freundlich isotherm with the  $R^2$  value of 0.999 indicating homogeneous adsorbate and monolayer adsorbent surface interactions. The process at 298K was endothermic with  $\Delta H$  value of +13,169.38KJ/mol, spontaneous with a  $\Delta G$  value of -60.998Kj/mol, and  $\Delta S$  as +41.969J/molK. This showed an increase in the randomness process, thus, suggesting that the solid/liquid interface interactions during the Hg(II) and the CS/ $\text{Fe}_3\text{O}_4$ . Furthermore, the adsorption-desorption study revealed that the adsorbent could retain its 85% potential after a few recycle adsorption processes. Jiang et al. [37] synthesized a new adsorbent of functionalized  $\text{SiO}_2$  coated MNPs with CS ( $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{CS}$ ) to remove Cr(VI) in an aqueous mixture. Three steps were involved in the synthesis process. Firstly, the preparation of  $\text{Fe}_3\text{O}_4$  by solvothermal reduction procedure, secondly, the preparation through silica coating of the  $\text{Fe}_3\text{O}_4$  to form  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  and lastly, by immobilizing of chitosan via glutaraldehyde as the cross-linker to form

$\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-CS}$  to increase the adsorption process. The FTIR characterization results showed the presence of the functional groups of -OH from adsorbed water molecules  $3436\text{ cm}^{-1}$  Fe-O at  $585\text{ cm}^{-1}$  from  $\text{Fe}_3\text{O}_4$ ,  $1083\text{ cm}^{-1}$  for Si-O, from  $\text{Fe}_3\text{O}_4/\text{SiO}_2$ , and  $-\text{NH}_2$  at  $1640\text{ cm}^{-1}$  from chitosan. The BET analysis showed  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4/\text{SiO}_2$  surface area as 24.0 and  $121.0\text{ m}^2/\text{g}$ , respectively, suggesting that porous silica was coated on top of magnetite to confirm the successful synthesis process. The possible adsorption mechanisms of the adsorbent towards Cr(VI) were reduction and electrostatic processes. The interferences adsorption experiment showed that the adsorbent had a strong affinity for Cr(VI) in the solution containing the ions of Zn(II), Cu(II), Cr(VI), Cd(II), and Ni(II). The researchers found that the adsorption capability of the adsorbent was high ( $336.7\text{ mg/g}$ ) towards Cr(VI), which was enhanced effectively via a simple technique of cross-linking. The pseudo-second order dynamic model for the adsorption methods well-fitted more than the pseudo-first-order kinetics with  $R^2 > 0.999$ , thus indicating a chemisorption process. The Langmuir isotherm model fitted better with the adsorption process than the Freundlich isotherm with  $R^2$  close to unity which showed a homogeneous phase with monolayer active sites. The recent advances in chitosan-based adsorbent materials for heavy metal removal [21-39] are summarized in Table 1.

Table 1. Chitosan-based adsorbent materials

Adsorbent	Metal Ions	q <sub>max</sub> (mg/g)	pH	Isotherm/Kinetics	References
Fe <sub>3</sub> O <sub>4</sub> /SH/CS	Pb(II)	235.5	7.0	Langmuir Pseudo 2 <sup>nd</sup> order kinetics	[21]
Fe <sub>3</sub> O <sub>4</sub> /ATP/EDTA/CS	Pb(II) Cu(II) Ni(II)	368.3 267.9 220.3		Langmuir Pseudo 2 <sup>nd</sup> order kinetics	[22]
MSCC/CS	Cu(II)	17.20	6.0	Langmuir Pseudo 2 <sup>nd</sup> order kinetics	[23]
MK <sub>a</sub> /4%CB	Cd(II) Pb(II)	90.988.50	6.0	Langmuir Pseudo 2 <sup>nd</sup> order kinetics	[24]
Fe <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> /CS/P	Pb(II)	0.75 L/g	1.0	Langmuir Pseudo 2 <sup>nd</sup> order kinetics	[25]
M/CS/AnGC	Pb(II) Cu(II)	97.97 83.65	6.0	Langmuir Freundlich isotherms	[26]
CNT/CS	Fe(II) Cu(II) Pb(II) Zn(II)	68.8 57.1 50.4 16.6	5.0	Langmuir Pseudo 2 <sup>nd</sup> order kinetics	[27]
CS/g/PMAm	Cu(II) Cd(II)	140.9 176.6	4-5	Langmuir Pseudo 2 <sup>nd</sup> order kinetics	[28]
CS/HAP/Fe <sub>3</sub> O <sub>4</sub>	Cu(II) Zn(II)	3.659 6.497	5.50	Langmuir Pseudo 2 <sup>nd</sup> order kinetics	[29]
Fe <sub>3</sub> O <sub>4</sub> /CS/BT	Cr(II)	62.01		Langmuir Pseudo 2 <sup>nd</sup> order	[30]
CS/TA	Cu(II) Cd(II)	684.9 813.0		Langmuir	[31]
SA/CCS/P	Cu(II)	5.515		Langmuir Pseudo 2 <sup>nd</sup> order	[32]
E/CS/M/BB	MO Cd(II) Zn(II)	305.4 63.3 50.8	5.0	Langmuir Pseudo 2 <sup>nd</sup> order	[33]
EDTA/M/CS	Zn(II) Cu(II) Cd(II)	-	5.3	Langmuir Pseudo 2 <sup>nd</sup> order	[34]
CS/Fe <sub>3</sub> O <sub>4</sub>	Hg(II)	-	3.0	Langmuir	[36]
Fe <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> /CS	Cr(VI)	336.7		Langmuir Pseudo 2 <sup>nd</sup> order	[37]

### Alginate-based adsorbents

Alginic acid or else its salt known as alginate is a biopolymer component of polysaccharides found in the colonies of a variety of algae species. It has a copolymer structure made up of layers of  $\beta$ -1,4-associated d-mannuronic acid (M-block) as well as  $\alpha$ -1,4-linked l-guluronic acid (G-block) [38]. The existence of a 2  $\mu$ m thick perforated holes wall of exine internal as well as the exterior surface of alginate, makes it easier for elements and compounds like heavy metals to adsorb. The recent advances in alginate-based adsorbent materials for heavy metal removal [39-44] are summarized in Table 2.

Ren et al. [39] produced new gel beads adsorbent from sodium alginate-carboxymethyl cellulose (SA/CMC) and utilized them to remove Pb(II) in a water mixture. The synthesis was successful via cross-linking of SA and CMC to enhance the adsorption of Pb(II). FTIR showed the functional groups of -OH and -COO in the complete synthesis of SA/CMC were responsible for complexation interactions with Pb(II). The authors verified parameters accountable for maximum adsorption of the Pb(II) and the results demonstrated that the initial adsorbate concentration was achieved at 5mg/L with adsorbent dose of 0.8g, and the temperature of 37 °C, and the vibration time of 18 hours. The adsorption experiment showed that Pb(II) adsorption unto the SA/CMC was greater than 99% under the optimum conditions. In addition, the author's comparative findings revealed that the Pb(II) removal efficiency of SA/CMC was significantly higher than that of traditional adsorbent CMC. Thus, they concluded that the SA could have improved the adsorption procedure possibly due to the functional groups on the SA. Additionally, the Pb(II) adsorption process unto the SA/CMC fitted the Langmuir adsorption isotherm, as well as the adsorption model depicted through a pseudo-second-order kinetic equation. Findings demonstrated that Langmuir  $R^2$  value of 0.718, Freundlich value of 1.96, while the Temkin of  $R^2$  was higher than 0.98. Thus, these demonstrated that both were homogeneous and heterogeneous adsorption sites of the adsorbent as well as both monolayer and multilayer surface sites were involved. The kinetic adsorption model also better fitted the pseudo-second order than the pseudo-first order

indicating chemisorption than the physisorption process. Cordova et al. [40] developed a new adsorbent made of alginate (Alg) as a matrix with xanthation (XA) to form adsorbent (XA/Alg) and employed it to remove Cu(II)Zn(II). The purpose of introducing Alg was to enhance the adsorption of metal ions through its suitable functional groups. The important parameters were studied such as the effect of reaction time and findings demonstrated that time ranged (from 4-12 hours), the types of the base suitable to control the pH values were discovered to be (NaOH-KOH), and the quantity of carbon disulphide was (2-10%v/v) to obtain the green materials. NMR methods were used to analyze the XA/SA adsorbent and the evidence of  $\beta$ -removal was found at 5.45 ppm. The findings from the NMR experiment in solid-state revealed that a shoulder was achieved at 182 ppm attributed to the C-S group. The EDS mapping procedure also confirmed the existence of the thiol (S element), whereas XRD showed a semi-crystalline structure. The chemical shifts of  $\delta$ (C=S) bands were at 863 to 805  $\text{cm}^{-1}$ , and  $\nu$ (C=S) bands were at 662 to 602  $\text{cm}^{-1}$ . The findings showed that the maximum adsorption capabilities of Zn(II) and Cu(II) occurred up to 47.30 and 86.40 mg/g, respectively higher than for maximum adsorption capabilities of values were 6.497 and 3.659mg/g respectively for Zn(II) and Cu(II) obtained by Pooladi et al. [29]

Fuks et al. [41] synthesized a new adsorbent by the combination of  $\text{Fe}_3\text{O}_4$  into calcium alginate gels (CaAlg) to form aggregate magnetic adsorbent material known as alginic ferrogels ( $\text{Fe}_3\text{O}_4/\text{CaAlg}$ ), utilized for the removal of cationic radionuclides; Am(III), Sr(II), Cs(I) and Eu(III) from aqueous mixtures. The removal of cations of radionuclides was achieved through the direct dosing of the solution mixed with sodium alginate/iron carbonyl with a 2 hours continuous stirring. The purpose of introducing alginate was to improve the adsorption of radionuclides metals through the suitable functional groups of -OH and -COO<sup>-</sup> through the modification by CaAlg. The optimized factors were obtained at 15g/L of iron carbonyl suspended in 1 L of an aqueous solution of sodium alginate and the addition of about 20 g  $\text{CaCl}_2$  to 1 L of the solution comprising the radioactive metals. These findings revealed that the percentage removals of the radionuclides were 30-100%. The author reported

the removal of cations of radionuclides were due to the calcium chloride ions exchange with Cs(I) which was less favorable because of the smaller charge of the ions except that it could be trapped in the adsorbent pores. On the other hand, the ions of Am(III) and Eu(III) could efficiently be removed from the aqueous solution much better than the monovalent Cs(I) and divalent Sr(II) ions. Consequently, the authors concluded that other metal salts could not considerably influence the removal efficiency as much as the roles played by the number of charges on the ions. Lee et al. [42] synthesized a new adsorbent by incorporating Ca/Alg, zinc-ferrocyanide (Zn/FC), and Cyanex 272 to yield an adsorbent composite beads of ZnFC-Cyanex 272-alginate (ZCA), which was then used to remove Cs(I) and Co(II) in water. The Ca/Alg beads were produced through the cation exchange and cross-linking between sodium alginate (Na/Alg) and calcium chloride ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) in the presence of water. FTIR results showed the -OH, and -COO- in Ca/Alg, -CH stretching vibrations in ZnFC-Cyanex 272 as well as spectral peaks at  $1164\text{cm}^{-1}$ ,  $960\text{cm}^{-1}$ , representing the P=O and C-O-P stretching vibration respectively: thus, confirming the successful synthesis process. By comparing the adsorbent's performances (Ca-Alg and ZCA), the latter was greater than the former due to the presence of some suitable functional groups of -OH, and -COO- in ZCA adsorbents which were responsible for binding with the metal ions. The maximum adsorption capability for Cs(I) and Co(II) was 71.73, and 34.92 mg/g, respectively. The adsorption procedure fitted both Langmuir isotherm, as well as pseudo-second-order kinetics, to support the adsorption process, indicating the isotherm revealed homogeneous and monolayer surface interactions and a well-fitting chemisorption kinetic process. Additionally, the ZCA composite beads could demonstrate an exceptional selectivity toward Cs(I) and Co(II) despite the presence of competitive cations of K(I), Fe(II), Na(I), and Ni(II). Consequently, the authors concluded that ZCA composite beads could be reused 3 times after the adsorption-desorption studies and could still maintain their excellent potential for the selective removal of Co(II) and Cs(I) in contaminated water.

Song et al. [43] synthesized a new adsorbent of Ca/Alg

and applied it for the removal of rare earth metals (i.e., La, Sr, and Li). The purpose of the composite through modification with alginate is to enhance the adsorption process. FTIR characterization showed the presence of -OH, -COO<sup>-</sup>, and -C-O functional groups in the Ca/Alg. Findings revealed that the adsorption capacities of Ca-Alg adsorbent towards La(I), Sr(I), and Li(I) were 0.562, 6.695 and 8.625mg/g, respectively. However, the adsorption capacities were generally low because the amount of adsorption depended on the number of the valences of the metal ions which was related to electrostatic interaction. The kinetics model and the isotherm studies were explored for the adsorption process and the findings demonstrated that Li(I) did not fit into both the pseudo-second-order and the pseudo-first-order process at both high and low initial concentrations with the  $R^2 = 0.781$  and  $0.825$  respectively, while data for Sr(I) and La(I) both matched the pseudo-first as well as the pseudo-second order with  $R^2$  values 0.999 as well as 1.00 respectively. This favored at lower and higher concentrations suggesting that both were physisorption and chemisorption processes. Additionally, the Freundlich isotherm data were more fitted for the adsorption process for La(I), Sr(I), and Li(I) with an  $R^2$  value of 0.981, 0.974, and 0.983, respectively, thus this was more than the Langmuir isotherm data with  $R^2$  values of 0.928, 0.927 and 0.814 respectively, indicated a heterogeneous layer surface interaction. Furthermore, the presence of co-existing ions could not largely affect the adsorption process towards the removal of trace metal ions. Dai et al. [44] developed a unique polysaccharide-based thermos-receptive hydrogel adsorbent material made from SA as well as 2-hydroxy-3- isopropoxy propyl/starch (HIPS) to form (HIPS/SA) and utilized it for the Cu(II) removal. The complex and permeable structure, laden with carboxyl groups, was to provide enough adsorption sites necessary for Cu(II) removal. The FTIR characterization results clearly showed the presence of suitable functional groups of O-H, C-H, C-O-C, -COO<sup>-</sup> and C=O in SA, HIPS/SA to confirm the successful synthesis process. The BET surface area of HIPS/SA hydrogel was  $2.7785\text{ m}^2/\text{g}$ , this was much greater than SA alone with  $0.284\text{ m}^2/\text{g}$  surface area, thus indicating a good surface area for adsorption for HIPS/SA. The conditions for the adsorbent's thermal

reversible responsive swelling/shrinking actions of adsorbent were examined as well as the effects of pH as well as the initial amounts of Cu(II) on adsorption ability. These findings showed that adsorbent dosage of 50 mg, pH 5.5, shaking speed, 200 rpm, temperature, 20 °C, contact time of 48 hours, and initial amounts of 100 mg/L. The maximum adsorption capacities of SA gel, as well as HIPS/SA, were 21.11 and 25.80 mg/g respectively indicating that there was a significant increase in adsorption upon the modification of SA by the HIPS. The adsorption isotherms and kinetics of the adsorbent further demonstrated that the adsorption of Cu(II) onto the HIPS/SA adsorbent which was a better fit for the Langmuir as well as the pseudo-second-order models, with both  $R^2$  as 0.999 and the maximum adsorption capacity for Cu(II) onto the HIPS/SA being 25.81 mg/g. Additionally, the adsorption studies revealed that the adsorbent could still be stable even after 5 cycles with the adsorption capacity of HIPS/SA decreasing from 19.83 to 15.23 mg/g.

Ahmed et al. [45] synthesized a new grafting polymer through the grafting of diphenylamine (DPA) on Na/Alg to form a composite (Na/Alg/g/DPA) adsorbent and applied it to remove Co(II) in wastewater solution. FTIR functional groups of -COOH, -COO-, -C-O, C=C, and C=N. From FTIR, they suggested a polymer structure, thus confirming that the grafting of DPA onto NaAlg in the synthesis process was successful. The adsorption performance of NaAlg-g-DPA was higher than NaAlg due to the existence of suitable functional groups as a result of the grafting of the DPA. The BET surface area of Na/Alg/g/DPA and Na/Alg was found to be 13.164 m<sup>2</sup>/g and 2.4459 m<sup>2</sup>/g, respectively, indicating that the grafting of DPA onto Na/Alg had greatly increased the surface area for the adsorption process, thus, making the adsorption of Co (II) more feasible. The enhancement of the external area for the one-step manufactured composite was linked to its mesoporous properties, which were crucial in Co(II) adsorption, according to the author's report. Additionally, the authors discovered that the best grafting efficiency was 97.5% at the initial concentration of 0.5M. The results of the kinetic study fitted well into the pseudo-second-order reaction mechanism of Na/Alg/g/DPA with adsorption capacity up to 17.2711 mg/g and an  $R^2 = 0.9998$ . Consequently,

the linear plot, the second order kinetics model had  $R^2 > 0.99$ , indicating a chemisorption process. Additionally, the adsorption isotherms studies revealed that the Langmuir, Freundlich, and Temkin data were all fitted with a linear plot with the coefficient of determination,  $R^2 > 0.9$  which indicated that the adsorption process was both homogeneous and heterogeneous surface interaction. Allouss et al. [46] used an ionotropic gelation approach to produce a new adsorbent from graphene-oxide (GO) combined with condensed carboxymethyl cellulose-Alginate (CMC/Alg) hydrogel nanoparticles as (CMC/Alg/GO) adsorbent and was applied to remove Cu(II) from water solution. FTIR results showed the presence of -OH, and -COOH functional groups in both graphene oxide and alginate to confirm the successful synthesis process and the functional groups were responsible for Cu(II) adsorption. The authors studied the adsorption of Cu(II) particles onto the adsorbent under various experimental settings and discovered that the best-optimized conditions were achieved at an adsorbent dosage of 2g/L, an initial amount of 150mg/L, a contact period of 90 minutes, a temperature of 398K, and a pH of 5. CMC, CMC/Alg, and CMC/Alg/GO were compared for the adsorbent's adsorption performances, thus results also demonstrated that embedded CMC-Alg/GO beads had a superior adsorption capacity to the natural CMC/Alg beads owing to a synergetic influence between the functional units of the GO and the CMC/Alg matrix. The adsorption capabilities at equilibrium for CMC/Alg, and CMC/Alg/GO, were 22.10 and 39.96 mg/g at 1% addition of GO. Subsequently, the adsorption capacity increases to 41.72 and 64.00 mg/g with the addition of 3 and 5% of GO, respectively, indicating that the adsorption capacity is GO dependent. It was clear that the modifications improved the adsorption process when the data were compared. Additionally, the pseudo-second-order adsorption kinetics was well fitted, with  $R^2$  values varying from 0.7974 to 0.989 which was better than the values within the range of 0.953 to 0.995 fittings for the pseudo-first order. Furthermore, both the Langmuir isotherm model and the Freundlich isotherm showed the  $R^2$  values of 0.999, indicating that both physisorption and chemisorption processes were the rate control mechanisms. The intraparticle distribution model was also investigated, with the conclusion that the

adsorption process was a progression of external adsorption as well as intraparticle distribution.

Hassan et al. [47] synthesized an efficient adsorbent by functionalizing a multi-walled carbon nanotube (CNT) (CNT/CONH<sub>2</sub>) with an amide functional group (CONH<sub>2</sub>) followed by an imprinted network of sodium alginate (NaAlg) containing hydroxyapatite (HAP) to form the new adsorbent (NaAlg/HAP/CNT). They then applied it to remove Co(II) from wastewater. The purpose of the -CONH<sub>2</sub> group addition and the modification was to enhance the metal adsorption process onto the adsorbent. The FTIR characterization revealed the presence of the functional group of -C-N from CNT, -CCOH from NaAlg, and the phosphate group from the HAP to confirm the successful synthesis process. The adsorption conditions were optimized and the findings revealed that the maximum adsorption capacity of Co(II) onto the NaAlg/HAP/CNT adsorbent

was 394.5mg/g with a BET surface area of 163.4m<sup>2</sup>/g greater than those of NaAlg/HAP with 33.1m<sup>2</sup>/g and NaAlg/CNT with 72.9m<sup>2</sup>/g, indicating a good surface area for adsorption of Co(II). By comparing the adsorption capacities of adsorbents, it was discovered that NaAlg/HAP/CNT with 394.5 mg/g was greater than NaAlg/HAP with 355.2 mg/g and greater than NaAlg/CNT with 354.7 mg/g, indicating that that the adsorption capacities were enhanced through the modifications. Furthermore, the investigated kinetics model was found to be fitted into the pseudo-second-order and the Langmuir isotherm with the R<sup>2</sup> higher than 0.99 indicating a chemisorption process and a monolayer surface, respectively.

The adsorption process was both endothermic and spontaneous. The recent advances in alginate-based adsorbent materials for heavy metal removal [39-47] are summarized in Table 2.

Table 2. Alginate-based adsorbent materials for the removal of metal particles in aqueous mixtures

Adsorbent	Metal Ions	q <sub>max</sub> (mg/g)	pH	Isotherm/Kinetics	References
SA/CMC	Pb(II)	-	5	Langmuir Pseudo 2 <sup>nd</sup> order	[39]
XA/Alg	Zn(II) Cu(II)	47.30 86.40	7.0	-	[40]
Ca/Fe <sub>3</sub> O <sub>4</sub> /Alg	Sr (I)Cs (I) Eu(I)	30.00% 80.00% 71.73%	3.5-4.5	-	[41]
Ca/Alg/ZnFC	Cs(I) Co(II)	71.73 34.92	-	Langmuir Pseudo 2 <sup>nd</sup> order	[42]
Ca/Alg beads	Cs(I) Sr(I) La(I)	01.64 93.82 99.30	7	Langmuir Freundlich	[43]
HIPS/SA	Cu(II)	25.81	4.5	Langmuir Pseudo 2 <sup>nd</sup> order	[44]
NaAlg/g/DPA	Co(II)	91.60	10.0	Temkin's Pseudo 2 <sup>nd</sup> order	[45]
CMC/Alg/GO	Cu(II)	-	5.0	Langmuir Pseudo 2 <sup>nd</sup> order	[46]
NaAlg/HAP/CNT	Co(II)	394.5	8.4-9.3	Freundlich Pseudo 2 <sup>nd</sup> order	[47]

### Sporopollenin-based adsorbents

*Lycopodium clavatum* (sporopollenin, (Sp)) is among the biopolymer materials which can be utilized as an adsorbent with an exceptionally safe biomacromolecule. It exists freely in nature as a segment of the external mass of spores and dust which makes it impervious to attacks by inorganic acids and soluble bases [49]. It possesses an exceptional property that can stay in topographical layers for more than a century while maintaining its full morphological qualities, and this proposed great steadiness of Sp at exceptional requirement. However, the complete chemical structure of the Sp is yet to be discovered, and it also has a stable inter-chain ring structure of aromatic compound containing carbon, hydrogen, and oxygen in a stoichiometry of  $C_{90}H_{144}O_{27}$ . Moreover, its functional group is the hydroxyl structure making it accessible for modification in huge quantities. Along these lines, the hydroxyl group fills in as anchorage targets for metal atom complexation just as an extension of the needed surface functional group and with the combination of different other materials with high affinity for metal [44]. MNPs can be manipulated with Sp to give magnetic sporopollenin (Msp). These manipulations of Msp have been reported to be utilized in the removal of a wide range of poisons, for example, metal ions pollutants [49].

The various Sp-based adsorbent materials for the removal of heavy metal particles in water solution are summarized in Table 3 [51-56]. Furthermore, Sayin, et al. [51] synthesized a new adsorbent calix[4]arene Sp-based on the adsorbent (SP-Calix) and applied it for the removal of Cr(VI) from an aqueous mixture. The adsorbent was made through the method of immobilization of dihydrazine amide derived from p-test-butylcalix [4] arene on the modified Sp. FTIR characterization. The results showed the presence of the required functional groups of carbonyl and isocyanate to confirm the successful synthesis process. The batch-wise adsorption method of analysis was used to optimize numerous experimental factors and the results were achieved at pH 5, shaking speed 175 rpm, initial concentration  $1.0 \times 10^{-4} \text{ mmol/dm}^3$ , and temperature of  $25^\circ\text{C}$ . Additionally, the maximum adsorption capability was calculated to be 28.07 mg/g. The isotherm study showed that among the three isotherms; Langmuir,

Freundlich, and Dubinin-Radushkevich, Freundlich were all found to be the most suitable to describe the adsorption process with the  $R^2$  value close to unity. Meanwhile, the  $R^2$  value for Langmuir was 0.8945. Additionally, the thermodynamic study showed that the value for  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  were found to be +41.01, +222.48, and +30.88KJ/mol which indicated endothermic, randomness, and spontaneous sorption process. Ünlü & Ersoz, [52], synthesized the new adsorbent dithiocarbonate/sporopollenin (DTC/SP) and applied it for Pb(II), Cd(II) as well as Cu(II) metal ions removal. The purpose of introducing sporopollenin was to enhance the adsorption performance of the dithiocarbonate. FTIR results showed the presence of the functional groups of DTC-SP was well captured from the functional groups of DTC and Sp to confirm the successful synthesis process. DTC/SP could adsorb metal ions better than the DTC when comparing the adsorbents, due to the presence of the functional groups of Sp. The mechanism of interaction was that of the DTC/SP chelating exchanger process. The operating pH for Cd(II), Pb(II), as well as Cu(II) metal particles were 7, 5.5, and 4, respectively, and the contact period ranged from 30 min to 7 hours, according to the author's findings. The isotherms studies revealed the maximal adsorption capacities for disclosed Cd(II), Pb(II), and Cu(II) were 7.09, 94.73, and 17.35 mg/g, in that order. The Langmuir  $R^2$  values for the metal ions of Cu(II), Pb(II), as well as Cd(II), were 1.00, 0.9976, and 0.9951, respectively indicating a good fit process, and a homogeneous adsorbate and a monolayer surface interaction. Additionally, the Freundlich correlation coefficients  $R^2$  for Cd(II), Pb(II), and Cu(II) were 0.9225, 0.9949, and 0.9572 in that order, while the Dubinin-Radushkevich(D-RK)  $R^2$  value for Cu(II), Pb(II), as well as Cd(II), were 0.9795, 0.9992, and 0.949, respectively. Both Langmuir and D-R isotherms were foreseen by the isotherm with homogeneous and conventional surfaces, i.e., homogeneous, and heterogeneous surfaces of the adsorbate unto the monolayer and multilayer sites of the adsorbent, hence, both Langmuir and D-R isotherms were predicted. Furthermore, the kinetic forecast of the pseudo-second-order process with  $R^2$  values of 0.9975, 0.9996, and 0.9997 for Cu(II), Pb(II), and Cd(II) respectively, outperformed the fit for the pseudo-first order process

with  $R^2$  values of 0.9791, 0.9902, and 0.9548 for Cu(II), Pb(II), as well as Cd(II) in that order. Furthermore, the thermodynamic parameters  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  values were computed as endothermic, randomness, and spontaneous after the graphical reading of the investigational data for the adsorption of Pb(II), and Cu(II), as well as Cd(II) ions to the DTC-SP. On top of this, the mechanism for the process of adsorption was revealed to be an ion exchange process in which the DST/SP is behaving as a chelating exchanger because the functionality present on the DST and adsorption took place through the exchange of valences between the resin and the adsorbent.

Hassan et al. [53] synthesized a new effective adsorbent through APTES functionalized magnetic sporopollenin-based silica-coated (MSP/SiO<sub>2</sub>/NH<sub>2</sub>) and graphene oxide (GO) to form GO/SiO<sub>2</sub>/MSP/SiO<sub>2</sub>/NH<sub>2</sub> and applied for hazardous Pb(II) ions removal from aqueous solution. The purpose of the modification and functionalization of the GO was to enhance the adsorption process. FTIR characterization results showed the presence of the -OH, and -COOH which confirmed the successful synthesis process, and these functional groups were responsible for the adsorption of the metal ions. The researchers discovered that the new adsorbent GO/SiO<sub>2</sub>/MSP/SiO<sub>2</sub>/NH<sub>2</sub> at the optimized experimental conditions of pH 6, with a 20 mg amount of adsorbent dosage, initial concentration of 100 mg/L the highest adsorption capabilities realized for Pb(II) was 323.5 mg/g. The adsorption process was studied by utilizing the Langmuir and Freundlich isotherms, and the kinetics with pseudo-first order along with pseudo-second-order models. Findings from this study revealed Langmuir isotherms with an  $R^2$  value of 0.9994 fitted better than the Freundlich adsorption isotherm with an  $R^2$  value of 0.5129. Meanwhile, the maximum adsorption capacity was found to be 323.5 mg/g for Pb(II). Additionally, findings showed that the pseudo-second order proved a better fitted with an  $R^2$  value of 0.9999 for Pb(II) than the pseudo-first-order with  $R^2$  values of 0.4262. In the same manner, the models affirmed a multilayer adsorption process followed by a chemisorption and physisorption model for the targeted metal ion. The thermodynamic study showed  $\Delta H$  value of +99.901KJ/mol,  $\Delta S$  value of +0.349KJ/mol, and  $\Delta G$  value of -6.627KJ/mol indicating endothermic,

randomness, and spontaneous process. The authors discovered that the generation studies showed that the potential of the adsorbent only decreased by 8.6% after the 10<sup>th</sup> round with adsorption capacity maintained at 295m/g thus showing a good recovery, eco-friendly and consequently concluded that the adsorbent shows good future potential to remove lead ions from wastewater.

Ren et al. [54] created a new modified EDTA/chitosan-SiO<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub> (EDCMS) adsorbent and used it for the removal of heavy metal ions (Pb(II), Cu(II), as well as Cd(II) from water solution. CMS was created by modifying the surface of chitosan-SiO<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub> with EDTA on top of the water/soluble carbodiimide as a cross-linker in a buffer blend. The purpose of EDTA was to enhance the adsorption process. FTIR characterization showed the functional groups of C=O, COO<sup>-</sup>, and N-H to confirm the successful synthesis process due to the combination of CMS and EDTA via the amide bonds. The most effective optimized conditions for the heavy metal ions removal by the EDCMS were achieved at pH 5, the dosage of 1.0g/L, and contact duration of 360 minutes. The maximal adsorption capacities of EDCMS for Cd(II), Pb(II), and Cu(II) ions were 64,41, 108.98, and 48.55 mg/g, respectively. The Langmuir isotherms investigation supported the sorption process with  $R^2$  values of 0.996, 0.995, and 0.999 for Cd(II), Pb(II), as well as Cu(II), respectively, over Freundlich, with  $R^2$  values of 0.812, 0.912, and 0.947 for Cu (II), Pb(II), and Cd (II) ions respectively. The kinetic study fitted well into the pseudo-second order with  $R^2$  values of 0.999 for Cu(II), Pb(II), and Cd(II) ions, respectively, better than the pseudo-first order with  $R^2$  values of 0.918, 0.980, and 0.906 for Cu(II), Pb(II), and Cd(II) ions correspondingly. Furthermore, both the EDCMS and CMS adsorption kinetics isotherm supported the mechanism of the pseudo-second-order kinetic model, and their equilibrium data were successfully matched with the Langmuir isothermal model. Additionally, at pH 5.0 (25 °C), the maximum adsorption capability of CMS was found to be 2.54, 9.32, and 55.64 mg/g for Cu(II), Pb(II), and Cd(II) ions, respectively, demonstrating the selective adsorption of Cu(II) ions, while the values of EDCMS were 64, 41, 108.98 and 48.55 mg/g, for Cd(II), Pb(II) and Cu(II) ions



correspondingly. The maximum adsorption capacities of EDCMS and CMS towards the removal of metal ions when compared clearly showed that the presence of EDTA enhanced the adsorption process through the modifications. Both EDCMS and CMS adsorption processes were endothermic, and the recycle studies demonstrated that after 12 rounds of reusability, EDCMS decreased by roughly 25% of its adsorption ability for heavy metal ions.

Recently, Bilgic et al. [55], prepared new adsorbent materials from a boron dipyrromethene (BODIPY) derivative which was immobilized on a sensor, then modified on 3-(Aminopropyltrimethoxysilane (APTES) to produce a microcapsule fluorescent sensor adsorbent (Sp/APTES/monoBODIPY) and applied it for Cu(II) the removal and selective sensitive detector. The Cd(II) used was from alkaline mixtures. FTIR results showed the presence of functional groups such as C=C, C=O, and -C=O, Si-O, OH, -NH<sub>2</sub> as well as the C-N bond present in both Sp-APTES and Sp-APTES-monoBODIPY adsorbent to confirm the successful synthesis process and the functional groups were responsible for the removal of Cu(II). The adsorbents Sp/APTES/monoBODIPY and Sp/APTES, when compared, in terms of adsorption performance, the former could adsorb Cu(II) better than Sp-APTES due to some suitable functional groups which was confirmed by FTIR. The maximum adsorption capacity of the Sp/APTES/monoBODIPY adsorbent unto Cu(II) was 25 mg/g. The authors reported that both the kinetics model and isotherms study revealed that pseudo-second-order kinetics and Langmuir adsorption were both fitted into the adsorption process with R<sup>2</sup> higher than 0.99.

Ahmad et al. [56] synthesized a new adsorbent of piperazine-functionalized/magnetic/sporopollenin hybrid adsorbent (MNPs/sp/HEP) and applied it used for the removal of Pb(II) as well as As(III) in water. The purpose of the functionalization with the HEP is to enhance the process of metal adsorption. FTIR results showed the presence of the functional groups of -OH, -COOH, C=N, and -NH<sub>2</sub> confirmed successful synthesis processes and the functional groups were also mainly responsible for the adsorption of the metal ions. The metal ions removal under optimized parameters was

achieved through a batch-wise method with optimum adsorption capacities ( $q_m$ ) be 13.36 mg/g and 69.85 mg/g for the Pb(II) and As(III), respectively. The experimental data analysis using the non-linear equations for the Langmuir and Freundlich isotherm model was additionally investigated. The findings revealed that the R<sup>2</sup> values of the linear for Pb(II) demonstrated higher for the non-linear plot for the analysis of both isotherms. However, the opposite results are shown in AS(III), where the R<sup>2</sup> values for the non-linear plot for both isotherms were relatively higher than the linear. Hence, AS(III) fitted better with the non-linear plots. The thermodynamic studies of the adsorption process revealed that the removal of both Pb(II) and As(III) ions was spontaneous and exothermic as  $\Delta G$  and  $\Delta H$  were both negative according to the findings by the researchers. This proved that the association of the adsorbate at the solid/solution interface was a random process. When comparing adsorbents performance, MNPs/sp/HEP showed a 119% rise in maximum adsorption capacity for Pb(II) as compared to MNPs/sp. This might be due to competition among the Pb(II) and As(III) ions for the insufficient active adsorption sites on MNPs/sp/HEP. Thus, based on the results the new adsorbent MNPs/sp/HEP proved to be an effective material for metal ions removal from aqueous solutions. Sargina et al. [57] synthesized natural polymers as biosorbents from two biomacromolecules and applied them for heavy metals removal. The components of the adsorbent were Cs, a versatile derivative of chitin, and Sp, a biopolymer with outstanding mechanical properties, and great resistance to chemical and biological reactions to form CS/Sp microcapsules which were prepared via a cross-linker. FTIR characterization showed the functional groups of hydroxyls, and carbonyl/carboxyl to confirm the combination of CS and Sp to form CS/Sp microcapsules. The adsorption performance of the microcapsules (CS/Sp) and the natural CS applied for the removal of Cu(II), Cd(II), Cr(III), Ni(II), and Zn(II) ions at various metal ions concentration, pH, amount of adsorbent, temperature, and contact time. The adsorption isotherm model fitted the Langmuir isotherm data and the adsorption capacity of the CS beads was found to be 85.16, 86.56, 51.47, 34.04, and 46.42 mg/g for Cu(II), Cd(II), Cr(III), Ni(II), and Zn(II), respectively. While,

the CS/Sp beads showed greater affinity for the ions at 92.78, 179.85, and 47.54 mg/g for Cu(II), Cr(III), and Ni(II), respectively, values of 16.86 and 16.34 mg/g for Cd(II), and Zn(II) were lower, respectively. Thus, the study revealed that the Sp enhanced ion sorption capacity of Cd(II) and Zn(II). Additionally, these findings from the adsorption isotherm studies revealed that both the Langmuir and the Freundlich isotherm fitted the adsorption process indicating both homogeneous and heterogeneous adsorbate and both monolayer and multilayer adsorbent interaction were involved. These authors stated that sporopollenin itself had an affinity for the metal ions due to the functional hydroxyl, carbonyl/carboxyl, and ether moieties present in its structure. Sargin et al. [58] synthesized bio-based sorbents, chitosan/sporopollenin (CS//Sp) especially by cross-linked chitosan (CS), with glutaraldehyde (GA) and combined with Sp to form (CS/GA/Sp) and applied for the removal of heavy metal. The metal adsorption behavior of chitosan-based sorbents was largely affected by the kind of cross-linking agent and degree of cross-linking. In the study, the authors described the preparation of chitosan/sporopollenin (CS/Sp) microcapsules cross-linked with various amounts of chitosan/glutaraldehyde (GA) ratios. The CS/GA/Sp were modified with 0.3, 0.9, and 1.5 mL of GA solution (in 25% water v:v) for 1.50 g of Cs. FTIR characterization. The results showed the presence of the functional groups of -OH, -C-N, -C=N, and -NH<sub>2</sub> to confirm the successful synthesis process. The adsorption performance of the microcapsules was studied for the removal of Cu(II) at different optimized conditions such as concentrations, contact time, amount of adsorbent, temperature, and pH. These findings showed that the maximum adsorption capacities of Cu(II) removal based on 0.3, 0.9, and 1.5mL GA impregnated CS microcapsules, which were 88.9, 100.4, and 80.7 mg/g, respectively. This indicated that the adsorption process could be best achieved at 0.9mL of GA. The outcomes

of the investigation of the equilibrium adsorption isotherm data of the microcapsules demonstrated a better fit to the Freundlich isotherm model than the Langmuir isotherm data. Additionally, the affinity of the CS microcapsules towards Zn(II), Cd(II), Ni(II), and Cr(III) in presence of Cu(II) was revealed upon further investigation. Similarly, the findings revealed that the GA/Cs ratio could greatly affect the metal ions adsorption performance and the physicochemical nature of the microcapsules. Consequently, the results unveiled, implies that when CS microcapsules were cross-linked with 0.9 mL of GA solution, this could give a superior Cu(II) ion adsorption capacity and could be cost-effective sorbents in water treatment. The sporopollenin-based adsorbent materials for the removal of heavy metals in water solution are summarized in Table3 [48-60].

#### **Tannic acid-based MNPs adsorbents**

Tannic acid (TA) is a natural organic polyphenol comprising sugar esters. Researchers have been modifying MNP with tannic acid to enhance surface properties and adsorption capacity [61]. Tannic acid, a humic substance comprising carboxyl and hydroxyl functional groups was a well-established metal scavenger, due to the abundant phenolic hydroxyl and carbonyl functional groups on the framework. The complexation and precipitation of polyphenols with polyvalent cations in aqueous mixtures were well understood from the works of the earlier investigator that the nano adsorbent (Fe<sub>3</sub>O<sub>4</sub>/TA NPs) had possible applications to remove metals from aqueous systems [62]. While some other industrial application of TA is known to be an adsorbent to remove various kinds of chemical species, it is also known to contain hydroxyl groups which show affinity as adsorbents for metal ions recovery [62,63].

Table 3. Sporopollenin-based adsorbents

Adsorbent	Metal Ions	q <sub>max</sub> (mg/g)	pH	Isotherm/Kinetics	References
<b>P-t-bCalix/Sp</b>	Cr(VI)	-	1.5	Freundlich	[51]
<b>DTC/SP</b>	Cu(II) Pb(II) Cd(II)	-	4	Langmuir	[52]
<b>MSP/ SiO<sub>2</sub>/NH<sub>2</sub></b>	Pb(II)	325.5	6.0	Langmuir	[53]
<b>EDCMS</b>	Cu(II) Pb(II) Cd(II)	-	5.0	Langmuir Pseudo-2 <sup>nd</sup> order	[54]
<b>Sp/APTES/ monoBODIPY</b>	Cu(II)	25	-	Langmuir Pseudo-2 <sup>nd</sup> order	[55]
<b>MNPS/sp/ HEP</b>	Pb(II) As(III)	-	6.5	Pseudo-2 <sup>nd</sup> order	[56]
<b>CS/Sp microcapsules</b>	Cu(II) Cd(II) Cr (II) Zn(II) Ni(II)	-	-	Langmuir	[57]
<b>CS/GA/Sp</b>	Cu(II)	100.4	-	Freundlich	[58]

Zou et al. [64], used a simple coordination procedure to produce a novel TA-based adsorbent (TA/Zr) and used it for the removal of Pb(II). The purpose of the TA is to introduce some phenolic carboxyl functional groups to enhance the metal ions adsorption process. FTIR characterization results confirmed the presence of some prominent phenolic hydroxyl and carbonyl functional to show the successful synthesis process. Batch adsorption experiments were used to explore the effect of varied initial Pb(II) concentrations on the adsorption capabilities of TA/Zr. The author's findings, disclosed that the maximum adsorption capability was achieved as 99.0 mg/g at 25 °C and an initial Pb(II) concentration of 170 mg/L. The Langmuir, as well as Freundlich models R<sup>2</sup> value of 0.99, which were well fitted into the adsorption process showing monolayer Pb(II)

adsorption on the surface of TA/Zr with the theoretical maximum adsorption capacity of 100 mg/g. The results explored for the kinetics of Pb(II) adsorption onto TA/Zr demonstrated that the pseudo-second-order > pseudo-first-order model, indicating that chemisorption was the dominant process. TA/Zr had adsorption selectivity for Pb(II) which was further investigated when mixed with binary solutions such as Zn(II), Cu(II), Co(II), Cd(II), Ni(II), and Pb(II) at a concentration of 150 mg/L. The Pb(II) removal was 64.62 mg/g significantly higher than the removal of other metal ions by the TA/Zr with values of 1.26, 3.68, 4.39, 1.14, 3.94 mg/g, for Zn(II), Cu(II), Co(II), Cd(II), Ni(II), respectively. Therefore, TA contributed substantially more to TA/Zr selectivity than the Zr species. Furthermore, the authors inferred that the presence of phenolic hydroxyl (e-OH) structures on the

surface of TA was responsible for the significant adsorption in which the hydroxyl groups of oxygen atoms synchronized with Pb(II), while hydrogen atoms of hydroxyl groups could be substituted and released as hydrogen ions, in this way showed, a proton exchange mechanism for the selective Pb(II) removal, as confirmed by the results of the characterization and batch adsorption assessments. Huang et al. [65] used a fast and scalable production strategy to produce tannin-based magnetic permeable organic polymers (TA/MOPs) adsorbent for the removal of methylene blue (MB) as well as Pb(II) from water mixtures by using workable tannin acid as construction blocks through an azo connection reaction without losing any phenolic eOH groups. FTIR characterization results showed the presence of some prominent phenolic hydroxyl and carbonyl functional to confirm the successful synthesis process. The results of VSM characterizations showed the value TA/MOPs saturation magnetization which was 17.6 emu/g. This indicated that the amount of MNPs separated throughout the reaction process could be controlled. For the BET surface area of TA/MOPs, results showed the presence of high unique surface areas of 110.7 m<sup>2</sup>/g for adsorption process, and plentiful phenolic eOH groups which were capable of providing ultrahigh adsorption capacities and quick adsorption kinetics. The researchers also discovered that MB and Pb(II) adsorption equilibrium capacities of 1696mg/g and 252 mg/g, in that order, could be achieved in 10 min of contact time. The subsequent linear R<sup>2</sup> obtained from the pseudo-first-order model were 0.9425 and 0.9425 for MB and Pb(II), respectively. While the pseudo-second-order model, finely matched better with a high positive R<sup>2</sup> of 0.999 and 0.9908 for MB and Pb(II) respectively. Thus, the rate-controlling step for both Pb(II) and MB adsorption revealed chemical adsorption. The Langmuir isotherm data with an R<sup>2</sup> value of 0.999 was more suitably fitted than the Freundlich isotherm with an R<sup>2</sup> value of 0.9768 which indicated a monolayer chemisorption process governing the interactions of the components. Consequently, the outstanding stability and superparamagnetic attraction properties of the adsorbent could allow 5 cycles with great results without any substantial performance degradation (i.e., the adsorbent still retains over 90% of its adsorption potential),

thereby justifying the low-cost efficiency.

Huang et al. [66], formulated an adsorbent from polyethylene polyamine (P/P) and tannic acid (TA) as (P/P/TA), and encapsulated them with Magaly-layered double hydroxide (LDH), to form an adsorbent (LDH-P-P/TA) and to remove Cu(II). The FTIR showed the broad spectral band at 3478cm<sup>-1</sup> for -OH due to LDH, 3478 cm<sup>-1</sup> spectra shifted to 3446 cm<sup>-1</sup> due to the formation of LDH/PP/TA, while spectral bands at 2880-2960 cm<sup>-1</sup> corresponded to C-H stretching vibration. New bands formed at 1707cm<sup>-1</sup> and attributed to TA and new bands at 1500 cm<sup>-1</sup> stand for C=C vibrational band in benzene and 1350 cm<sup>-1</sup> for C-O stretching vibration for TA acid groups and 1199 cm<sup>-1</sup> due to TA esters groups thus, confirming the successful synthesis process. The optimized conditions were all investigated as, contact time, solution pH, starting Cu(II) concentration, and temperature. The produced adsorbents LDH, PP/TA, and LDH/PP/TA gave the maximum adsorption of Cu(II) as 23.39, 27.78, and 41.56 mg/g respectively. Therefore, this indicated a progressive rise in the adsorption capacities with modifications. The adsorption ability of Cu(II) was considerably increased when LHD was added to the PP/TA polymer. Furthermore, the adsorption of Cu(II) onto the LDH/PP/TA was fitted into the pseudo-second order with an R<sup>2</sup> value of 0.997, as against the pseudo-first order with an R<sup>2</sup> value of 0.9766. In addition, the calculated q<sub>e</sub> full term? (q<sub>e</sub>) was close to the experimental with values of 42.62 and 41.56 mg/g in that order, indicating a good fit. Additionally, the isotherm favored the Langmuir isotherm over the Freundlich isotherm data, with an R<sup>2</sup> value of 0.9897 and 0.8488 respectively. Furthermore, the thermodynamic adsorption capacity was 58.70 mg/g with ΔG = -8.25KJ/mol and ΔH = 22.97KJ/mol, thus, revealing that the adsorption procedure was spontaneous as well as endothermic. The mechanisms of interaction were shown to be primarily mediated by electrostatic and complexation interactions towards the removal of Cu(II). Shi et al. [67], fabricated (TA/CS/MOF) a membrane-type adsorbent by blending and depositing chitosan, TA, and metal-organic structure (MOF, UIO-66) on the surface of polyether sulfone (PES) membrane. The adsorption-desorption of N<sub>2</sub> isotherm

demonstrated the specific surface area of TA/CS/MOF reduced from 598.2m<sup>2</sup>/g to 135.77m<sup>2</sup>/g after the addition of UIO-66 which reduced the pore volume to confirm the success of the modification in the synthesis process. FTIR characterization showed the presence of -OH, -C-O-C, and -NH<sub>2</sub> to confirm the synthesis process. The SEM images of MOF showed an open-pore surface, while TA/CS/MOF image confirm the successful coating. All these results showed that the MOF contributed a core to the disperse of the tannic acid/chitosan mixture in order to enhance the removal of pollutants. Additionally, under optimized conditions, the findings showed that when the proportion of MOF/Chitosan was combined, at 30%, pH at 3.5, and then the filtration for 200min, the pollutant removal achieved 99%. The improved driving force induced by the concentration polarity in the filtration was assumed to alter the capacity of the adsorbent in the dynamic filtration, which proved a pollutant load-up capacity was 3 times better than that of the static adsorption. The findings from the dynamic filtration process demonstrated that the data fitted both the pseudo-first order and pseudo-second order for most of the adsorption processes for the adsorbate with the  $R^2 \geq 0.99$ , suggested the process as a chemisorption rate-controlling step. Similarly, the Elovich model fitted the data with the value of  $R^2 \geq 0.99$  which showed that the diffusion was also influenced by the adsorption process.

Liu et al. [68], produced adsorbents from, poly(tannin-hexamethylenediamine) (PTHA), by changing the mole proportion of TA as well as hexamethylenediamine (HA) in a one-pot combination to produce a new adsorbent (PEG/PTHA) to remove Cr(VI). The results given were based on the effectiveness of Cr(VI) removal versus all made adsorbents according to the mole ratio formulation. The PEG/PTHA demonstrated an excellent adsorption performance with the mole ratio at TA/HA as 1:12.5. FTIR characterization results showed the presence of some phenolic hydroxyl and carbonyl functional to confirm the successful synthesis process. The adsorption experiment's optimum conditions were achieved at 24 h, pH 2 to 6, and an initial amount of 100mg/L. The process of adsorption for the kinetic equation was demonstrated to conform to the pseudo-second-order isotherm model with an  $R^2$  value of

0.99293 which was better than the pseudo-first-order kinetic,  $R^2$  value of 0.97335. This showed the chemisorption process dominating. Additionally, the highest adsorption capacity for the removal of Cr(VI) was 283.29 mg/g at 30 °C, depending on the isothermal curve appropriately described by the Langmuir model. On top of that, findings from the isotherm analysis revealed that Langmuir isotherm proved superior ( $R^2 = 0.9939$ ) over Freundlich ( $R^2 = 0.9084$ ) specified homogeneous adsorbate and monolayer as surface interactions. Meanwhile, the authors discovered and stated that the amount of highly toxic Cr(VI) had remained lowered to the less toxic Cr(III) for the duration of the adsorption process. Gao et al. [69], created a new adsorbent from TA/templated mesoporous silica nanoparticles (T/MSNs) by using a simple non-surfactant template technique. The dopamine functionalized T/MSNs to form (Dop/TMSNs) adsorbent, achieved by using a superficial and biomimetic coating approach and used to remove Cu(II). The purpose of functionalization of Dop on top of T/MSNs was to enhance the process of adsorption of the Cu(II) from an aqueous solution. FTIR characterization results showed the presence of some prominent phenolic hydroxyl and carbonyl functional to confirm the successful synthesis process. The results of the adsorption under optimized conditions were achieved at an initial concentration of 100 mg/L, a temperature of 298 K, a contact time of 180min, a pH of 5.5, and an adsorbent dose of 1.0mg/L. Additionally, the kinetic model investigation revealed that the pseudo-second-order model was better preferred ( $R^2 = 0.995$ ), above the pseudo-first-order model ( $R^2 = 0.827$ ). Meanwhile, the calculated adsorption capacity for the pseudo-second-order model was 45.4 mg/g, close to the experimental value of 42.8 mg/g. Furthermore, the results of the adsorption isotherm model revealed that the Langmuir model had a better fit with an  $R^2$  value of 0.994 as compared to the Freundlich model's  $R^2$  value of 0.948. This implied a homogenous adsorbate process and a monolayer adsorbent active site interaction. Moreover, Langmuir model's adsorption capacity was 58.7 mg/g, which was close to the experimental value of 55.6 mg/g. As for the K(I) and Na(I) concentrations had only a little impact on the adsorption process. The adsorbent's adsorption capacity was maintained at 89.2% efficiency

even after four recycling rounds. Yun Zhang et al. [70], developed a novel adsorbent multi-functional polymer hydrogel (Zr/DETA/TS) with a three-dimensional network structure and used it for the removal of Pb(II), Hg(II), as well as CrO<sub>2</sub>(IV) via organic-inorganic crosslinking. FTIR characterization results showed the presence of amino, hydroxyl, carbonyl, and phenolic hydroxyl in the as-prepared composite adsorbent to confirm the successful synthesis process, which was responsible for the metal adsorption process. The peak spectral band at 150cm<sup>-1</sup> due to N-H bending vibrations of amino in the adsorbent was shifted to 1494 cm<sup>-1</sup> as well as 1497 cm<sup>-1</sup> after the adsorption of Pb(II) and Hg(II), respectively, indicated that ionic exchange and electrostatic interactions were the major adsorption mechanisms for Pb(II) as well as Hg(II) removal, while electrostatic attraction, inner-sphere complex, and esterification played a significant role in CrO<sub>2</sub>(IV). The optimal parameters for Pb(II), Hg(II), as well as CrO<sub>2</sub>(IV), were 200mg/L initial concentration, 780 min contact time, and pH 5, respectively. The Langmuir model adsorption capacity was 384.61, 416.66, and 125.00 mg/g for Pb(II), Hg(II), as well as CrO<sub>2</sub>(IV), respectively. The Langmuir model, fitted better with R<sup>2</sup> values of 0.9957, 0.9930, and 0.9949 for Pb(II), Hg(II), as well as CrO<sub>2</sub>(IV), than the Freundlich model, with R<sup>2</sup> values of 0.8314, 0.8817, and 0.8435, while the Dubinin-Radushkevich(DRK) isotherm model, with R<sup>2</sup> values of 0.9750, 0.9422, and 0.8940 for Pb(II), Hg(II), as well as CrO<sub>2</sub>(IV). The pseudo-second order was also found to be better at fitting the data than the first order, as shown by the kinetic models, which had R<sup>2</sup> values of 0.9995, 0.9999, and 0.9973, respectively. This indicated a chemisorption process over the pseudo-first order model, which had values of 0.9598, 0.9728, and 0.8290 for Pb(II), Hg(II), and CrO<sub>2</sub>(IV), respectively.

Deng et al. [71], fabricated out of MnO<sub>2</sub>(Mn), polyethyleneimine (PEI), and TA, which was a new adsorbent called (Mn/PEI/TA) and used it to remove Cu(II) and Cr(VI) from effluent solution. FTIR characterization showed phenolic hydroxyl groups on the surface of TA and O-N on the surface of functional groups on the MnO<sub>2</sub>. This improved the removal of metal ions by complexation. According to the results of the experiment, the maximal adsorption capabilities of

the Mn/PEI/TA adsorbent towards Cu(II) as well as Cr(VI) were 121.5 and 790.2 mg/g correspondingly. The physicochemical interaction mechanism in the process of Cu(II) and Cr(VI) co-adsorption on the Mn/PEI/TA was also described using the surface complexation structure model. The complexation, solvation action, electrostatic force, and adsorbate-adsorbate lateral interaction, could be the factors for spontaneous interactions. Although chemical action was the major force significant to adsorption equilibrium, physical electrostatic contact was discovered to be the dominant factor in the primary stage. The scientists then remarked, however, that studying the adsorption on the adsorbent's surface, demonstrated that the Cr(VI) reacted with a few reducing agents. These reducing agents converted it into Cr(III) with the help of functional groups (hydroxylamine-NH<sub>2</sub>). The understanding of the adsorption mechanism could have aided in the advancement of heavy metal adsorbents and the addition of PEI/TA considerably aided the adsorption process, demonstrating that the Mn/PEI/TA adsorbent nanocomposite. Consequently, the authors discovered that the results from adsorption-desorption studies revealed that the adsorption capacity was reduced by 12% after recycling 5-times, showing favorable adsorbent for removing heavy metal ions. Zhu et al. [72] prepared TA-based on graphene aerogel adsorbent via the hydrothermal method by incorporating both graphene oxide(GO) and TA in a one-step method to form aerogel composite adsorbent (TRGA) and applied it to the removal of Pb(II) and Cd(II) from wastewater. FTIR results showed the presence of -OH broadband at 1120cm<sup>-1</sup>, and spectral peaks in 1750, 1695 cm<sup>-1</sup>, and 1614 cm<sup>-1</sup>. They were due to the stretching vibration of the ester group and ketone groups. The spectral, C=O. 3383 cm<sup>-1</sup> peak appeared for -OH groups while the peak at 1695 cm<sup>-1</sup> and 1614 cm<sup>-1</sup> disappeared to confirm that GO was present. BET surface area was confirmed to have a value of 122.2 m<sup>2</sup>/g with high porosity to enable the adsorption of metal ions. The TRGA maximum adsorption capacity toward Pb (II) and Cd (II) was achieved at 803.84 mg/g and 395.80 mg/g, respectively at pH 4. Findings from the isotherm studies revealed that both Langmuir and Freundlich's isotherm could adequately explain the adsorption process with R<sup>2</sup> values of 0.9924 and 0.9741, respectively.

Ucer et al. [73], developed a new TA immobilized on activated carbon (TA/AC) adsorbent and used it for the removal of Fe(III), Mn(II), Zn(II), Cd(II), and Cu(II). FTIR characterization results. This showed the presence of -COOH and -OH functional groups which were known to be metal ions scavengers. The optimal adsorption parameters were achieved at pH 2-8, a contact period of 60 min, and an adsorbent dosage range of 0.02-2mg. The percent metal ions removed for Zn(II), Cd(II), Cu(II), Mn(II), as well as Fe(III) under optimum conditions were 49.0, 60.1, 89.0, 45.0, and 70.4%, respectively at pH ranging from 5-8. Furthermore, the isotherm adsorption data revealed, that both Langmuir and Freundlich could appropriately explain the adsorption process. Langmuir  $R^2$  values for Zn(II), Cd(II), Cu(II), Mn(II), as well as Fe(III) were 0.989, 0.965, 0.992, 0.990, and 0.966, correspondingly, while Freundlich  $R^2$  values for Zn(II), Cd(II), Cu(II), Mn(II), as well as Fe(III) were 0.978, 0.955, 0.905, 0.989, and 0.935 correspondingly. Furthermore, the order of attraction based on removal by TA/AC and natural carbon was similar, with Mn(II) < Zn(II) < Cd(II) < Fe(III) < Cu(II) and electronegativities values being identical. Furthermore, in separate systems, the adsorption capacity of TA/AC increasing order of Mn(1.13) < Zn(1.23) < Cd(1.51) < Fe(1.77) < Cu(2.23) and in Cu(II) mixed competitive systems, Mn(1.11) < Zn(1.19) < Cd(1.48) < Fe(1.56) also in increased order. Thus, the principal adsorption mechanisms participating in the binding of metal ions were a combination of complex formation, ion exchange, and surface adsorption activities. Findings from the reusability study showed that the adsorbed-desorbed metal ions efficiently ranged from 90.2 to 98.4% by utilizing 0.1 M HCl without damaging the improved adsorbent. In

another development, a research conducted by Fan et al. [74] and core workers, a core-shell nano-structured MNPs biopolymer-based composite sorbent was synthesized by immobilizing persimmon-tannin (PT) on top of the overlay of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> microspheres to produce (Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/PT) adsorbent and applied for the removal of Pd(II), as well as Au(III). The main purpose of PT immobilization of the Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> microspheres is to introduce the presence of some phenolic hydroxyl functional groups to enhance the adsorption of metal ions. FTIR findings showed spectra at 575-589cm<sup>-1</sup> for Fe-O bond in Fe<sub>3</sub>O<sub>4</sub>, 794 cm<sup>-1</sup> and 1082 cm<sup>-1</sup> for Si-O-Si bond for coating of SiO<sub>2</sub> on top of Fe<sub>3</sub>O<sub>4</sub>, 3410 cm<sup>-1</sup> for -NH due to PT functionalization on top of Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>. 3396 cm<sup>-1</sup> and 1446 cm<sup>-1</sup> stretching vibrations were for O-H and C-C confirming the presence of phenolic -OH groups from tannin, thereby confirming the successful synthesis of the process. The adsorption capacities of the Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/PT unto Pd(II) and Au(III) under optimized conditions were shown to be 196.46 and 917.43 mg/g respectively, as applied for metal ions removal. The kinetic study revealed that pseudo-second-order with the correlation coefficient  $R^2$  value 0.9969 and 0.9996 for Au(III) and Pd(II) respectively, proved superior over pseudo-first-order with  $R^2$  0.9860 and 0.8712 for Au(III) and Pd(II). Hence, this indicated the chemisorption process. The Langmuir adsorption isotherm showed a better fit with  $R^2$  values of 0.9940 and 0.9937 for Au(III) and Pd(II) respectively than the Freundlich model with  $R^2$  values of 0.9279 and 0.8457 for Au(III) and Pd(II), thus, indicating a homogeneous adsorbate monolayer interaction surface site. The tannic acid-based adsorbent material for the removal of metal in an aqueous solution [61-74] is summarized in Table 4.

Table 4. Tannic acid-based adsorbents

Adsorbent	Metal ions	$q_{max}$ (mg/g)	pH	Isotherm/Kinetics	References
CS /TA	Cu(II)	6810	9.0	Langmuir	[ 61]
	Cd(II)	84.93			
TA/Zr	Pb(II)	170.0	3.3-3.7	-	[64]
TA/MOFs	Pb(II)	252.0	2-7	-	[65]
LDH/PP/TA	Cu(II)	41.56	-	Langmuir Pseudo 1 <sup>st</sup> 2 <sup>nd</sup> order	[66]
TA/CS/MOF	Cr(II)	99.0%	3.5	Pseudo 1 <sup>st</sup> 2 <sup>nd</sup> order	[67]
PEG/PTHA	Cr(IV)	283.3	2-6	Langmuir 2 <sup>nd</sup> order	[68]
DOP/TMSNS	Pb(II)	58.70	5.5	-	[69]
Zr/DETA/TS	Pb(II)	384.6	3-5	Pseudo 1 <sup>st</sup> 2 <sup>nd</sup> order	[70]
	Hg(II)	416.7			
	Cr (II)	125.0			
Mn/PEI/TA	Cu (II)	12.50	5.5	Langmuir	[71]
	Cr(II)	790.2			
TRGA	Pb(II)	803.8	4.0	Langmuir Freundlich	[72]
	Cd(II)	395.8			
TA/AC	Cu(II)	23.50	-	Langmuir Freundlich	[73]
	Cd(II)	17.80			
	Mn(II)	14.88			
		11.30			
Fe <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> /PT	Au(III)	917.4	5.0	Langmuir Freundlich Pseudo 1 <sup>st</sup> 2 <sup>nd</sup> order	[74]
	Pd(II)	196.4			



### Silica coated MNPs adsorbent

Numerous published works on the applications of the functionalized silica coated MNPs materials utilized as adsorbent raw material for heavy metal ions removal in aqueous media are readily available. For example, Zhang, et al. [75] produced a new MNPs adsorbent material of  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{NH}_2$  core-shell by the sol-gel controllable method and applied it to remove Pb(II) in contaminated natural water. The purpose of the functionalization of the  $\text{SiO}_2$  coated MNPs materials was to enhance the adsorption capacity of the adsorbent due to some suitable functional group.  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4/\text{SiO}_2$ , and  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{NH}_2$  were compared for the performances of adsorbents, the adsorption capacities towards Pb(II) which were 6.94, 42.85, 243.9 mg/g, respectively. These progressive increases were due to the adsorption of the -OH groups on  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{NH}_2$  caused by  $\text{SiO}_2$  coating of  $\text{Fe}_3\text{O}_4$  and the - $\text{NH}_2$  functionalization of the  $\text{Fe}_3\text{O}_4/\text{SiO}_2$ , to form  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{NH}_2$ . FTIR characterization results showed the presence of the spectral bands at  $1630\text{cm}^{-1}$  and  $3430\text{cm}^{-1}$  corresponding to the O-H vibration from water molecules as well as the presence of  $\text{NH}_2$  groups due to functionalization. BET results also showed the surface area of  $77\text{m}^2/\text{g}$  for  $\text{Fe}_3\text{O}_4$  and  $138\text{m}^2/\text{g}$  for  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{NH}_2$  hence, confirming the coating of  $\text{SiO}_2$  on top of  $\text{Fe}_3\text{O}_4$  with its surface endowed with functionalization due to APTMS. Under optimum parameters for uniform core-shell formation with a relatively high loading amino functionality at 5.45%, with the use of TEOS and APTMS for the sol-gel process, the researchers were able to remove the metal ions were ease with the aid of an external magnet. More findings demonstrated that the adsorbent could effectively remove Pb(II) with an adsorption capability of 243.9 mg/g at 25 °C. Both the Langmuir model and kinetic data were well fitted into the pseudo-second-order model with  $R^2 = 0.994$  against the Freundlich model with  $R^2 = 0.9684$ . This, indicated homogeneous adsorbate and a chemisorption process, upon the interpretation of the adsorption equilibrium process results. Additionally, the thermodynamic study showed that  $\Delta H = +18.058\text{KJ/mol}$ ,  $\Delta S = +73.237\text{KJ/mol}$  and  $\Delta G = -5.233\text{KJ/mol}$  showed endothermic, randomness and spontaneous process.

Zhang, et al. [76] synthesized a novel adsorbent of thiol-functionalized MNPs materials ( $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{SH}$ ) for effluent solutions. The surface-functionalized MNPs were exceptionally viable for the additional removal of Ag, Cd, Pb, Hg, As, and Ti metal ions from water solutions. The purpose of the surface modifications with the -SH group was to enhance the adsorption process through the functional groups. Findings from their experiments indicated that all metals bonded successfully with the -SH functional groups of the ligand, except for As, which binds more to the MNPs. Similarly, the MNPs materials were functionalized in conjunction with mesoporous silica, by further introducing an aminopropyl functional unit to produce the adsorbent ( $\text{Fe}_3\text{O}_4/\text{mSiO}_2/\text{NH}_2$ ) and applied for the removal of Cr(III) as a liquid solution and this was achieved with greater recovery. The adsorption capacity of the adsorbent containing just mesoporous silica ( $\text{Fe}_3\text{O}_4/\text{mSiO}_2$ ), was found to show an adsorption capacity of 36.91 mg/g at pH 5.4. However, further functionalization with aminopropyl ( $\text{Fe}_3\text{O}_4/\text{mSiO}_2/\text{NH}_2$ ) resulted in the rise in the adsorption capacity to 108.14 mg/g. This showed the - $\text{NH}_2$  group enhanced the adsorption process. The mechanisms of interaction between the adsorbent and the metal ions were ascribed to be the coordination of Cr(III) with the amine functional groups (- $\text{NH}_2$ ) combined with the electrostatic impacts of the silica surface. Additionally, the results from the isothermal studies revealed that Freundlich isotherms were better fitted into the isotherm data than the Langmuir isotherms with the  $R^2$  value of 0.99, indicating a heterogeneous solution and multilayer active surface interaction. Sabermahani et al. [77], reported the synthesis of a new adsorbent of polyaniline/maghemite magnetic nanocomposite ( $\text{PANI}/\text{Fe}_2\text{O}_3/\text{MNC}$ ) in which the polyaniline was used as an active agent by the method of polymerization of aniline and applied to remove Pb(II). The purpose of polymerization with aniline was to improve the adsorption process. FTIR characterization results confirmed the presence of some prominent aminophenol functional groups to show the successful synthesis process. The batch method was used for the adsorption study and the findings showed at optimized conditions were achieved at pH 6.0, adsorbent dosage of 40mg, and the equilibrium contact time was enhanced at

90 min. Additionally, the Freundlich adsorption isotherms were revealed to have a better fit with an  $R^2$  value of 0.97 than the Langmuir isotherm with an  $R^2$  value of 0.80. They found that pseudo-second order ( $R^2 = 0.984$ ) > the pseudo-first order ( $R^2 = 0.447$ ). This proved that a chemisorption process more than heterogeneous adsorbate interacting with multilayer active sites.

Similarly, Lin et al. [78], produced a new adsorbent of amino-functionalized  $\text{SiO}_2$  coated MNPs ( $\text{NH}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4$ ) to remove Cu(II) in water solution. An amino-functionalized  $\text{SiO}_2$  magnetite was synthesized with N-(3-trimethoxypropyl) ethylenediamine (TPED) as the surface modifier to enhance the metal removal. The adsorption performances of the adsorbents,  $\text{Fe}_3\text{O}_4$ ,  $\text{SiO}_2/\text{Fe}_3\text{O}_4$ , and  $\text{NH}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4$ , when compared, was obvious that there was a progressive increase in that order due to the modification which was expected to enhance the adsorption process. FTIR characterization showed that the  $-\text{NH}_2$  functional groups were key to the adsorption process. The optimum pH solution was achieved between the range of 5-6, and the maximum adsorption capacity was 10.41 mg/g. Adsorption isotherms studies revealed that equilibrium adsorption data were well fitted into the Langmuir isotherm equations with the  $R^2$  value close to unity than the Freundlich isotherms, indicating homogeneous adsorbate and monolayer adsorbent surface-active sites. Additionally, the kinetic isotherm revealed that the pseudo-second order best explained the adsorption kinetics with the  $R^2$  value close to unity than the pseudo-first order indicating the chemisorption process. The enthalpy energy  $\Delta H$  was found to be endothermic with the value of +26.92 kJ/mol. The authors discovered that the optimum conditions for adsorption of Cu(II) with the adsorbent  $\text{NH}_2/\text{SiO}_2/\text{Fe}_3\text{O}_4$  could also be better optimized by using the desorption solvent of a 0.1 M  $\text{HNO}_3$  concentration.

Jin, et al. [79], synthesized new magnetic mesoporous  $\text{SiO}_2$ -coated core-shell nanoparticles ( $\text{Fe}_3\text{O}_4/\text{m}/\text{SiO}_2$ ) adsorbents based on different  $\text{Fe}_3\text{O}_4$  core sizes. This was to evaluate the impact of the magnetic core sizes on the adsorption capability of adsorbent and to remove Cu(II). Meanwhile, the adsorption capability was discovered to

be 84.4mg/g for Cu(II). The findings revealed that magnetic core sizes were pH-dependent and have an influence on the magnetic properties of the various adsorbents as well as the structure of the mesoporous silica, specific surface area, and the different interactions with the surface moieties. The adsorption kinetics study for the various adsorptions unto the adsorbent revealed to be fitted to the pseudo-second-order kinetic model. This had well-proven that the adsorption process was a chemisorption process. Nodeh et al. [80] synthesized a new modified magnetic graphene oxide composite adsorbent ( $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{GO}$ ) and intended to remove As(III) and As(V) from ecological samples. The purpose of the modification with the GO was to enhance the adsorption process. Peaks in the FTIR spectrum for O-H at 3400  $\text{cm}^{-1}$ , C=O stretching vibrations at 1714  $\text{cm}^{-1}$  for carboxylic groups, C-O vibrations at 1036  $\text{cm}^{-1}$ , and C=C aromatic vibrations in GO at 1437  $\text{cm}^{-1}$  all indicated effective synthesis. The findings showed that the  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{GO}$  adsorbent exhibited a superior adsorption capacity towards As(III) along with As(V) with values of 7.51 and 11.40 mg/g, respectively. The adsorbent demonstrated the linearity of 0.05-2.0  $\text{ngml}^{-1}$  and the magnetic solid-phase extraction (MSPE) procedure was used for the pre-concentrations of the metal ions. The Langmuir model was better fitted into the adsorption process with the coefficient of determination;  $R^2$  being 0.9992 and 0.9985 for the ions of As(III) and As(V), in that order, than the Freundlich model with  $R^2$  0.9256 and 0.9754. The pseudo-second-order was better fitted with  $R^2$  0.9984 and 0.9968 than the pseudo-first order with  $R^2$  0.8181 and 0.9447 for As(III) as well as As(V), indicating the chemisorption process. The thermodynamic parameters gave correspondingly  $R^2$  0.9990 and 0.9998 as well. The  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  were 29.27KJ/mol, 0.09KJ/mol, and -0.45J/molK for As(III) and 40.75KJ/mol, 0.14KJ/mol, and -2.15KJ/mol for As(V) accordingly indicating endothermic and spontaneous process. Both As(III) and As(V) adsorption on the adsorbent were spontaneously negative when the adsorbent material was applied using the lake, tap water, spring water, and river tap water. The technique could give good relative recoveries of 72.55-109.71% and RSD of 0.1- 4.3 %, with  $n = 3$ . The reusability studies showed that the adsorbent could be reused 15 times in

an adsorption-desorption experiment with about 80% potential, to prove that the adsorbent was economically feasible.

Purwanto et al. [81]., synthesized a new adsorbent of a composite of rice husk and ash/activated carbon (AC) made from coconut shell which was subsequently combined with silica gel(SG) and also modified with 3-aminopropyltrimethoxysilane (APTES), through the technique of sol-gel to form (SG/APTES/AC) adsorbent, and was used to remove Pb(II) in aqueous solutions. FTIR characterization showed the functional groups of Si-O-Si from silica gel and -NH<sub>2</sub> from APTES to confirm the successful synthesis process. BET surface area of the SG/APTES/AC adsorbent was 290.23m<sup>2</sup>/g at 22°C, which showed a good surface area for adsorption. The results of the investigations revealed that the optimum pH for the adsorption was achieved at 5.0 and the adsorption equilibrium for Pb(II) was achieved within 20 min of the contact time. The Pb(II) adsorption onto the composite adsorbent was well fitted into the Langmuir isotherm model >Freundlich with the R<sup>2</sup> > 0.99 and the maximum and minimum adsorption capacity values were 46.94 mg/g and 29.72 mg/g, respectively.

Ahmad et al. [82] synthesized an adsorbent based on MNPs coated mixture of inorganic-organic material of nanocomposite (MNPs/SiO<sub>2</sub>/TSD/TEOS) to remove Ni(II) and Pb(II). Meanwhile, the purpose of the TSD-TEOS was used as a modifier hybrid to enhance the adsorption of the metal ions pollutants. FTIR results showed the spectral peaks at 3405cm<sup>-1</sup>, 2934 cm<sup>-1</sup>, 2873 cm<sup>-1</sup>, 1580 cm<sup>-1</sup>, 1475 cm<sup>-1</sup>, 1317 cm<sup>-1</sup>, 1051 cm<sup>-1</sup>, 788 cm<sup>-1</sup>, and 578 cm<sup>-1</sup> for the bonds of N-H, -CH<sub>3</sub>, -CH<sub>2</sub>, C-C, C-N, -NH<sub>2</sub>, Si-O, Si-C and Fe-O respectively. Extra spectral peaks of 3294 cm<sup>-1</sup>, 2934 cm<sup>-1</sup>, 1580 cm<sup>-1</sup>, 1317 cm<sup>-1</sup>, and 788 cm<sup>-1</sup> were observed for N-H, C-H, C-N, NH<sub>2</sub>, and Si-C, thus, confirming the successful synthesis process. The researchers discovered that the new adsorbent MNPs/SiO<sub>2</sub>/TSD/TEOS at the optimized experimental conditions of PH 5, with a 20 mg amount of adsorbent dosage, the highest adsorption capacity realized for Pb(II) and Ni(II) particles were 417, and 357 mg/g, respectively. The adsorption studies were conducted by utilizing the Langmuir and Freundlich

isotherms. The results showed that the Freundlich adsorption isotherm fitted more with the value R<sup>2</sup> of 0.997. This was higher than the Langmuir isotherms with an R<sup>2</sup> value, of 0.871, indicating more heterogeneous adsorbate and multilayer adsorbent active sites interaction. Additionally, findings from the kinetic study showed that the pseudo-second-order proved a better fit with R<sup>2</sup>-values 1.00 and 0.998 for Pb(II) and Ni(II) respectively than the pseudo-first-order with R<sup>2</sup> values 0.666 and 0.641 for Pb(II) and Ni(II) indicating a chemisorption process. The authors then argued that the newly synthesized adsorbent was different in structure and ability from those most prepared sol-gel-based adsorbents. The results gave a higher adsorption capacity for Pb(II) and Ni(II). Wang, et al. [83] synthesized a new adsorbent of thiol SiO<sub>2</sub> shell coated onto MNPs (Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/SH) by the hydroxylation method of Na<sub>2</sub>SiO<sub>3</sub> modified with thiol groups(-SH) and applied to remove Hg (II). The purpose of the -SH group is to enhance the metal adsorption process. FTIR revealed a Fe-O bond with an intense absorption band at 587cm<sup>-1</sup>, then after the silica coatings, a Fe-O band appeared at 1087 cm<sup>-1</sup> and for the thiol functionalization, a new spectral band appeared at 2586 cm<sup>-1</sup> for the -SH bond, thus Fe<sub>3</sub>O<sub>4</sub> was successfully coated by SiO<sub>2</sub> and functionalized by the -SH to confirm the success of the synthesis process. The researchers used SiO<sub>2</sub> shells as a protection to the iron core from being corroded or dispersed in acid solution. Their results have demonstrated that the adsorbent coating of the functionalized material, Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/SH showed an excellent adsorption property due to its superior adsorption capability with a rapid adsorption rate. The adsorbent exhibited a good adsorption capacity of 132.0 mg/g owing to the powerful interaction between the -SH group of the adsorbent material and the mercury. They were able to observe that the presence of the -SH groups and was also responsible for the step-up of the adsorption capacities model. The R<sup>2</sup> values were 1.00, 0.920, 0.985, and 0.934 for Langmuir, Freundlich, Temkin, and D-R isotherm models respectively. All R<sup>2</sup> > 0.920 implies that all four isothermal data could be used to explain the equilibrium adsorption process of the Hg(II) onto adsorbent. Additionally, the adsorption mechanisms depended mostly on the electrostatic interactions of the active sites of the adsorbent and the

Hg(II). Furthermore after five rounds of adsorption-desorption studies, the high adsorption capacity of the adsorbent was achieved in the first round and the subsequent values for the second to fifth rounds as 51.1, 42.3, 40.5, and 34.3 mg/g, respectively.

In another related development, Ghorbani et al.[84], a new adsorbent from magnetic-ethylene-diamine-modified graphene oxide (MEDFGO) was prepared to remove Cd(II) and Pb(II). The purpose of the modification with EDTA was to enhance the adsorption process through the  $-NH_2$  functional groups. FTIR results showed the functional groups of C-O, C-N from amide, and C-N from amine at  $1624$ ,  $1400\text{ cm}^{-1}$ , and  $1045\text{ cm}^{-1}$ , respectively, indicating the interaction between graphene oxide and ethylenediamine and the presence of a peak at  $578\text{ cm}^{-1}$  from  $Fe_3O_4$ . This confirmed the successful binding of EDGO and  $Fe_3O_4$ . The optimized parameters, namely pH, sorbent dosage, shaking rate, and desorption time, were found to be 6, 33.0 mg, 500 rpm, and 11 mins, respectively. The adsorption capacity of Pb(II) as well as Cd(II) onto the synthesized adsorbent was 10.9 and 10.3 mg/g, respectively. The pseudo-first order and pseudo-second-order equations, both well interpreted the kinetic process with  $R^2$  (0.9102-0.9901) and  $R^2$  (0.9584-0.9935) for Pb (II) and Cd (II), respectively. The Freundlich model data for the metal ions adsorption was better fitted with  $R^2$  0.9719 and 0.9795 for Pb(II) and Cd(II), respectively. The Langmuir model with  $R^2$  0.0100 and 0.9630 for Pb(II) and Cd (II), indicated a heterogeneous adsorbate and a multilayer active sites adsorbent interaction. The thermodynamic parameters were well fitted for both Pb(II) and Cd(II) with  $R^2$  0.9908 and 0.9894 respectively. Meanwhile, the  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  were 37.50KJ/mol, 217.08J/molK, and -39.13KJ/mol and 31.82KJ/mol, 176.12J/molK, and -30.35KJ/mol for Pb(II) and Cd(II) respectively indicated and endothermic as well as the spontaneous process of adsorption. Furthermore, the metal ions removal was discovered to be 99.6 and 99.4% for Pb(II) and Cd(II) respectively recovery after six times of the adsorption-desorption experiment. Santhosh et al.[85] synthesized a new MNPs composite adsorbent of ( $SiO_2/Co/Fe_3O_4$ ) nanoparticles, amine-functionalized with APTES ( $SiO_2/Co/Fe_3O_4/NH_2$ ) adorned on graphene oxide by

using solvothermal along with sol-gel processes to generate the adsorbent ( $SiO_2/Co/Fe_3O_4/NH_2/GO$ ) and applied the adsorbent for the removal of organic (black dye 1) and inorganic pollutants (Cr(VI) in effluent solutions. The purpose of the modification with APTES was to enhance the adsorption process through the  $-NH_2$  functional groups. FTIR characterization showed the presence of the functional groups of Si-O-Si in  $SiO_2$  coating of  $Fe_3O_4$ ,  $-NH_2$  in APTES functionalization and (epoxides,  $-OH$ , and  $-COOH$ ) groups from GO to confirm the successful synthesis process. The results showed that the synthesis processes were well captured in the characterization methods which showed that the  $SiO_2/Co/Fe_3O_4/NH_2/GO$  adsorbent was of good quality. Furthermore, black dye 1 and Cr(VI) had respective adsorption capacities of 130.7 and 136.4 mg/g on the  $SiO_2/Co/Fe_3O_4/NH_2/GO$  adsorbent, which were well fitted into the Langmuir isotherm than the Freundlich with  $R^2$  close to unity. . More so, the results showed that the adsorption was influenced by a maximum value of PH 2. Additionally, the kinetics study interpretation showed compliance with the pseudo-second-order kinetics model with a good fit for both pollutants. Furthermore, the adsorption-desorption studies demonstrated that  $SiO_2/Co/Fe_3O_4/NH_2/GO$  could retain its potential with 92% and 65% of Black dye 1 and Cr(VI), respectively even after five rounds to prove its worthiness as a material. Hence, it could be concluded that the material was good for the removal of organic and inorganic pollutants in effluent solutions.

### Conclusion

The environmental safety of water supply and efficient management of wastewater remains one of the global concerns. It is discovered that over the last seven years, there have been more notable advances in the development of biopolymer and magnetic-based adsorbents for the removal of pollutants from water and wastewater. The formulation of the adsorbent and the mechanism of the adsorption i.e., chelation, ions exchange, coordination, chemisorption, and electrostatic attraction adsorptions isotherms models, kinetic models, and thermodynamic parameters was applied for the elimination of different heavy metal pollutants in an aqueous environment were specifically discussed. The impact of physicochemical factors on the

performance of these adsorbents was also reviewed. Meanwhile, these magnetic biopolymers sorbents offered a faraway benefit of chemical interaction due to the presence of functional groups like the -OH and -NH<sub>2</sub> groups and magnetic properties for the separation during heavy metal removal. Accordingly, it could be established that the types of functional groups, as well as the surface area presented in the adsorbents, play significant roles in the removal of metals in both aqueous and wastewater environments. It was also discovered in the review that good proportion removal and optimum adsorption capabilities were achieved at optimal conditions. Consequently, the adsorption of these metals was either one of Langmuir, Freundlich, or some additional linear plot adsorption isotherms models. In addition, pseudo-second and first-order kinetics were crucial in determining the nature of the adsorption processes. However, much of the adsorbent produced by the scientists was in an aqueous solution that comprises the heavy metal of concern without the real sample interferences. Therefore, the potential researchers must perform research in real samples as well as in the industrial natural environment.

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