Original Article
cnj.araku.ac.ir

☑ Cite This: Colloid Nanosci. J. 3(1) (2025) 478-498 DOI: 10.61882/CNJ.3.1.478

Removal of Some Potentially Toxic Metal Ions and Dyes from Aqueous Solutions by Nanobiosorbent: A Review

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ARTICLE INFO

Article History:
Received Feb 16, 2025
Revised May 4, 2025
Accepted May 4, 2025
Published July 15, 2025

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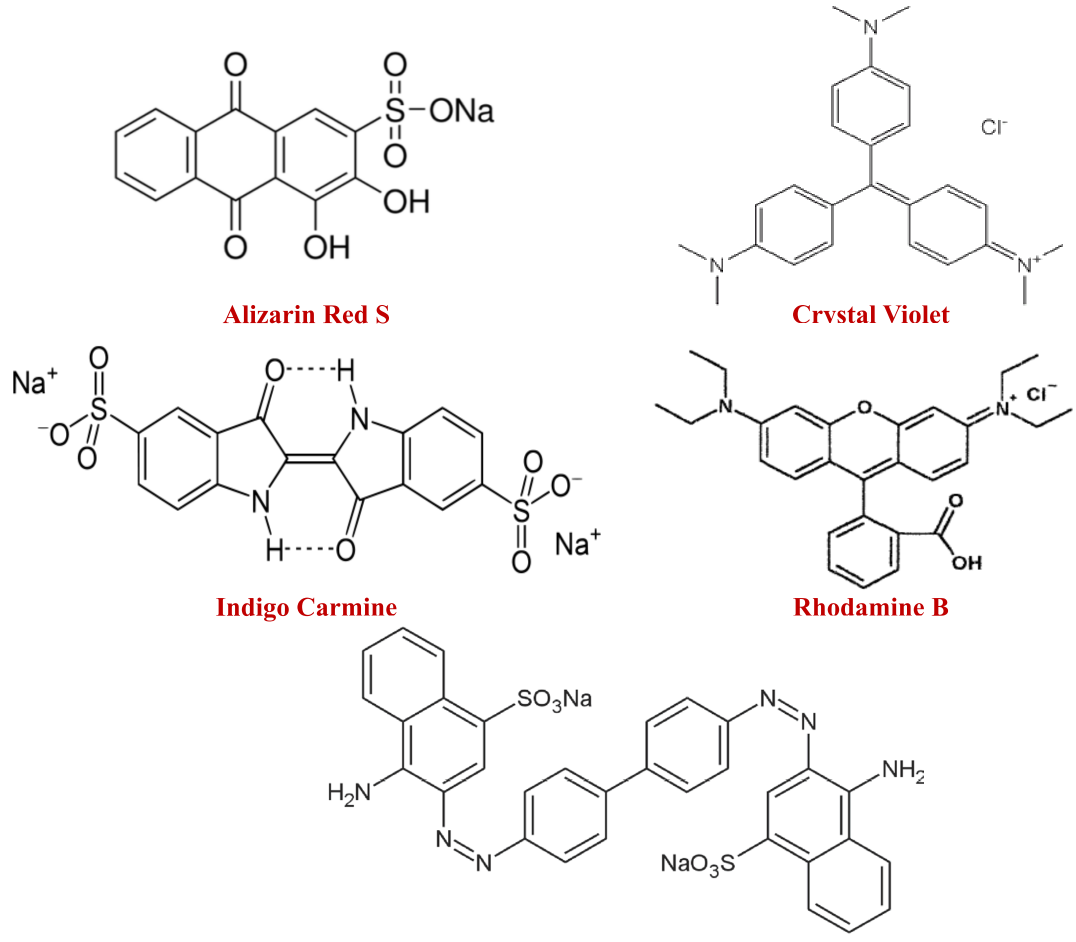
ABSTRACT

Adsorption techniques are widely used to remove certain groups of inorganic and organic pollutants from waters, especially those that are not easily biodegradable. Dyes and heavy metals represent one of the problematic classes. Currently, a combination of biosorption treatment and adsorption on nanomaterials is becoming more common for removal of pollutants from wastewater. This paper reviews the current nano-biosorbents applied to treat contaminants wastewater and their characteristics. Nanosized materials provide high surface area and specific affinity for heavy metals and dye adsorption from aqueous systems and biosorbents as inexpensive and biocompatible substances pose high efficiency to remove pollutants due to functional groups present in their structure viz. acetamido, alcoholic, carbonyl, phenolic, amido, amino, sulphydryl groups etc. This review examines some new nano-biosorbents, which are capable of uptake of hazardous pollutants, discusses the effects of various parameters such as pH, temperature, concentrations of pollutant, other ions, and biomass dose in solution, pretreatment method, etc. on adsorption, reports some elution and regeneration methods for adsorbent and summarizes the equilibrium and kinetic models used in batch and continuous biosorption systems which are important to determine the adsorption capacity of nano-biosorbents and to design of treatment processes.

KEYWORDS: *Nano biosorbent, Water treatment, Heavy metals, Synthetic dyes*

1.Introduction

Water pollution by toxic organic chemicals and heavy metals from the various industrial wastewater discharges has become a worldwide environmental concern. Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 g/cm^3 [1]. Water contamination by heavy metal ions is one of the most serious environmental problems due to their higher toxicities, nature of non-biodegradability, higher bioaccumulation in human body and food chain, and most likely carcinogenicities to humans [2-4]. These toxic ions usually come from several industrial activities viz. mining, refining ores, fertilizer industries, tanneries, batteries, paper industries, pesticides etc. and pose a serious threat to environment. The major toxic metal ions hazardous to humans as well as other forms of life found in contaminated surface water and groundwater as well as industrial wastewater are Cr, Fe, Se, V, Cu, Co, Ni, Cd, Hg, As, Pb, Zn, etc [5]. The release of these ions in water causes great threats to humans and other living organisms [6-9]. To date, numerous methods have been proposed for efficient heavy metal removal from aqueous solutions, i. e., chemical precipitation, chemical oxidation and reduction, filtration, ion exchange, reverse osmosis, electrochemical treatment, evaporative recovery and solvent extraction [5, 10–13]. Moreover, many industries such as textile, paper and pulp, printing, iron-steel, paint, petroleum, pesticide, coke, solvent, pharmaceutics, wood preserving chemicals, consume large quantities of water, and organic based



Alizarin Red S

Crvstal Violet

Indigo Carmine

Rhodamine B

Congo Red

Fig. 1. The chemical structure of some synthetic dyes frequently studied in adsorption.

chemicals such as synthetic dyestuffs [14]. Effluents of these industries may also contain undesired amounts of dyes and need to be treated. Synthetic dyes are classified as follows: anionic direct, acid and reactive dyes; cationic-basic dyes; non-ionic-disperse dyes [15-18]. The more common chemical classes of dyes used at industrial scale are the azo, anthraquinone, sulfur, triphenylmethyl, indigoid, and phthalocyanine derivates (Fig. 1) [19].

Dyes usually have a synthetic origin and complex aromatic molecular structures which make them more stable and more difficult to biodegrade. They may impart toxicity to aquatic life and may be mutagenic, carcinogenic and may cause severe damage to human beings, such as dysfunction of the kidneys, reproductive system, liver, brain and central nervous system [20–22]. Therefore, it is greatly essential to develop cost-effective technologies that can effectively remove toxic dyes from contaminated soil and water as heavy metallic waste has been increasingly discharged to the natural environment in many places in the world. In spite of the accessibility of many techniques to remove these pollutants from wastewaters as legal requirements, such as chemical oxidation, coagulation, membrane separation process, electrochemical and aerobic and anaerobic microbial degradation, these methods are not very successful due to suffering from many limitations [18, 23].

Among different approaches, adsorption has been found to be superior to other techniques for water reuse regarding initial cost, flexibility in design and operation and, in many cases, it will generate high-quality treated effluent. In addition, owing to the reversible nature of most adsorption processes, the adsorbents can be regenerated by suitable desorption processes for multiple use [5, 24], and many desorption procedures are of low maintenance cost, high efficiency, and ease of operation [25]. Adsorption also as a well known equilibrium separation process and an effective method for water decontamination applications does not result in the formation of harmful substances [26–29]. To date, numerous approaches have been studied for the development of cheaper and effective adsorbents. Many non-conventional low-cost adsorbents, including natural materials, biosorbents, nano-sized materials and wastes from industry and agriculture, have been proposed by several researchers. Some of the reported sorbents include clay materials (bentonite, kaolinite), zeolites, siliceous material (silica beads, alunite, perlite), agricultural wastes (bagasse pith, maize cob, rice husk, coconut shell), industrial waste products (waste carbon slurries, metal hydroxide sludge), biosorbents (chitosan, peat, biomass) and others (starch, cyclodextrin, cotton) [30-32].

The present review article deals the compilation of the newer achievements in the adsorption processes developed for the removal of dyes and heavy metals from water and wastewater and the technical applicability of various non-conventional low-cost adsorbents based on nano-biosorbents for water treatment. On the other hand, the current review highlights the various nanosized biosorbents as well as composites of nanomaterials and biosorbents that have been used as sorbents for pollutant removal and critically discusses the efficiency of contaminant removal from aqueous solution vs. nano-biosorbents characteristics. Moreover, the aim of this review is to develop a vision for nano-biosorbents as adsorbents of the future for wastewater treatment by discussing highly promising yet so far under- or unexplored nano-biosorbents. For this, a list of adsorbents literature has been compiled.

2. Adsorbent literature

2.1. Nanosorbents

Nanomaterials are mainly classified into groups due to their role in adsorption applications which is dependent on their innate surface property and further external functionalization. Nanoparticles include metallic nanoparticles (gold NPs), metallic oxide NPs (TiO_2, SiO_2, Al_2O_3, MgO, ZnO, CeO_2 and ferric oxides: goethite (α-FeOOH) and hematite (α-Fe_2O_3), hydrous ferric oxide: maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4)), and nanostructured mixed oxides (nanostructured binary iron– titanium mixed oxide particles). Carbonaceous nanomaterials (CNMs) are another important class based on sorbent properties that include carbon nanotubes (CNTs), carbon nanoparticles (CNPs), and carbon nanosheets (CNSs). In the same way, silicon nanomaterials (SiNMs) include silicon nanotubes (SiNTs), silicon nanoparticles (SiNPs), and silicon nanosheets (SiNSs). Other nanomaterials for adsorption processes are nanofibers (NFs), nanoclays, polymer-based nanomaterials (PNMs), and xerogels and aerogels [31, 33]. However, decrease in the size of particles from micrometer to nanometer levels, results in increase of fraction of the "surface" atoms and the surface energy fraction. Consequently, it is the key reason for a series of unique physical and chemical properties of small particles. A very important one is that most of the atoms that have high chemical activity and adsorption capacity to many metal ions are on the surface of the nanomaterials and large surface areas caused by the size-quantization effect. The surface atoms are unsaturated and are thus subject to combination with other element ions by static electricity. Therefore, nanomaterials can strongly adsorb numerous substances including trace metals and polar organic compounds. Among the various nanosorbents, nanosized metal oxides (NMOs) are classified as the promising ones for pollutant removal from aqueous effluents [34–43]. To improve the feasibility of NMOs in real wastewater treatment, they were then combined with other materials or impregnated into porous supports of large size to obtain composite adsorbents [34]. The widely used porous supports include activated carbon, natural materials, biomasses, synthetic polymeric hosts, etc.

2.2. Bio-sorbents

Biosorption is a sorption procedure, where biomaterial or biopolymer is used as sorbent. The phenomenon of biosorption was reported in early 1970s when the radioactive elements (also heavy metals) in the wastewater discharged from a nuclear power station were found to be concentrated by several algae. To date, some reviews have been published that mainly focused on different aspects of heavy metal biosorption [44–63]. Early research conducted in laboratory studies had showed that biosorption was a favorable and cost-effective

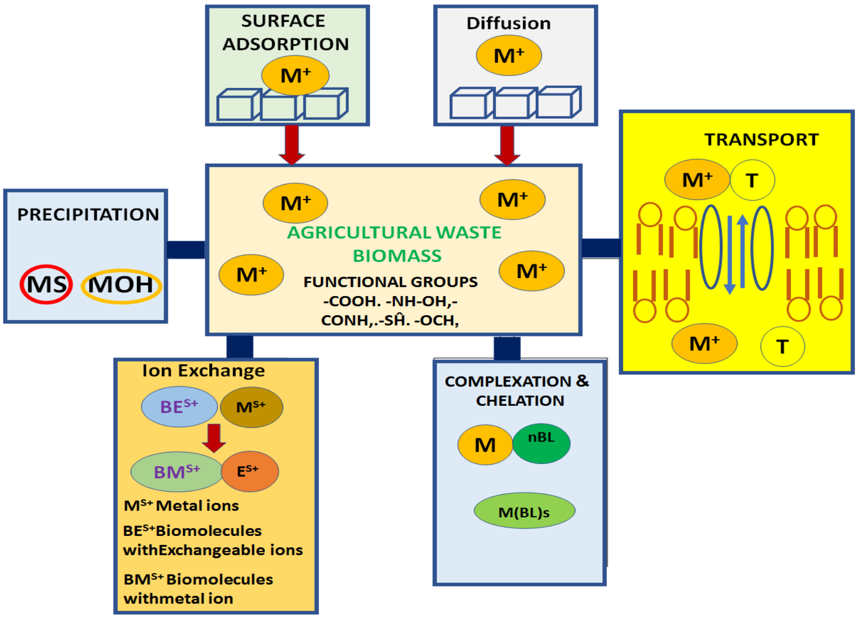


Fig. 2. Plausible mechanism of biosorption.

technology for the removal of heavy metals from aqueous solutions. Compared with such conventional methods as precipitation, chemical reduction, ion exchange, and membrane separation, biosorption technology has several advantages: low operating cost, high efficiency in detoxifying heavy metals that have lower concentrations, less amount of spent biosorbent for final disposal, and no nutrient requirements [5]. On the other hand, biosorption is an alternative technology for the removal of metal ions and organic pollutants from dilute aqueous solutions using biomass as the adsorbent, e. g., agricultural and fermentation wastes and various kinds of microorganisms. For simplicity the biosorbents have been subdivided into some classes including algae, fungi, bacteria, plants, wood, grasses, compost, peat moss, chitin and chitosan.

It has been found that biosorbents are rich in organic ligands or the functional groups, which play a dominant role in removal of various heavy metal and other contaminants. The important functional groups are hydroxyl, carboxyl, sulfate, phosphate, and amine groups. Due to high affinity of the biosorbent for the metal ion species, the latter is attracted and bound by rather complex process affected by several mechanisms involving chemisorption, complexation, adsorption on surface and pores, chelation, ion exchange, adsorption by physical forces, entrapment in inter and intrafibrillar capillaries and spaces of the structural polysaccharides network as a result of the concentration gradient and diffusion through cell wall and membrane (Fig. 2) [53, 64-66]. So far, a wide variety of biosorbentes have been employed by researchers [67-70].

2.3. Nano-Biosorbents

The synthesis and application of new composites of nanomaterials and biosorbents and also nanosized biosorbents are especially considered recently. The high adsorption capacity exhibited by these new sorbents, nano-biosorbents, may be explained by their nano-scale particle size giving access to a larger surface area as well as the incorporation of a large number of various functional groups of biomaterials, which provided effective adsorption sites for the binding of metal ions or dyes. Some nano-biosorbents for pollutant removal are summarized in Table 1. The major advantages of these novel sorbents are their effectiveness in reducing the concentration of pollutants to very low levels and using inexpensive materials. For instance, NMOs provide an effective and specific adsorption toward heavy metals. They are usually present as fine or ultrafine particles, which often lead to problems such as agglomeration due to Vander Waals forces or other

Table 1. Nano-biosorbents for heavy metal and dye removal from water.

Adsorbent	Shape and size (nm)	Target pollutant	Adsorption capacity	Isotherm method	Refs.
Orange peel powder modified magnetic nanoparticles	Spherical particles, mean size 32–35 nm	Cd(II)	71.43 mg/g	Langmuir isotherm	[102]
Nano-Fe_3O_4 modified Baker's yeast	Spherical and granular nanoparticles	Methyl violet	60.84 mg/g	Langmuir isotherm	[105]
EDTA dianhydride treated nano-Fe_3O_4 modified Baker's yeast	Nanoparticles	Ca(II), Cd(II), Pb(II)	99.26 mg/g for Pb(II) at pH 5.5, 48.70 mg/g for Cd(II) at pH 6.0, 33.46 mg/g for Ca(II) at pH 6.0	Langmuir isotherm	[110]
Composite of activated carbon adsorbent-immobilized-nano Fe_3O_4-impregnated-baker's yeast	Spherical particles, mean size 25–42 nm	Hg(II)	250–800 µmol/g	Langmuir isotherm	[111]
Magnetic chitosan nanoparticles	Nanoparticles in the range of 8 nm–40 nm	Cu(II)	35.5 mg/g	Langmuir isotherm	[117]
Chitosan-coated magnetic nanoparticles-immobilized Saccharomyces cerevisiae	Spherical nanoparticles	Cu(II)	144.9mg/g	Langmuir model	[118]
Magnetic graphene/ Fe_3O_4/chitosan nanocomposite	Nanoparticles with about 20–50 nm	Acid Orange 7	42.7 mg/g	Langmuir isotherm	[119]
Gum kondagogu modified magnetic nanoparticles	Spherical nanoparticles in the range of 8–15 nm	Cd(II), Cu(II), Pb(II), Ni(II), Zn(II), Hg(II)	106.8 mg/g for Cd(II), 85.9 mg/g for Cu(II), 56.6 mg/g for Pb(II), 49.0 mg/g for Ni(II), 37.0 mg/g for Zn(II), 35.0 mg/g for Hg(II)	Langmuir isotherm	[127]
Nanocomposite based Gum ghatti and Fe_3O_4 magnetic nanoparticles	Nanoparticles 70 nm	Rhodamie B	654.87 mg/g	Langmuir isotherm	[137]
Magnetic nanoparticles impregnated chitosan beads	-	As(V), As(III)	35.7 mg/g for As(V), 35.3 mg/g for As(III)	Langmuir isotherm	[138]

Table 1. (Continue) Nano-biosorbents for heavy metal and dye removal from water.

Adsorbent	Shape and size (nm)	Target pollutant	Adsorption capacity	Isotherm method	Refs.
Modified Fe_3O_4 nano-particles with the extracted pectin from the cell wall of *Azolla filicoloides*	-	methyl orange	0.498 mmol/g		[139]
Poly(γ-glutamic acid) coated magnetite nanoparticles	Average particle diameter 12.4 nm	methylene blue	78.67 mg/g	Redlich–Peterson, Langmuir isotherm	[140]
Mussel-inspired Polydopamine polymer decorated with magnetic nanoparticles	quasi-spherical shape, particle size with an average diameter of about 7 nm	Methylene blue, Tartrazine, Cu(II), Ag(I), and Hg(II)	204.1 for methylene blue, 100.0 for tartrazine, 112.9 for Cu(II), 259.1for Ag(I), 467.3 mg/g for Hg(II)	Langmuir isotherm	[141]
NaOH-treated wheat straw impregnated with Fe_3O_4 magnetic nanoparticles	-	Methylene blue	1374.6 mg/g	Freundlich isotherm	[142]
Silicon dioxide nanopowder-combined-heat inactivated Aspergillus ustus	Nanoparticles	Cd(II)	1000 μmol/g	Langmuir and Freundlich isotherms	[143]
SiO_2-nanoparticles-immobilized-Penicillium funiculosum	Nanoparticles	Pb(II)	1266.7 μmol/g	Langmuir, Freundlich, Dubinin–Radushkevich isotherms	[144]
Bio-silica/ chitosan nanocomposite	20 nm	Acid Red 88	25.84 mg/g	Langmuir isotherm	[145]
Filamentous fungal biomass-loaded TiO_2 nanoparticles	Nanoparticles	Pb(II)	-	-	[146]
Guar gum–nano zinc oxide biocomposite	Spherical nanoparticles	Cr(VI)	55.56 mg/g	Langmuir and Freundlich isotherms	[147]

Table 1. (Continue) Nano-biosorbents for heavy metal and dye removal from water.

Adsorbent	Shape and size (nm)	Target pollutant	Adsorption capacity	Isotherm method	Refs.
Nano-sized hydroxyapatite incorporated alginate polymer	-	Pb(II)	270.3 mg/g	Langmuir isotherm	[157]
Nano-hydroxyapatite/chitosan composite	Nanorods ~5 nm in diameter and 20–50 nm in length	Cd(II)	122 mg/g	Langmuir isotherm	[158]
Single-walled carbon nanotubes-doped walnut shell composite	-	Pb(II)	185.2 mg/g	Langmuir isotherm	[160]
Magnetic guar gum-grafted carbon nanotubes	-	Neutral red and Methylene blue			[161]
Xanthated nano banana cellulose	Nano fiber 100nm	Cd(II)	154.26mg/g	Langmuir and the Redlich–Peterson isotherms	[162]
Pleurotus ostreatus nano-particles	Spherical or approximately spherical nanoparticles	Mn(II)	130.625 mg/g	Langmuir isotherm	[169]
Spirulina platensis nanoparticles	Spherical particles with mean size 120 to 350 nm	FD&C red no. 40 and Acid blue	295 mg/g for FD&C red no. 40, 1450 mg/g for acid blue	-	[170]
Polydopamine nanospheres	150–200 nm	Hg(II)	1861.7 mg/g	Langmuir isotherm	[175]

interactions [71], and greatly decrease or even lost the high capacity and selectivity of NMOs, difficult separation, and excessive pressure drops when used in flow-through systems [72]. An effective approach to overcome these technical drawbacks is to construct hybrid adsorbents by impregnating or coating NMOs particles into/onto porous supports of larger size [73–76]. The widely used porous supports include activated carbon, natural hosts such as bentonite [77,78], sand [79,80], metallic oxide materials such as Al_2O_3 membrane [81] and porous manganese oxide complex [82], and synthetic polymer hosts such as cross-linked ion-exchange resins [83–85]. In the following sections, recent advances in pollutant removal from water and wastewater by nano-biosorbents are presented in terms of their synthesis, characterization, and application perspectives and are classified by the components of nano-biosorbents.

2.4. Composites of nanosized ferric oxides and biosorbents

Nanosized ferric oxides (NFeOs) are known as low-cost adsorbents for toxic metal sorption due to their facileness of resource and ease in synthesis. Since elemental iron is environmentally friendly, NFeOs can be pumped directly to contaminated sites with negligible risks of secondary contamination [86]. The most commonly studied NFeOs for water/wastewater treatments include goethite (α-FeOOH), hematite (α-Fe_2O_3) [87,88], amorphous hydrous Fe oxides [89], maghemite (γ-Fe_2O_3) [90,91], magnetite (Fe_3O_4) [92,93] and iron/iron oxide ($Fe@Fe_xO_y$) [94]. Recently, magnetic nanoparticles (MNPs) have attracted substantial interest in various scientific fields because of their special properties such as their super paramagnetic properties, high dispersibility, low toxicity, biocompatibility and easiness of their surface modification [95]. Moreover, magnetic nanoparticles are new adsorbents that have attracted to separation or purification methods substantially because of their unique properties such as excellent magnetic responsivity, significantly higher surface area-to-volume ratio and a short diffusion route, resulting in high adsorption capacity, rapid adsorption dynamics and high adsorption efficiencies [95-98]. To date, many studies are available on the use of different synthetic polymeric agents as a supporting material for the immobilization of microbial biosorbents, but a limited number of studies have been focused on the use of magnetic nanoparticles for the biosorbent immobilization so far. Recently, relatively good removal capabilities of magnetic nano-biosorbents to uptake pollutants have been demonstrated by many researchers. The Fe_3O_4 nanoparticles have been applied in enzyme immobilization by Lee et al. [99]. Yong et al. made use of polymer-grafted magnetic nanoparticles for lipase immobilization [100]. The adsorption of Cu(II) by carboxymethylated chitosan-conjugated Fe_3O_4 nanoparticles was studied by Chang and Chen [101]. Gupta et al. [102] prepared a novel magnetic nano-adsorbent by the surface modification of magnetic Fe_3O_4 nanoparticles (MNP) with orange peel powder (OPP), an agricultural waste, to explore its applicability as an adsorbent for the removal of cadmium from aqueous solutions. Orange peel, a low cost, non-toxic biosorbent, containing active functional groups of hydroxyl and carboxyl present in cellulose, hemi-cellulose and pectin components [103,104] was selected for its better application and management for wastewater treatment. MNP and MNP–OPP were synthesized by co-precipitation method and their characterization investigated with respect to BET, FE-SEM, and TEM. The BET surface area of OPP, MNP and MNP–OPP was found to be 47.03, 76.32 and 65.19 m^2/g, respectively. Although MNP–OPP had a lower surface area than MNP, its adsorption capacity is higher which shows that the multiple functional groups on MNP–OPP played an important role in the enhancement of the adsorption capacity. The TEM image revealed that the average diameter of such a structure was 32–35 nm. The high adsorption capacity exhibited by MNP–OPP may be explained by its nano-scale particle size giving access to a larger surface area as well as the incorporation of a large number of hydroxyl functional groups of OPP, which provided effective adsorption sites for the binding of Cd(II) ions. The effect of some variables on cadmium adsorption onto MNP–OPP, MNP and OPP including pH, ionic strength, natural organic matter, adsorbate concentration, contact time and temperature was studied. Results revealed a faster kinetics and efficiency of MNP–OPP in comparison to those of MNP and OPP and further confirmed a complexation and ion exchange mechanism to be operative in metal binding. Thermodynamic studies revealed the feasibility and endothermic nature of the system and the kinetic data were well described by the pseudo-second-order model.

The magnetic baker's yeast biomass (MB) was prepared by combining baker's yeast and nano-Fe_3O_4 using glutaraldehyde as a cross link agent by Tian et al [105]. Yeasts are extensively used in a variety of large-scale industrial fermentation processes and waste biomass from these processes is a potential source of cheap adsorbent material. Baker's yeast is an inexpensive biomass and is readily available. Numerous researchers have devoted their time to verifying the applicability of this material for remediation of heavy metals [106-109]. Yu et al. [106] used FTIR results to detect the presence of various functional groups on the surface of modified baker's yeast, which explains its surface mechanism complexity. These phenomena highlighted the fact that carboxyl, hydroxyl and amide groups were all engaged in the adsorption of metals. MB, as a potential reusable dye nano-biosorbent, was successfully used for the biosorption of methyl violet (MV) and was easily recycled using an applied magnetic field. Fig. 3 shows the synthesis route used to prepare MB and a suggested mechanism for MV biosorption/desorption onto MB.

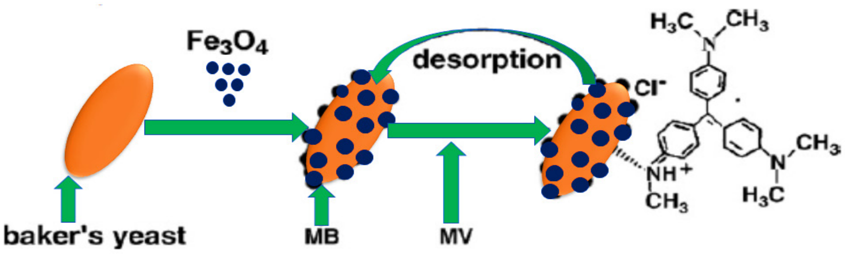


Fig. 3. The synthesis route used to prepare MB and a suggested mechanism for MV biosorption/desorption onto MB.

The SEM image revealed that nano-Fe_3O_4, with spherical and granular morphology, was distributed on the surface of baker's yeast biomass. The optimum biosorption conditions for dye removal were determined as pH 6.0, initial MV concentration 300 mg/L and contact time 30 min. According to regeneration studies, the HAc solution (0.05 mol/L) was the optimal eluent and MB could be effectively utilized for the removal of MV after recycling. Also the thermodynamic parameters ΔG°, ΔH° and ΔS° showed that the biosorption was feasible, spontaneous and endothermic.

In another study conducted by Xu et al. [110], a new magnetic nano-biosorbent was prepared by combining baker's yeast biomass and nano-Fe_3O_4 (FB) using glutaraldehyde as a cross-link agent, and was chemically treated with ethylenediaminetetraacetic dianhydride (EDTAD). The adsorption properties of EDTAD-treated FB (EFB) for Pb(II), Cd(II), and Ca(II) ions were evaluated. The results showed that the uptakes of EFB for the three metal ions were higher than that of FB, and the adsorption capability of Pb(II), Cd(II), and Ca(II) ions increased with an increase in pH. The adsorption process was followed by the pseudo-second-order kinetic model and Langmuir isotherm equation. The maximum adsorption capacities of 99.26 mg/g for Pb(II) at pH 5.5, 48.70 mg/g for Cd(II) at pH 6.0, and 33.46 mg/g for Ca(II) at pH 6.0 were observed at 30 °C. The regeneration experiments showed that the EFB could be successfully reused.

A novel composite of activated carbon adsorbent-immobilized-nano Fe_3O_4-impregnated-baker's yeast (AC@Nano- Fe_3O_4-BY) for removal of Hg(II) from various water matrices introduced by Mahmoud et al. [111]. Activated carbon, the most traditional adsorbent for removal of organic and inorganic pollutants from aqueous as well as gaseous environments, is used widely in water and wastewater treatments due to the high surface area, well developed internal micro-porosity structure and the presence of some surface loaded functional groups [112–114]. Chemical or biological modification of activated carbon surface has been recognized as an effective approach for enhancing the metal adsorption characteristics of the modified adsorbents [115]. Removal of Hg(II) from various samples was explored, studied, optimized and evaluated using the combined sorption characteristics of a novel composite based on three sorbent–biosorbent systems. A schematic diagram for the immobilization of Nano-Fe_3O_4 and baker's yeast on the surface of AC is represented in Fig. 4.

Combination of nanomaterials and biopolymers is being favorable for water treatment. Chitosan, β-(1-4) acetyl-D-glucosamine, a linear biopolymer of glucosamine, is the second most abundant polymeric material in nature after cellulose. It can be produced commercially by chemical deacetylation of chitin, a major component of the exoskeleton of crustaceans such as crabs, lobster and shrimp [116]. It is shown that magnetic chitosan nanoparticles is a promising adsorbent for removing heavy metals. This new adsorbent has not only strong metal chelating capability due to presence of the amine and hydroxyl groups in chitosan chain, but also the feature of nanomaterials. In addition, due to magnetic properties, it can easily be separated from the sorption system using magnetic field. Recently, many researchers have reported the preparation of the magnetic chitosan/Fe_3O_4 composites and their applications for removing metal ions. Yuwei et al. [117] reported a novel magnetic chitosan nanoparticle synthesized through a simple one-step in situ co-precipitation method. Their performance was characterized, and the sorption property for removing Cu(II) from aqueous solution was investigated. The experimental results

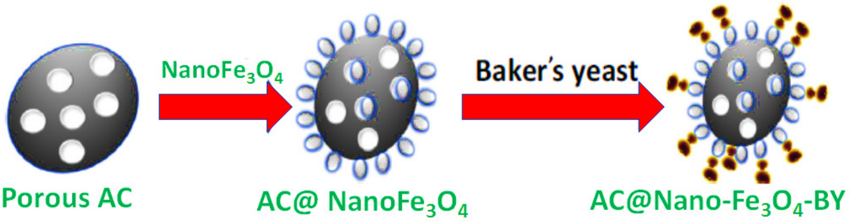


Fig. 4. Schematic diagram for the immobilization of Nano-Fe$_3$O$_4$ and baker's yeast on the surface of AC.

showed that the particles were super-paramagnetic, with the saturation magnetization about 36 emu/g. The maximum sorption capacity was calculated to be 35.5 mg/g using the Langmuir isotherm model. TEM image shows that the size of magnetic chitosan nanoparticles is in the range of 8 nm–40 nm. Moreover, TEM image also indicates different contrasts of chitosan–Fe$_3$O$_4$: the dark areas present for crystalline Fe$_3$O$_4$ while the bright ones are associated with chitosan.

Recently, immobilized Saccharomyces cerevisiae on the surface of chitosan-coated magnetic nanoparticles (SICCM) was employed as a new magnetic sorbent for the adsorption of Cu(II) from aqueous system [118]. Presence of large number of hydroxyls, acetamido, and primary amino groups results in excellent adsorption characteristics of SICCM for heavy metals. The biosorption process was studied with regard to the effects of initial pH, initial Cu(II) concentration and contact time. The highest removal efficiency of 96.8% was reached when the initial Cu(II) concentration was 60mg/L, and the adsorption capacity was increased with the increase of initial concentration of Cu(II). In particular, SICCM was highly efficient for the fast adsorption of Cu(II) within the first 10 min, and adsorption equilibrium could be achieved in 1 h. The maximum adsorption capacity for Cu(II) was estimated to be 144.9 mg/g with a Langmuir adsorption equilibrium constant of 0.0719 L/mg at 301 K.

Magnetic graphene/chitosan (MGCh) nanocomposite was constructed through a facile chemical route and its application as a new adsorbent for Acid Orange 7 (AO7) removal was also investigated by Sheshmani et al [119]. Recently, different kinds of materials have been used to form composites with chitosan such as graphene oxide (GO) and magnetite. These composites have been affirmed to present better adsorption capacity to remove synthetic dyes and resistance to acidic environment [120-122]. GO is a highly-oxidized planar material containing 25–33% oxygen with good adsorption between layers. Compared with conventional adsorbents, the merits of GO as adsorbents are its structure type sand diverse compositions, tunable pore size, large surface area, and coordinatively unsaturated or saturated metal sites to regulate the adsorption ability [123-125]. For this reason, it has been reported that GO based nanocomposites can serve as a dye remover in aqueous solutions [126]. The maximum absorption capacity of MGCh for AO7 was reached at initial pH=3 and, 120 min contact time. The batch adsorption experiments showed that the adsorption of the AO7 is considerably dependent on pH of milieu, amount of adsorbent, and contact time. The adsorption kinetics and isotherms were investigated to indicate that the kinetic and equilibrium adsorption were well-described by pseudo-firstorder kinetic and Langmuir isotherm model, respectively. The adsorption behavior suggested that the adsorbent surface was homogeneous in nature. The study suggests that the MGCh is a promising nanoadsorbent for removal of anionic azo dyes from aqueous solution.

Saravanan et al. prepared Gum kondagogu modified magnetic iron oxide nanoparticles (GK-MNP) by coprecipitating Fe^{2+} and Fe^{3+} ions using ammonia solution in presence of GK biomacromolecules [127]. Magnetic nanocomposites based on natural biomacromolecules such as gum arabic and chitosan have been successfully demonstrated as biosorbents for toxic metal ions [128,129]. GK, a novel biopolymer derived from Cochlospermum gossypium tree, is a partially acetylated, rhamnogalactouran type of polysaccharide with a high molecular mass of 3.6×107 Da [130,131]. This gum is rich in acidic sugar residues such as, galacturonic and glucuronic acids, which accounts for 52% of the total carbohydrates, rest being accounted by neutral sugars such as glucose, galactose, rhamnose and arabinose. In addition, GK also contains tannins, proteins and minerals [132,133]. Fourier transform infrared spectroscopic analysis of GK revealed that this gum contains carboxyl groups (R–COO–), hydroxyl (–OH–), ether (C–O–C), acetyl (CH_3CO–), aliphatic (–CH) and carbonyl (C=O) functional groups [134]. This gum is non-toxic and has potential application as a food additive [135]. Besides, it is shown that the native gum itself can be used as a potential biosorbent for removal of toxic metal contaminants [130,136]. In order to further improve their adsorption capacity and enhance the separation rate, the native gum modified in the form of magnetic nano-adsorbent by functionalizing the gum network with the iron oxide nanoparticles. The processing of GK grafted magnetic nanoparticles (GK-MNP) was carried out in one-step process, i.e. synthesis of magnetic iron oxide nanoparticles have been directly carried out in an aqueous medium containing the biopolymer GK. The native gum contains various functional groups [131] that facilitate in trapping the magnetic nanoparticles effectively within the gum network. The removal efficiencies for a variety of metal cations by the GK–MNP were determined quantitatively in the order: Cd^{2+}> Cu^{2+}> Pb^{2+}> Ni^{2+}> Zn^{2+}> Hg^{2+} at a pH of 5.0±0.1 and at a temperature of 30.0±1.0 ˚C. Mittal et al. [137] reported the development of a new nanocomposite using gum ghatti crosslinked with poly(acrylic acid-co-acrylamide) reinforced with iron oxide magnetic nanoparticles for the removal of Rhodamine B (RhB). The adsorption isotherm data was used to study Langmuir, Freundlich and Dubinin–Kaganer–Radushkevich isotherm models. The value of correlation coefficient confirmed the applicability of Langmuir isotherm model with maximum adsorption efficiency of 654.87 mg/g. Wang et al. [138] investigated removal of arsenic by magnetic nanoparticles impregnated chitosan beads (MICB) and showed that the hydroxyl groups on the adsorbent surface were involved in arsenic adsorption. Another magnetic nano-biosorbent synthesized by modification of Fe_3O_4 nanoparticles with the extracted pectin from the cell wall of *Azolla filicoloides* (FN-EP). This new sorbent can remove methyl orange as a water-soluble azo dye from waste water better than Azolla and the extracted pectin from Azolla (EPA), alone [139]. Magnetite nanoparticles coated with an anionic biopolymer poly(γ-glutamic acid) (PGA-MNPs) were synthesized and characterized for methylene blue dye adsorption capability by Inbaraj et al [140]. Dye removal mechanism by PGA-MNPs was probably due to electrostatic interaction through exchange of protons from side-chain α-carboxyl groups on PGA-MNPs surface. The Mussel-inspired polydopamine biopolymer decorated with magnetic nanoparticles (Fe_3O_4/PDA) was synthesized and used for removal of multiple pollutants including methylene blue, tartrazine, Cu(II), Ag(I), and Hg(II) [141]. Another new magnetic nanoadsorbent, NaOH-treated wheat straw from agriculture biomass impregnated with Fe_3O_4 magnetic nanoparticles (MNP-NWS), introduced by Pirbazari et al. [142] for removal of methylene blue from aqueous solution. The results presented above show that magnetic nano-biosorbents may be promising adsorbents from environmental and purification point of views.

2.5. Composites of miscellaneous nanosized metal oxides and biosorbents

Heat inactivated Aspergillus ustus (Asp), a fungal biomass, silicon dioxide-nano-powder (N-Si), and silicon dioxide nanopowder- combined-heat inactivated Aspergillus ustus (N-Si-Asp) were employed to study the biosorption of Cd(II) from aqueous solutions via batch equilibrium technique [143]. Cadmium biosorption processes were investigated under the effect of pH, contact time, sorbent dosage and initial metal concentration. The three examined sorbents were found to exhibit maximum capacity values in pH 7.0. The maximum determined cadmium capacity by N-Si (600 µmol/g) was found higher than that exhibited by Asp (400 µmol/g). However, N-Si-Asp showed the highest sorption cadmium capacity (1000 µmol/g) as a combined behavior of both silicon dioxide nano-powder and Aspergillus ustus units. Sorption equilibria were established in 20 min and their data were well described by both Langmuir and Freundlich models. Also Mahmoud et al. established a novel high performance biosorbent based on the combination of SiO_2-nanoparticles (N-Si) with Penicillium funiculosum fungus (Pen) and applied for biosorption of Pb(II) from aqueous solutions [144]. They introduced a batch equilibrium technique used to follow-up the adsorption processes of lead under the effect of pH, contact time, sorbent dosage and initial metal concentration. The maximum capacity values were

1200.0 and 1266.7 μmol/g for (Pen) and (N-Si-Pen), respectively at pH 5. Sorption equilibria were established in ~20 min and their data were well described by Langmuir, Freundlich and Dubinin–Radushkevich models. Soltani et al. evaluated the efficiency of immobilized nanosized bio-silica (average crystalline size of 20 nm) within chitosan as a nanocomposite adsorbent for removing Acid Red 88 (AR88) in aqueous phase [145]. As result, the amount of adsorbed AR88 (mg/g) was increased with increasing reaction time and adsorbate concentration and decreasing temperature and initial pH. A rapid increase in the adsorption was happened with increasing adsorbent dosage from 1 to 3 g/l, while further increase in the adsorbent dosage resulted in an insignificant increase in the adsorption (1.66 mg/g). The kinetic study was performed and the results indicated the suitability of pseudo-second order kinetic model. The fitness of experimental data to the intra-particle diffusion model demonstrated that the adsorption process occurred via a multi-step mechanism. But the intra-particle diffusion was not the sole rate-limiting stage. Regarding the negative ΔG° and ΔH° values obtained through thermodynamic study the adsorption of AR88 onto nanocomposite was simultaneous and exothermic in nature, respectively.

The biosorption of lead(II) ions by filamentous fungal biomass-loaded TiO_2 nanoparticles using flow-injection system coupled to flame atomic absorption spectrometry studied [146]. The effects of pH, sample volume, loading and elution flow rates, eluent type and volume on the recovery of lead were investigated. Lead ions were sorbed on a biosorbent minicolumn at pH 4.0 followed by an elution step using 288μL of 1.0 mol/L hydrochloric acid solution. The limit of detection was 0.78μg/L.

Guar gum–nano zinc oxide (GG/nZnO) biocomposite was used as an adsorbent for enhanced removal of Cr(VI) from aqueous solution [147]. The maximum adsorption was achieved at 50 min contact time, 25 mg/L Cr(VI) conc., 1.0 g/L adsorbent dose and 7.0 pH. Langmuir, Freundlich, Dubinin–Kaganer–Radushkevich (DKR) and Temkin isotherm models were used to interpret the experimental data. The data obeyed both Langmuir and Freundlich models (R^2 = 0.99) indicating a multilayer adsorption of Cr(VI) onto the heterogeneous surface. The linear plots of Temkin isotherm showed adsorbent-adsorbate interactions. Moreover, the energy obtained from DKR isotherm (1.58–2.24 kJ/mol) indicated a physical adsorption of the metal ions onto the adsorbent surface, which implies more feasibility of the regeneration of the adsorbent. GG/nZnO biocomposite adsorbent showed a good adsorption capacity for Cr(VI) (q_m = 55.56 mg/g). Adsorption process followed pseudo-second order kinetics; controlled by both liquid-film and intra-particle diffusion mechanisms. Thermodynamic parameters (ΔG^o, ΔH^o and ΔS^o) reflected the feasibility, spontaneity and exothermic nature of adsorption. The results suggested that GG/nZnO biocomposite is economical, eco-friendly and capable to remove Cr(VI) from natural water resources.

2.6. Combination of miscellaneous nanosized materials with biosorbents

Various other nanosized materials have also been put to use for preparing new and efficient nano-biosorbents. Polymeric composites made up of nano-hydroxyapatite (n-HAp) with chitin and chitosan have been prepared and studied for the removal of Cu(II) ions from the aqueous solution [148]. Chitin and chitosan have more applications as biopolymers reported for their high potential of adsorption of metal ions [149] and biomedical applications [150-152]. It has been known for a long time that various biocomposites which are made from organic matrix and inorganic fraction possess good mechanical strength [153]; biocompatibility and biodegradability which would make the material desirable for practical applications [153]. Chitin and chitosan blended with n-HAp have been reported to have good mechanical and chemical properties which have been recommended for the development of defluoridation technology [154]. The powdered hydroxyapatite cannot be directly used in fixed bed columns or any other flow-through systems because it causes excessive pressure drops. To circumvent such technological bottlenecks, polymeric hybrid composites were prepared by dispersing powdered hydroxyapatite particles onto porous polymeric substrates [154-156]. The sorption capacity of n-HAp, n-HAp/chitin (n-HApC) composite and n-HAp/chitosan (n-HApCs) composite for Cu(II) removal were found to be 4.7, 5.4 and 6.2 mg/g respectively with a minimum contact time of 30 min.

Another nanocomposite adsorbent based on hydroxyapatite was prepared by incorporating natural nano-sized hydroxyapatite (nHAp) into alginate polymer [157]. Bead and film form composite adsorbents with two different compositions were used for the Pb(II) removal from aqueous solutions. The adsorption results were compared with the results obtained using pure alginate films and beads as well as pure nHAp particles. In case of bead form adsorbents, incorporating nHAp particles into alginate decreased the adsorption capacity. SEM and EDX analysis proved that it was due to agglomeration of nHAP particles on the bead surface and reduction in Pb(II) diffusion in the beads. However, composite films had greater sorption capacities than pure alginate film and nHAp powder. Maximum equilibrium capacity of 270.3 mg/g was obtained after 6 h for composite film from adsorbent containing 50 wt% of nHAp. Kinetics studies showed that the pseudo-second-order kinetic model was able to describe the dynamic behavior of the adsorption process by composite adsorbents used. Also hydroxyapatite nanorods (nHAp) and nano-hydroxyapatite chitosan composites (nHApCs) were proposed for the removal of Cd(II) ions in water treatment by Salah et al. [158].

Soluble starch-functionalized multiwall carbon nanotube composites (MWCNT-starch) were prepared to improve the hydrophilicity and biocompatibility of MWCNTs [159]. Characterization of the MWCNT-starch by FTIR, UV–vis, XRD, TEM and thermogravimetric analysis (TG), showed that the starch component (about 14.3 wt%) was covalently grafted onto the surface of MWCNT. MWCNT-starch-iron oxide composites, intended for use as adsorbents for the removal of dyes from aqueous solutions, were prepared by synthesizing iron oxide nanoparticles at the surface of MWCNT-starch. MWCNT-starch-iron oxide exhibited better adsorption for anionic methyl orange (MO) and cationic methylene blue (MB) dyes than MWCNT-iron oxide.

Saadat et al. [160] introduced a novel adsorbent, highly pure (99%) single-walled carbon nanotubes-doped walnut shell composite (SWCNTs/WSh), was then prepared by immobilizing SWCNT particles on the surface of walnut shell. This adsorbent was examined to evaluate its potential to remove Pb(II) ions from aqueous solutions. In conclusion, the SWCNTs/WSh composite can be used as an effective adsorbent for the removal of Pb(II) ions from aqueous solutions.

The hydrophobicity of carbon nanotubes (CNTs) limits their extensive application. The hydrophilicity and biocompatibility of CNTs can be improved by modifying them with biopolymers. Guar gum (GG), a natural biopolymer, was covalently grafted on the surfaces of multiwall carbon nanotube (MWCNT) to obtain GG–MWCNT composite. Then iron oxide nanoparticles were synthesized on the GG–MWCNT to prepare the magnetic GG–MWCNT–Fe_3O_4. GG–MWCNT–Fe_3O_4 exhibited good adsorption on neutral red and methylene blue. GG–MWCNT–Fe_3O_4 could be easily separated from the aqueous solution in a magnetic field [161].

2.7. Nanosized biosorbents

Pillai et al. explored the biosorption capacity of xanthated nano banana cellulose (XNBC) for Cd(II) from aqueous solution. Cellulose nanofibers have enormous unique characteristics such as very high surface area to volume ratio, high surface area, and thermal stability, contain 96 percent cellulose [160]. Banana fiber was used for the production of nano fibrils by steam explosion. The advantages of steam explosion include low energy consumption, eco-friendly and less hazardous chemicals. Sulfur group can be introduced into this nanocellulose by xanthation. The biosorbent containing sulfur-bearing groups have a high affinity for heavy metals but a low affinity for light metals. The maximum percentage removal of Cd(II) was obtained at pH 6.0 and the percentage removal of Cd(II) increased with the increment of biosorbent amount.

Chitosan, an antibacterial, biocompatible, environment friendly, biodegradable material, has great potential for sorption of metal ions due to amino and hydroxyl groups in its chemical structure [161–163]. Investigations reveal that chitin and chitosan are easily processed into gels, membranes, nanofibers, beads, microparticles, nanoparticles, scaffolds and sponges [164]. In terms of higher capacities of nano-sized adsorbents compared to traditional micro-sized adsorbents for removal of metal ions Sivakami et al synthesized chitosan nanoparticles by ionic gelation of chitosan and tripolyphosphate and evaluated its sorption capacity for Cr (VI) by varying the operational factors (pH of solution, agitation time, ion concentration and adsorbent concentration) that are responsible for adsorption [165]. Also adsorption of an azo reactive dye, C.I. Reactive Red 120 (RR120), from aqueous solution on chitosan and on chitosan nanodispersion has been studied [166]. The nanodispersion was prepared using a mixture of chitosan and sodium tripolyphosphate. The results revealed that the adsorption of RR120 on dissolved chitosan and on the chitosan nanodispersion was affected significantly by initial dye concentration, temperature, sorbent amount, pH and ionic strength of the solution. Maximum dye removal for both adsorbents was at a pH of 4–5 and the adsorption of the reactive dye on both dissolved chitosan and the nanodispersion gave good fit to the Langmuir isotherm model. The adsorption capacity of the nanodispersion was around 910 mg/g, much higher than of dissolved chitosan, which was 51 mg/g. The adsorption of the dye on the chitosan nanodispersion reached equilibrium much faster than on dissolved chitosan. The kinetics of the adsorption correlated well with the pseudo-second order model.

Pleurotus ostreatus (P. ostreatus), a normal edible mushroom, nano-particles (PONP) investigated by Ma et al. as a new nano-biosorbent to remove Mn(II) from aqueous solution [167]. Dotto et al. used micro and nanoparticles of Spirulina platensis dead biomass, a member of blue-green algae, to remove FD&C red no. 40 and acid blue 9 synthetic dyes from aqueous solutions [168]. Spirulina platensis involves proteins, polysaccharides, lipids, and vitamins [169]. Hence it contains a variety of functional groups such as carboxyl, hydroxyl, sulfate, phosphate and other charged groups [170–172] which can be responsible for dye binding. In addition, the nanobiotechnology enables the obtaining of micro and nanoparticles from S. platensis biomass [173], suggesting that studies should be realized to verify its potential as a biosorbent. Therefore, the feasibility of micro and nanoparticles of S. platensis dead biomass as biosorbents to removal synthetic dyes studied. The best results for removal of both dyes were found using 250 mg of nanoparticles, in these conditions, the biosorption capacities were 295 mg/g and 1450 mg/g, and the percentages of dye removal were 15.0 and 72.5% for the FD&C red no. 40 and acid blue 9, respectively. The EDS results suggested that the dyes biosorption onto microparticles occurred mainly by physical interactions, and for the nanoparticles, chemisorption was dominant.

The potential of using nano-sized aragonite mollusk shell (nano-Bio-ARA) to remove Cd(II) from contaminated water was investigated by comparing the sorption kinetics and isotherms with the nano-sized calcite-type mollusk shell (nano-Bio-CAL) and nano-sized geological calcite (nano-Geo-CAL) [174]. Nano-Bio-ARA displayed extremely high sorption capacity to Cd(II) (8.91 mmol/g), much higher than nano-Bio/Geo-CAL, and many other natural or engineered materials. The results of thermodynamic experiments indicated that the sorption of Cd(II) on the nano-ARA was a spontaneous and endothermic process. The coexisting metals in the solution displayed competition effect to the sorption of Cd(II) on nano-Bio-ARA in the following order: $Cu^{2+} > Cr^{3+} > Pb^{2+} > Zn^{2+} > Ca^{2+}$. The results demonstrate that nano-Bio-ARA is a potential high-effective material to treat Cd(II) contaminated water.

A new biosorbent for efficient removal of Hg(II) from contaminated water using highly selective adsorptive polydopamine (PDA) nanospheres with a small diameter 150–200 nm reported [175]. Adsorption of Hg(II) was very fast and efficient as adsorption equilibrium was completed within 4 h and the maximum adsorption capacities were 1861.72 mg/g, 2037.22 mg/g, and 2076.81 mg/g at 298 K, 313 K, and 328 K respectively, increasing with increasing of temperature. The PDA nanospheres exhibited highly selective adsorption of Hg(II) and had a total desorption capacity of 100% in hydrochloric acid solution, pH 1. The results showed that the structure of PDA nanospheres remained almost unchanged after recycling five times. Considering their efficient and highly Hg(II) selective adsorption, total recycle capacity, and high stability, PDA nanospheres will be feasible in a number of practical applications.

Biosorption processes based on the nanotechnology are particularly suitable for the treatment of solutions containing dilute pollutant concentration. Nano-Biosorption can be a promising potential alternative to conventional processes for the removal of pollutant. However, these technologies are still in the developing stage and much more work is required.

3. Conclusion

Water pollution is one of the most important environmental problems throughout the world. To meet the increased more and more stringent environmental regulations, numerous adsorbents have been developed for pollutant removal from wastewater. It is evident from the literature survey of recent articles that biosorbents and nanomaterials are the most frequently studied for the wastewater treatment. Adsorption of contaminants by biosorbents due to a physico-chemical interaction between the pollutant and already present functional groups on the biomass (such as; carboxyl, hydroxyl, thiol, ketones, aldehydes, amino, phosphate, sulfonate and imidazole groups) results in high efficiency for removal and recovery of dyes and heavy metals from aqueous media. Furthermore, the immobilization of biosorbents on either natural or synthetic polymeric matrices via entrapment was found to enhance the performance, biosorptive capacity and increasing the life time of these biosorbents for regeneration and recycling by several orders of magnitude. Recently, nanometer solid materials have been become more effective solid supports as well as efficient sorbents for removal of pollutants due to numerous atoms with high chemical activity and adsorption capacities to many contaminants on the surface of the nanoparticles. Therefore, as illustrated throughout the article, nano biosorbents have significant advantages of established adsorbents for water treatment, most notably (i) their simple production, (ii) excellent performance, and (iii) high efficiency due to probably the most important of all, a tremendous economic advantage. In spite of this, nano- biosorption have not yet reached its full potential and further work on all levels from the research laboratory to the large scale engineering development stage is necessary to fully realize the potential of this highly versatile and powerful yet cheap technique. Already the currently available data however show that nanobiosorbents are among the promising materials for water treatment by adsorption.

Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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