Sequestering Nickel(II) Ions from Aqueous Solutions Using Various Adsorbents: A Review

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Abstract

Adsorption process has proven to be one of the best water treatment technologies around the world and activated carbon is undoubtedly considered as a universal adsorbent for the removal of different types of pollutants from water. However, widespread use of commercial activated carbon is sometimes restricted due to its high cost. Attempts have been made to develop inexpensive adsorbents utilizing numerous agro-industrial and municipal waste materials. Use of agricultural waste materials as low-cost adsorbents is attractive because it reduces the cost of waste disposal, thereby leading to environmental protection. In this review, agricultural, synthetic and other adsorbents used for adsorbing Nickel(II) ion from aqueous solutions are reported. Different ways to improve their efficiencies are also discussed.

Keywords: Nickel; Wastewater; Adsorption; Adsorbents; Heavy metals.

Introduction

Water is a source of life and energy, although millions of people worldwide are suffering from shortage of fresh and clean drinking water. Rapid pace of industrialization, population expansion, and unplanned urbanization have contributed largely to severe water pollution and surrounding soils. This has stimulated a growing research interest in establishing a leading selective, reliable and durable alternative for environmental conservation [1]. The main source of freshwater pollution can be attributed to discharge of untreated sanitary and toxic industrial wastes, dumping of industrial effluent, and runoff from agricultural fields. It is well known that 70–80% of all illnesses in developing countries are related to water contamination; particularly susceptible are women and children [2]. Pollutants discharged in wastewaters can be toxic to aquatic life and cause natural waters to be unfit as potable water sources. Stringent regulations have been introduced by many countries with respect to the presence of these chemicals in water which binds industries to treat industrial effluents properly before discharging it into the natural water-bodies containing clean water. Therefore, it is essential to remov Ni from industrial wastewaters before discharging it into the environment. A number of technologies are available with varying degree of success to control water pollution. Some of them are coagulation [3], froth flotation [4], filtration [5], ion exchange [6], aerobic and anaerobic treatment [7, 8], advanced oxidation processes [9], solvent extraction [10], adsorption [11], electrolysis [12], microbial reduction [13], and activated sludge [14]. However, most of them require substantial financial input and their use is restricted because of cost factors overriding the importance of pollution control. Among various available water treatment technologies, adsorption process is considered best because of convenience,

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ease of operation and simplicity of design [11]. Furthermore, adsorption process remove/minimize different pollutants; thus, it has a wider applicability in water pollution control [15].

Deleterious effects of Nickel(II) ions in the ecosystem

Heavy metals are persistent environmental contaminants since they cannot be degraded or destroyed, heavy metal pollution represents an important problem due to its toxic effect and accumulation throughout the food chain leading to serious ecological and health problems even at very low concentration [16-19]. Nickel(II) is one common heavy metal. It is an essential nutrient needed by the body in trace amounts; it takes part in the synthesis of vitamin B12, however, an increase in the intake of Nickel(II) and its compounds can lead to birth defects, embolism, chronic bronchitis [20-23]. The tolerance limit of nickel in drinking water is 0.02 mgL^{-1}, and for industrial wastewater it is 2.0 mgL^{-1}. It is a non-biodegradable toxic heavy metal ion present in wastewater. The main source of nickel pollution in water comes from industrial production processes such as galvanization, smelting, mining, dyeing operation, batteries manufacturing and metal finishing. Trace amounts of nickel are beneficial to man, it serves as an activator of some enzyme systems, but if it is beyond the permissive level, different types of diseases occur such as lung cancer, renal oedema, skin dermatitis and gastrointestinal disorder. It is toxic to the plant and causes dermatitis, headache, nausea, and carcinogenesis in humans [22-24]. It exists mostly as Nickel(II) in aqueous media posing threat to living beings owing to its acute neurotoxic and carcinogenic effects. Nickel(II) is also found to be an embryo toxin; a teratogen which makes the removal of this ecotoxic species a serious concern. According to WHO guidelines, the maximum permissible concentration of Nickel(II) in drinking water is 0.02 mgL^{-1} [37]. However, the major contributors of higher concentrations of Nickel(II) in aqueous media are the industries related to stainless steel, electroplating, jewellery, coinage, catalyst, and batteries [24-27].

Due to the mounting demand for such industries, there is a possibility of higher level of Nickel(II) in the effluents or the water bodies which are in close proximity to such industries [28-29]. Therefore, the removal of Nickel(II) from water and wastewater is important. These pollutants constitute serious problems to human health and environment. For example the symptoms of drinking water containing nickel ion above the recommended limit results in headaches, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness [28-32].

Therefore the removal of nickel ions from wastewater is of necessity for human survival and an eco-friendly environment. The toxicity and effect of trace heavy metals on human health and the environment has attracted considerable attention and concern in recent years [32]. Heavy metals are categorized as environmentally toxic materials that can harm the natural environment at low concentrations, with an inherent toxicity, a tendency to accumulate in the food chain, and a particularly low decomposition rate [33-34]. Nickel is a moderately toxic element compared to other transition metals that can lead to serious illness, malignant tumours and nasopharynx, lung, and dermatological diseases when ingested. [34].

It's widespread and varied use has led to an increase in the release of nickel into the environment, resulting in environmental, pollution. For instance, the concentrations of Ni in industrial wastewaters range from 3.40 to 900 mgL^{-1} [33-35]. This concentration is higher than the maximum limit for Ni in terms of the regulation, which is 0.20 mgL^{-1} for wastewater [36]. The accumulation of nickel and its compounds in the environment causes serious hazards to plants, animals and human health. Some of the adverse effects are skin allergies, lung fibrosis, and cancer of the respiratory tract [32]. Several forms of nickel, including its water soluble compounds, have been found to be carcinogenic in humans. The World Health Organisation (WHO) and the European Economic Community have restricted the concentration of nickel in drinking water to 0.02 and 0.05 mgL^{-1} respectively. [37].

Agricultural waste adsorbents used for Nickel(II) ion removal
Cashew nut shell

The adsorptive behaviour of Nickel(II) from aqueous solution onto agricultural waste such as cashew nut shell (CNS) was investigated as a function of parameters such as solution pH, CNS dose, contact time, initial Nickel(II) concentration and temperature [38-39]. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich models were applied to describe the equilibrium isotherms using nonlinear regression analysis. The equilibrium data fits well for the both Langmuir and Freundlich adsorption isotherms. The Langmuir monolayer adsorption capacity of CNS was found to be 18.868 mg^{-1}. Thermodynamic parameters such as ΔG^0, ΔH^0 and ΔS^0 have also been evaluated and it has been found that the sorption process was feasible, spontaneous and exothermic in nature. Pseudo-first-order, pseudo-second-order and Elovich kinetic models were used to describe the kinetic data and the rate constants were evaluated. The result of the kinetic study shows that the adsorption of Nickel(II) could be described by the pseudo-second-order equation, suggesting that the adsorption process is presumably chemisorption. The adsorption process was found to be controlled by both surface and pore diffusion, with surface diffusion at the earlier stages followed by pore diffusion at the later stages. Analysis of adsorption data using a Boyd kinetic plot confirmed that external mass transfer as the rate determining step in the sorption process. A single-stage batch adsorber was designed for different CNS dose/effluent volume ratios using the Freundlich equation. [39-41].

It was observed that the adsorption was pH dependent and the maximum adsorption of 73.89 % occurred at pH of 5.0 for an initial Nickel(II) ion concentration of 20 mgL^{-1}. With increase in the CNS dose increase in Nickel(II) adsorption was found to increase owing to a corresponding increase in the number of active sites. The adsorption was rapid and equilibrium was achieved within 30 min. The percentage removal of Nickel(II) ions decreased with increase in temperature. The data obtained from the thermodynamic study at different temperatures were used to calculate the thermodynamic

quantities such as ΔG^o, ΔH^o and ΔS^o of adsorption. Results indicated that Nickel(II) adsorption onto CNS was found to be spontaneous and exothermic. Based on the results obtained from these studies, it was concluded that since the CNS is an easily, locally available, low-cost adsorbent and has a considerable high adsorption capacity, it could serve as an alternative adsorbent for treatment of wastewater containing Nickel(II) ions. Several studies are also reported affirming that CNS could be used as efficient adsorbent for removing pollutant from aqueous solution [39-44]

Starch, activated charcoal, wood charcoal and clay (type-bleaching earth)

The batch removal of divalent nickel (Ni^{2+}) from wastewater under different experimental conditions using economic adsorbents has also been investigated [45-47]. These natural adsorbents were from different sources i.e. starch, activated charcoal, wood charcoal and clay (type-bleaching earth). The effect of pH and concentration of biomass on the adsorption kinetics was studied. These adsorbents were shown to have comparable performance with the commercial one. The result indicate that the optimum pH for the removal of Nickel(II) ions by starch, wood charcoal, activated charcoal and clay (type bleaching earth) are 7.5 and 6.5 respectively. Clay was efficient in removing nickel ions [47-50]. The adsorption process is endothermic. The pseudo-first-order chemical reaction model provides the best correlation of the data [45].

Rice husk ash

Rice husk ash (RHA) was found to be an effective adsorbent for the removal of Nickel(II) ions from aqueous solution. The study deals with the competitive adsorption of nickel and Nickel(II) ions from aqueous solution onto RHA [51-59]. Non-competitive Redlich–Peterson (R–P) and Freundlich models represent the single metal ion equilibrium sorption data. The combined equilibrium sorption of Nickel(II) ion onto RHA is found to be antagonistic in nature and the extended Freundlich model was found to best represent the binary equilibrium isotherm data. Higher percentage of metal ion removal was possible provided that the initial adsorbate concentration in

the solution was low. Freundlich and R–P isotherms predicted the single-component sorption equilibrium data well. In the binary metal mixtures, the affinity of the RHA for Nickel(II) ion was efficient, from both single-component and the binary solutions under the same experimental conditions. The simultaneous adsorption phenomena of Nickel(II) ions on the RHA were explained by various multi-component equilibrium sorption models. Based on Marquardt's percent standard deviation error function, the extended Freundlich adsorption model, showed the best fit to the binary experimental sorption data [51-53].

Peat

The use of peat for the removal of nickel from aqueous solutions was investigated at various pH values by means of static conditions [60-64]. The outcome of the research shows that the ability of Ni to bind to peat increases as the pH value increases. Adsorption of nickel onto peat is more favourable at higher pH values, which is evidenced by the values of ΔG^o and R_L. The Langmuir model correlated most at different temperatures. The solutions reach adsorption equilibrium rapidly [60]. A reasonable kinetic model, first-order in nickel concentration, was developed and fitted to the adsorption of Nickel(II) onto peat. Kinetically, the first-order model gave the best correlation to the experimental data. The characteristic parameters of the Langmuir isotherm were determined at various temperatures. The relationship between kinetics and equilibrium isotherms was established through the forward- and backward-rate-constants, k_1 and k_2, and the equilibrium constant, K. A bridge from kinetics to thermodynamics was established through the forward and backward rate constants, k_1 and k_2, and the equilibrium constant, K. The forward and backward first order rate constants, the equilibrium constant and the free energy change were determined from the modified first-order equations without knowing any parameter beforehand [60-67].

Clay mixture containing boron impurity

The use of clay mixture containing boron impurity (BC) from boron enrichment plant for the removal of Nickel(II) from aqueous solutions was investigated [68-70]. The effects of pH, contact time, initial dye concentration, adsorbent dosage, and temperature on the adsorption process were examined [71-73]. Residual nickel concentration reached equilibrium in 90 min and the rate of adsorption by BC was rapid in the first 45 min of the reaction time. The pseudo-second-order kinetic model best described the kinetic of the adsorption. Batch adsorption studies showed that the adsorption patterns followed Langmuir isotherm model. The adsorption of heavy metal ions from solution onto BC was determined. It was rapid for the first 45 min and then decreased gradually. About 81.86% of Nickel(II) was adsorbed from single component solution. The rate of adsorption was directly proportional to pH value of the solution. The uptake of metal ions depends appreciably on the amount of BC. Experimental data obtained from batch studies gave a good fit for the Langmuir isotherm model. BC-metal interactions are thermodynamically favourable and exothermic in nature. The study showed that BC has the potential to effectively remove Nickel(II) ions from aqueous solutions, consequently, clay mixture containing boron impurity can be used as a substitute for more expensive adsorbents [69-74].

Cellulose

Cellulose is a linear polymer chain which is formed by joining the anhydroglucose units into glucose chains [75-77]. These anhydroglucose units are bound together by -(1,4)-glycosidic linkages. Due to this linkage, cellubiose is established as the repeat unit for cellulose chains. Cellulose must be hydrolyzed to glucose before fermentation to ethanol. By forming intramolecular and intermolecular hydrogen bonds between OH groups within the same cellulose chain and the surrounding cellulose chains, the chains tend to be arranged parallel and form a crystalline supermolecular structure. Then, bundles of linear cellulose chains (in the longitudinal direction) form a microfibril which is oriented in the cell wall structure [78]. Cellulose is insoluble in most solvents and has a low accessibility to acid and enzymatic hydrolysis. Chemical modification of cellulose is a promising technique for modifying its physical and chemical properties to improve the adsorption property toward dye removal.

Adsorbents based on direct modification of cellulose were evaluated initially and subsequently modifications resulting from the grafting of selected monomers to the cellulose backbone with subsequent fictionalization were assessed [77]. The heavy metal adsorption capacities for these modified cellulose materials were found to be significant and levels of uptake were comparable, in many instances, to both other naturally occurring adsorbent materials and commercial ion exchange resins. Most of the modified cellulose adsorbents proved regenerable and re-usable over a number of adsorption/desorption cycles allowing recovery of the adsorbed heavy metal in a more concentrated form. The advantages of using cellulose as the basis for new adsorbent design lie primarily in its high abundance, low cost and the relative ease with which it can be modified chemically. Approaches to its modification, as reviewed in this paper, is based around a direct chemical modification approach or by grafting of suitable polymeric chains to the cellulose backbone followed by functionalization. The latter has been achieved by the addition of amine, amide, amidoxime, carboxyl, hydroxyl and imidazole type binding ligands to the adsorbent backbone. Both broad methodologies produced adsorbents with a range of heavy metal binding capacities, comparable to other naturally occurring materials and in some cases comparable to the more commercial type of ion exchange resins. Generally, optimum pH conditions for the heavy metal binding on the modified cellulose tend to occur in the range of pH 4.0–6.0. In the context of wastewaters, this pH range is quite narrow whereas most of the commercial resins reviewed are effective ion exchangers over a wide range of pH conditions. Regeneration and reuse of a number of modified cellulose adsorbents is demonstrated in a number of papers reviewed in this work. Many of the adsorption interactions between the modified cellulose adsorbents and heavy metals have been characterised by the Langmuir approach or in a lesser number of cases by the Freundlich model of adsorption [75-76].

Chemically modified orange peel cellulose adsorbents

Li and co-workers reported the preparation of chemically modified orange peel cellulose adsorbents and the bio-sorption behaviour of Nickel(II) was studied [76,79-83]. Effects of different chemical modifications on the adsorbent properties including different alkalis saponification (NaOH, NH_4OH, and $Ca(OH)_2$) and different acids ($C_6H_6O_7 \cdot H_2O$, $H_2C_2O_4$, and H_3PO_4) modification after saponification with NaOH were investigated [9]. The FT-IR spectra showed that there are different functional groups in the adsorbents, which are able to complex with metal ions in aqueous solution. The maximum adsorption capacities of Nickel(II) for SPA is obtained as 1.28 mol kg^{-1} and have increased by 95% compared to raw orange peel. Effects of initial pH, initial metal ions concentrations, shaking time and solid/liquid ratio on metal ions biosorption were also investigated. Biosorption equilibriums were rapidly established in about 60 min and the adsorption kinetics followed the Lagergren first-order kinetics model. The Langmuir and Freundlich adsorption isotherms models fitted the experimental data best with regression coefficient $R^2 > 0.95$ for all the metal ions. Elution efficiencies with different concentrations of HCl were evaluated. The biosorption kinetic studies indicated that the experimental data followed the first-order kinetic reaction. Recoveries of sorbed heavy metal ions could be achieved by desorbing with different concentrations of HCl, which were capable of regenerating the biomass.

Sugarcane bagasse

Bioavailability of nickel in the form of hydrated Nickel(II) resulted to its toxicological effects and hence its removal from aqueous solution is of great concern Activated carbon obtained from sugarcane bagasse pith (SBP-AC), a waste biomass collected from juice shops in Sarkara Devi Temple, Chirayinkeezhu, Trivandrum, India during annual festival was used as adsorbent in their study [84]. The process of adsorption is highly dependent on solution pH, significant removal occurs in the pH range of 4.0–8.0. The maximum adsorption of Nickel(II) was observed at pH 6.5. Moreover, the amount of Nickel(II) adsorbed onto SBP-AC increased with increase in time. Equilibrium was reached in four hours. Adsorption kinetic and equilibrium data were analyzed by determining the best fit kinetic and isotherm models. The overall study reveals the

potential value of steam pyrolyzed SBP-AC as a possible commercial adsorbent in wastewater treatment strategies. SBP-AC is more effective than CAC for the adsorption of Nickel(II) from aqueous phase [84-85]. The adsorption of Nickel(II) onto SBP-AC was influenced by initial concentration of Nickel(II), contact time, agitation speed and adsorbent dose as well as solution pH. The pseudo-second-order kinetic and Langmuir isotherm model precisely fitted both the kinetic and equilibrium data respectively. SBP-AC showed higher adsorption capacity of 140.85 mg g^{-1} for the removal of Nickel(II) from aqueous solutions [86-93].

Garg and co-worker studied the effect of adsorbent dose, pH and agitation speed on nickel removal from aqueous medium using sugarcane bagasse, an agricultural waste biomass [94]. Sugarcane bagasse has been investigated using Response Surface methodology (RSM) [95-96]. RSM is undoubtedly a good technique for studying the influence of major process parameters on response factor by significantly reducing the number of experiments and henceforth, facilitating the optimum conditions. Batch mode experiments were carried out to assess the adsorption equilibrium. The influence of three parameters on the removal of nickel was also examined using RSM approach. The central composite face-centered experimental design in RSM by Design Expert Version 6.0.10 (Stat Ease, USA) was used for designing the experiments as well as for full response surface estimation. The optimum conditions for maximum removal of nickel from an aqueous solution of 50 mg L^{-1} were as follows: adsorbent dose (1500 mg L^{-1}), pH (7.52) and stirring speed (150 rpm). This was evidenced by the higher value of coefficient of determination (R^2 = 0.9873). SCB is readily available in India, so it can be used by small-scale industries having low concentrations of Nickel(II) in wastewater using batched or stirred-tank flow reactors. The kinetic data provided would be useful for the fabrication and design of treatment plant where standard material such as activated carbon is not readily available. Many other works, correlated with this thus confirming the efficiency of this adsorbent for the sequestering of Nickel(II) from aqueous solution [90-94].

Coir pith

Coir pith, an agricultural solid waste has been assessed for the adsorption of Nickel(II) from single-ion solutions as well as from a mixture of them. The efficiency of the adsorbent was investigated using batch adsorption technique under different experimental conditions namely solution pH, initial metal-ion concentration and contact time. Optimum pH values for maximum metal-ion adsorption were determined as 5.3 for nickel [108]. The adsorption of Ni (II) on coir pith followed pseudo second- order kinetics [108-112]. Adsorption isotherms were expressed by Langmuir and Freundlich adsorption models. The Langmuir adsorption model fits the experimental data reasonably well than Freundlich model for the three metal ions studied. The maximum adsorption capacity of coir pith was found to be 15.95 mg g^{-1} nickel. The competitive adsorption of multi-metals onto coir pith was studied [108]. Adsorption efficiency of coir pith to remove these three metal ions from synthetic nuclear power plant coolant water samples was also tested. The studies showed that this low cost adsorbent could be used as an efficient adsorbent material for the quantitative removal of nickel from water and synthetic nuclear power plant coolant water. Although, the adsorptive capacity of coir pith is not excessively high for nickel, low cost of the material together with its adsorptive ability could offer a promising procedure for the pollution of industrial wastewaters [108-115].

However, coir pith and modified coir pith have been investigated. The study confirmed the effectiveness of the adsorbent for nickel removal [116-119] because the coir pith contains high lignin (36%) and cellulose (44%) and is suitable to adsorb nickel from electroplating rinse water [116]. This was in correlation with previous studies reported by other researchers [117]. The optimum condition for nickel removal by coir pith in batch system was solution pH 4–7, adsorbent dosage of 5% (w/v), an equilibrium contact time of 10 min and a temperature of 30^0C. Nickel adsorption was fitted to both Langmuir and Freundlich isotherms. It showed that the maximum value of nickel adsorption (q_{max}) by coir pith and modified coir pith were 9.5 and 38.9 mg/g respectively. Sodium hydroxide increased metal binding site (free O^-) of

modified coir pith. The advantages of this adsorbent are; low cost, availability in high quantities and high adsorption capacity. However, the efficiency of adsorption of coir pith was low. As a result of this, it was modified with NaOH to increase nickel adsorption from 9.5 to 38.9 mg g^{-1} coir pith. The mechanism of Nickel adsorption by the coconut coir pith was confirmed by elution with sulphuric acid, which implied that it was chemisorption. The evidence showed that lignin and holo-cellulose are the main components in coir pith that played the major role in nickel adsorption. The main functional groups in coir pith that were involved in nickel adsorption were hydroxyl and methoxyl groups. It was confirmed by X-ray adsorption spectroscopy (XAS) that the oxidation species of nickel involved in nickel adsorption by

coir pith and modified coir pith was Nickel(II). Sodium hydroxide increased metal binding site (free O $^-$) of modified coir pith. [116,120].

Chemically prepared activated carbon from waste apricot

Waste apricot supplied by Malatya apricot plant (Turkey) was activated by using chemical activation method and K_2CO_3 was chosen as the activating agent. Activation temperature was varied over the temperature range of 400–900^{0}C and N_2 atmosphere was used with 10^{0}C/min heat rate. The maximum surface area (1214 m^2/g) and micropore volume (0.355 cm^3/g) were obtained at 900^{0}C, but activated carbon was predominantly microporous at 700^{0}C.
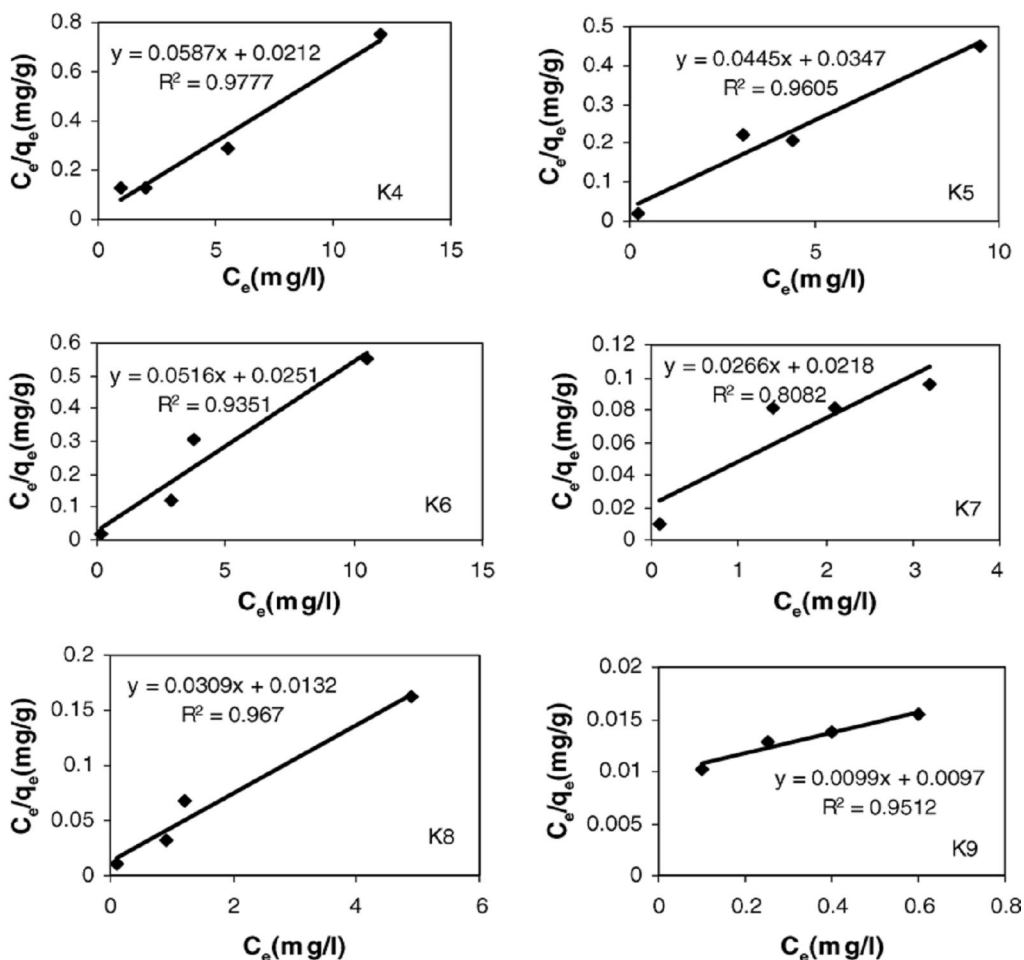

*Figure 1.* **The Langmuir isotherms for activated carbon sample [121]**

The resulting activated carbon was used for removal of Nickel(II) ions from aqueous solution and adsorption properties were investigated under various conditions such as pH, activation temperature, adsorbent dosage and nickel concentration [121]. Optimal condition was determined as; pH 5, 0.7 g/10 ml adsorbent dosage, 10 mg L^{-1} Nickel(II) concentration and 60 min contact time. Results indicated that the effective uptake of Nickel(II) ions was obtained by activating the carbon at 900^0C. Adsorption percentage of all activated carbon samples was determined in the range of 40–100 % [121]. Maximum adsorption percentage was determined and the experiments carried out with the sample by using different adsorbent dosage. The adsorption data fitted reasonably well the Langmuir isotherm (Fig. 1) for activated carbon samples prepared from waste apricot under different activation temperature. Maximum Langmuir adsorption capacity was 101.01 mg g^{-1} [121]. The adsorption capacities of activated carbon samples are compared with other adsorbents examined for removal of Nickel(II) under similar conditions reported in literature 122-133]. Activated carbon samples in this study had the highest adsorption capacity. R_L values were determined, it ranges between 0 and 1, indicating favourable adsorption.

Synthetic materials and other adsorbents used for Nickel(II) ion removal
Sodium polyacrylate-grafted activated carbon

A novel sodium polyacrylate grafted activated carbon was produced by using gamma radiation to increase the number of functional groups on the surface. After irradiation the capacity for nickel adsorption was studied [134] and found to have increased from 44.1 to 55.7 mg g^{-1}. X-ray absorption spectroscopy, Desorption and FTIR showed that the adsorbed nickel on activated carbon and irradiation-grafted activated carbon was coordinated with 6 oxygen atoms from carboxyl groups at 2.04–2.06 Å in first shell (Scheme 1 and Figure 2). It is proposed that this grafting technique could be applied to other adsorbents to increase the efficiency of metal adsorption. From the result obtained, the grafting technique with gamma rays, could be applied to other polymers in order to increase metal adsorption capacity. This technique will help the

treatment of industrial wastewater economically [132-141].
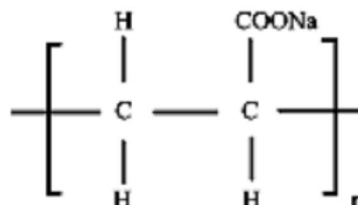
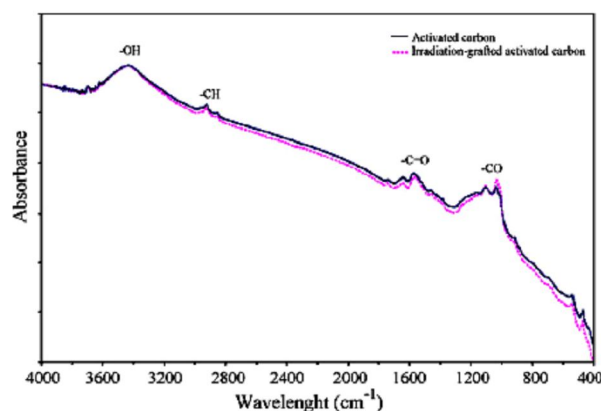*Scheme 1.* **The structure of sodium polyacrylate.[134]**

Figure 2. **IR spectra of activated carbon and irradiation-grafted activated carbon [134]**

Sewage sludge

The adsorbent derived from sewage sludge through chemical pyrolysis has been used for the adsorption of Nickel(II) from aqueous solution. Parameters such as the agitation time, metal ion concentration, adsorbent dosage and pH were studied [95-96]. The adsorption data fit well with the Langmuir and Freundlich isotherm models. The capacity of adsorption calculated from the Langmuir isotherm was 16.9 mg g^{-1} for Nickel(II) at the initial pH of 5.8 at 25^0C. Agitation time of 60 min was necessary for the adsorption to reach equilibrium, the optimum pH value in the range of 5.5–6.0. Desorption studies were performed with dilute hydrochloric acid. Quantitative recovery of the metal ion was possible. The mechanism of adsorption seems to be ion exchange. As the sewage sludge is discarded as waste from wastewater treatment processing, the adsorbent derived from sewage sludge is expected to be an economical product for metal ion remediation from water and wastewater [96-101]. The optimum

adsorption conditions were as follow: the pH range 5.5–6.0, the equilibrium time was 60 minutes; the initial concentration was 30 mg L^{-1} adsorbent dosage was not less than 10 g L^{-1} for Nickel(II). The desorption experiment indicate that the quantitative recovery of Nickel(II) is possible from the metal-loaded adsorbent and that the ion exchange seems to be an important process in the adsorption of metal ion by adsorbent [97-107].

Surface molecular imprinting adsorbent

The expanded-bed adsorption of Nickel(II) from aqueous solution using surface molecular imprinting adsorbent was experimentally and theoretically studied [121]. An expanded bed is a stabilized liquid fluidized bed with a solid phase (adsorbent) of defined size and density distribution [122-124]. Expanded bed adsorption technology has been widely applied to capture proteins directly from crude feed stocks such as Escherichia coli homogenate, yeast, fermentation, mammalian cell cultures, milk, and animal tissue extracts. Various applications have been reported ranging from lab-scale to pilot-plant to large-scale production. A large number of reports have appeared which have successfully demonstrated the utility of the concept of adsorption in expanded beds and have used adsorbents that have specific properties for expanded bed operation [125-127].

A new surface molecular imprinting adsorbent (SMIA) was used in the expanded bed. The expansion ratio and adsorption performance were studied at different volumetric rates, inlet concentrations, and pH values [129]. A model based on the Adams–Bohart adsorption model of breakthrough curves was established to predict the breakthrough curves for the expanded bed adsorption. The predicted curves had good agreement with the experimental curves. The breakthrough time ($T_{1/2}$) decreased with increasing inlet concentration when the outlet concentration was half the initial concentration ($C/C_0 = 0.5$). The inlet concentration had little effect on the adsorption rate constant *(k_1)* value when the initial concentration (C_0) was above 150 mg/L. However, $T_{1/2}$ values increased with increasing initial pH of the inlet solution, and the k_1 value decreased due to the competition between H^+ and Nickel(II).

The expansion of the bed height showed a linear relationship with the flow rate of Nickel(II) solution. The expansion of the bed height decreased with increasing adsorbent size. pH had an obvious effect on the adsorption of Nickel(II). When the pH was 2, the H^+ in the solution used most of the adsorption sites on the adsorbent leading to a rapid decrease in adsorption capacity. When the volumetric flow rate of the Nickel(II) solution increased from 5 to 35 mL/min, the breakthrough time was shortened, and for higher flow rates of the Nickel(II) solution the total outlet volume increased. $T_{1/2}$ values decreased with increasing inlet concentrations. However, the inlet concentration had little effect on the k_1 value when C_0 was above 150 mg L^{-1}. Both Q_e and $T_{1/2}$ values increased with increasing initial pH of the inlet solution, whereas the k value decreased because of the competition between H^+ and Nickel(II). The predicted values show good agreement with the experimental values [121].

Su and co-worker reported the adsorption mechanism for the imprinted ion (Nickel(II)) of a novel surface molecular imprinting adsorbent (SMIA) prepared by the imprinting technique method [128]. The interaction mechanism for the imprinted ion (Nickel(II)) with–OH and –NH_2 groups on the chitosan molecules was testified by FT-IR and X-ray photoelectron spectroscopy (XPS). By means of FT-IR and XPS analysis, there exist two kinds of –NH_2 groups on the chitosan molecule. Most –NH_2 groups showed higher adsorption activity as a result of the imprinting technique in the adsorbent preparation, whereas a few –NH_2 groups displayed a lower adsorption activity because of the cross linking in the preparation, which caused different adsorption mechanisms for Nickel(II). Compared with the surface molecular non-imprinting adsorbent (non-SMIA), both –OH and –NH_2 groups on the imprinted adsorbent surface could provide higher adsorption activity to Nickel(II) based on FT-IR and XPS analyses. SMIA had more pores and higher specific surface area than non-SMIA according to the distribution of the pore diameter and specific surface area analyses [121-126, 128].

The adsorption mechanism for Nickel(II) on the –OH and –NH_2 groups on the adsorbent

surface was confirmed by FT-IR and XPS analyses. There existed two kinds of –NH$_2$ groups on the chitosan molecules, most –NH$_2$ groups protected and only a few –NH$_2$ groups cross-linked, which caused different adsorption mechanism with Nickel(II). The cross-linking bands could only be opened after the adsorbent was reused for 10 batches, the adsorbent coat appeared with some cracks. This made some interior –OH groups and a few cross-linked NH$_2$ groups made some contribution to the removal of Nickel(II). In contrast to non-SMIA, the BE of N element on SMIA increased by 0.5 eV, thereby enhancing the adsorptive ability of Nickel(II) on –NH$_2$ groups. The distribution of the pore diameter on SMIA was mainly at 33Å. The non-SMIA had only few pores, but the specific surface area decreased by 8% compared with SMIA. The pore on the SMIA surface was very flat and the adsorption process for Nickel(II) occurred mainly on the adsorbent surface. The study revealed that if the adsorbent was imprinted during preparation, the –OH and –NH$_2$ groups will have greater activity and a better selectivity for the imprinted ions (Nickel(II)) than non-SMIA [129-136].

Waste rubber tire

A novel carbon (RTAC) developed by physical activation from waste tire rubber, was used as adsorbent for assessing its removal capacity of nickel ions from aqueous solutions [142-164]. A well-developed mesoporous structure in RTAC was conducive for its enhanced batch adsorption capacity of the studied metal ions removal in comparison to a microporous commercial carbon (CAC) [143].
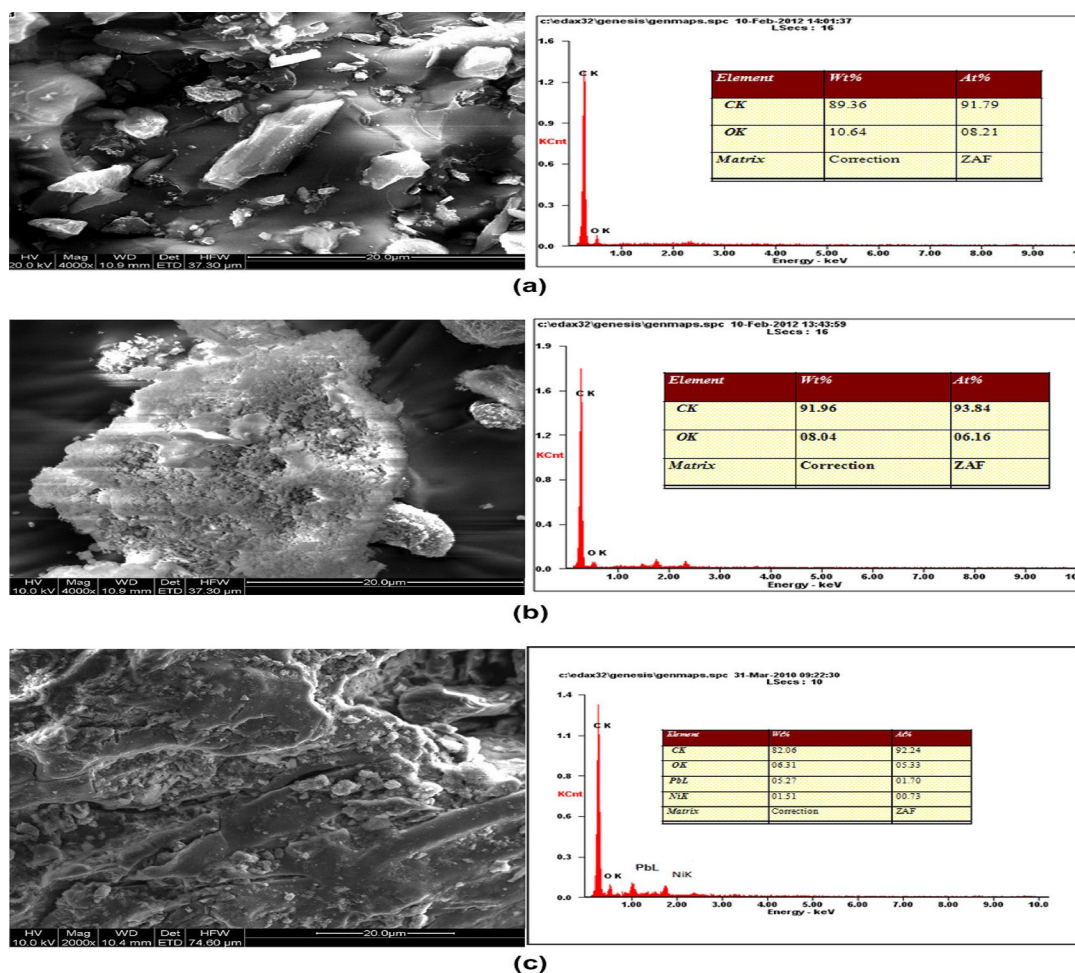

Figure 3. **SEM micrograph and EDAX of (a) CAC (b) RTAC before adsorption (c) RTAC after adsorption of Nickel(II) [143]**

RTAC and CAC exhibited a similar surface chemistry as revealed by FTIR and pH$_{pzc}$ studies, the higher mesoporosity played a significant role in enhancing the adsorption capacity of RTAC for liquid phase adsorption of lead and nickel removal. Uptake trend of RTAC for Nickel(II) revealed the adsorbate properties of electronegativity and ionic radii to play a contributory role. Effect of various operating parameters along with equilibrium, kinetic and thermodynamic studies reveals the efficacy of the RTAC for nickel removal (Fig. 3). The adsorption equilibrium data obeyed the Langmuir model and the kinetic data were well described by the pseudo-second-order model. A physical electrostatic adsorbate–adsorbent interaction is revealed from pH$_{pzc}$ studies and from D–R model constants. The adsorption process is believed to proceed by an initial surface adsorption followed by intraparticle diffusion [143-150]. Thermodynamic studies revealed the feasibility and endothermic nature of the system. Results were confirmed by column experiments [141-153]. Adequate desorption as well as reusability without significant loss of efficiency established the practicality of the developed system and demonstrated an important criterion of advanced adsorbent in RTAC for waste water treatment. Approximately 96% nickel removal was achieved by RTAC from a simulated electroplating industrial wastewater. Experimental results reveal the technical feasibility of RTAC, it's easy to synthesize, economical, eco-friendly and a promising advanced adsorbent in environmental pollution clean-up [143-156].

Aerobic activated sludge with the influence of three different surfactants

The effects of different surfactants (SDBS, C14BDMA, Tween 20) on the sorption of Nickel(II) onto aerobic activated sludge were studied [153]. Results showed that the influence of surfactants on the adsorption of Nickel(II) strongly depended on the type of the surfactants. The presence of SDBS enhanced Nickel(II) sorption, in contrast, the presence of C14BDMA and Tween 20 both caused a Nickel(II) sorption reduction, but Tween 20 had a slighter effect. With the presence of individual surfactant, the sorption kinetics and isotherms were in good agreement with pseudo-second-order kinetic model and Langmuir

isotherms respectively [153-159]. The surfactant impelled the Nickel(II) adsorption process onto aerobic activated sludge to transform from chemisorption to physisorption [154-161], and the existence of SDBS in solution even changed the exothermic nature. From FT-IR and zeta potential measurements, there was competitive relationship between C14BDMA and Nickel(II) as they adsorbed onto sludge. The FT-IR and zeta potential measurements confirmed the competitive relationship between C14BDMA and Nickel(II) for their adsorption onto sludge as shown in the Figures 4-5 below. Tween 20's effort mechanisms on the Nickel(II) adsorption were unapparent [154-160].
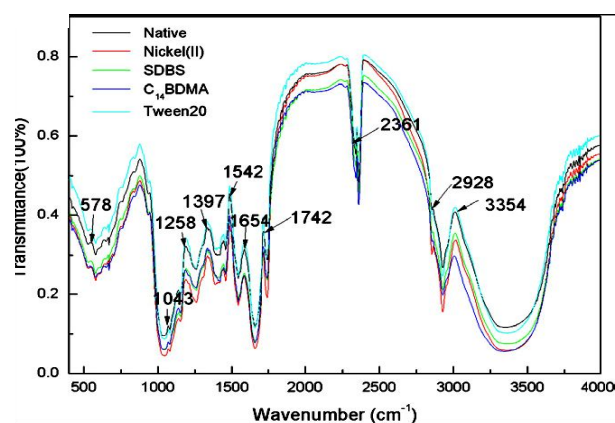

Figure 4. **FTIR analysis of native activated sludge, after Nickel(II) biosorption, after SDBS biosorption, after C14BDMA biosorption and after Tween 20 biosorption, indicating the involvement of various functional groups Nickel(II) and surfactants biosorption [154]**
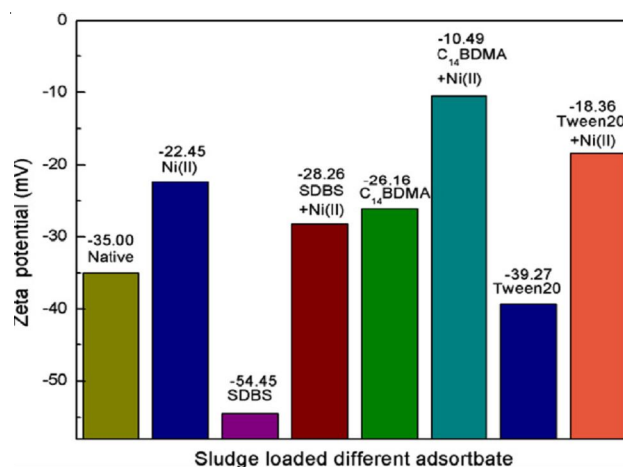

Figure 5. **Zeta potential changes in presence of different surfactants [154]**

In summary, there are other adsorbents that have been used to remove nickel from aqueous solution. Table 1 shows the summary of work done by various researchers using different waste materials for the removal of nickel

Table 1. **Summary of other work done by various researchers using different agricultural waste materials for the removal of nickel.**

Agricultural waste	Results	Reference
Hazelnut shell activated carbon	Effective removal	[162]
Casia fistula biomass	100%	[163]
Maple saw dust	75%	[164]
Sugarcane bagasse	>80%	[165]
Tea waste	86%	[166]
Defatted rice bran, chemically treated soybean & cottonseed hulls	87%	[167]
Waste tea leaves	92%	[168]
Saw dust of oak and black locust hard wood (modified & unmodified)	70–90%	[169]
Hazelnut shell, orange peel, maize cob, peanut hulls, soyabean hulls treated with NaOH & jack fruits	High metal adsorption	[170]
Mustard oil cake	Upto 94%	[171]
Coir fiber chemically modified with hydrogen peroxide	>70%	[164]
Dye loaded groundnut shells and sawdust	Up to 90%	[164]
PFP (petiolar felt sheath palm)-peelings from trunk of palm tree	>70%	[172]
Agro waste of black gram husk	Up to 93%	[173]
Modified & unmodified kenaf core, kenaf bast, sugarcane bagasse, cotton, coconut coir, spruce	Up to 88%	[169]

Future challenges

Despite the tremendous progress achieved from the use of agricultural and synthetic waste materials in the removal of Nickel(II) from aqueous solutions, there are still some challenges and limitations to be addressed, some of them are highlighted below:

(1) Selection and identification of an appropriate low-cost adsorbent is one of the key issues to achieve the maximum removal/adsorption of specific type of pollutant depending upon the adsorbent–adsorbate characteristics.

(2) The conditions for the production of low-cost adsorbents after surface modification for higher uptake of pollutants need to be optimized.

(3) Cost factor should not be ignored. Low production cost with higher removal efficiency of adsorbents would make the process economical and efficient.

(4) Mechanistic studies need to be performed in detail to propose a correct binding mechanism of aquatic pollutants with low cost adsorbents.

(5) Regeneration studies need to be performed in detail with the pollutants-laden adsorbent to recover the adsorbate as well as adsorbent. It will enhance the economic feasibility of the process.

(6) The potential of low-cost adsorbents under multi-component pollutants needs to be assessed. This would make a significant impact on the potential commercial application of low-cost adsorbents to industrial systems.

(7) There is scarce data available for the competitive adsorption of pollutants (metal ions adsorption in presence of phenols, dyes and other contaminants and vice-versa). Therefore, more research should be conducted in this direction.

(8) It is further suggested that the research should not be limited to only lab scale batch studies, but pilot-plant studies should also be conducted utilizing low-cost adsorbents to check their feasibility on commercial scale.

(9) The effectiveness of the treatment depends not only on the properties of the adsorbent and adsorbate, but also on various environmental conditions and variables used for the adsorption process, e.g. pH, ionic strength, temperature, existence of competing organic or inorganic compounds in solution, initial adsorbate/adsorbent concentration, contact time and speed of rotation, particle size of adsorbent, etc. These parameters should also be taken into account while examining the potential of low-cost adsorbents.

(10) The development in the field of adsorption process using low-cost adsorbents essentially

requires further investigation of testing these materials with real industrial effluents.

(11) Environmentally safe disposal of pollutants-laden adsorbents is another important topic of concern which should not be overlooked.

If it is possible to develop such adsorbents having all the above-mentioned characteristics, then these adsorbents may offer significant advantages over currently available expensive commercially activated carbons and, in addition contribute to an overall waste minimization strategy.

Conclusions

In recent years, increasing costs and environmental considerations associated with the use of commercial adsorbents, has led to a significant body of research work aimed at developing new low cost adsorbents derived from renewable resources. In this review, an attempt has been made to focus on the recent developments related to the detoxification of water and wastewater by low-cost adsorbents derived from agro-industrial and municipal wastes. It is important to note here that the maximum adsorption capacities reported in this paper provide some idea of adsorbent's effectiveness for Nickel(II), it mainly depend on experimental conditions. The use of waste materials as low-cost adsorbents for removing various pollutants from water and wastewater presents many attractive features especially their contribution in the reduction of costs for waste disposal, therefore contributing to environmental protection. Although the amount of available literature data on the use of low-cost adsorbents in water and wastewater treatment is increasing at a tremendous pace, there are still several gaps which need to be filled.

Acknowledgements

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