# REMOVAL OF NICKEL (II) IONS FROM WASTE WATER USING LOW COST ADSORBENTS: A REVIEW

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## ABSTRACT

Due to rapid industrialization and urbanization in developing countries has increased the toxin levels in industrial effluent which rise the importance of water and waste water treatment. Very small concentrations of metallic ions present in water increase the health risks to human and animals. Though there are many treatment methods used for removal of heavy metals from waste water like chemical precipitation, membrane filtration, ion exchange, coagulation, flocculation, electrochemical treatment, adsorption and co-precipitation. Yet various researchers have studied that adsorption is a highly effective and economical technique for the removal of heavy metals from waste water and from ancient times activated carbon has extensively used as an adsorbent but it found to be an expensive material which triggered the need for synthesizing low cost adsorbents from Agro and horticultural wastes and by products such as coconut husk, tamarind fruit shell, saw dust, oil palm shell, cow bone charcoal and bagasse fly ash(sugar industry waste) etc., for the nickel removal from waste water. These Agro and horticultural wastes would have been the sources to pollute our environment. The removal of nickel ions from waste water using low cost adsorbents and utilization of Agro and horticultural wastes and by products to avoid environment pollution is discussed in this paper.

**Key words:** adsorption, frendlich isotherm, Langmuir isotherm.

## INTRODUCTION

Water is the most essential element to life on earth. In its purest form it is odourless, colourless and tasteless. Level of contaminants in aquatic ecosystems has increased due to discharge of industrial effluents in water which in turn has led to water demand for domestic and industrial purpose. Heavy metals like Zn, Cr, Pb, Hg, Ni and As originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries etc (MukeshParmar, 2013). These metals are non-biodegradable in nature and affect living organisms, causes various disease and disorders. Removal of toxic metals is necessary when the heavy metals level exceeds the permissible discharge level in industrial effluent. Various techniques which have been used for the removal of heavy metal ions from industrial effluents include ion exchange, chemical precipitation, electrode dialysis, membrane filtration, reverse osmosis, ultra-filtration, coagulation, floatation and adsorption. From the above mentioned techniques adsorption method is widely used because of its cost effective nature. Activated carbon is a well-known adsorbent used in the removal of metals but the high cost of activated carbon inhibits its large scale use as an adsorbent. To overcome this problem, several studies have been carried out for synthesizing the low cost adsorbent that are obtained from various wastes and by-products such as rice husk ash, coconut husk, Neem bark, pellets of peanut hull, tea wastes, sugarcane bagasse, cow bone charcoal, tamarind fruit shell, moringaoleifera pods. In this article, the technical ability and feasibility of various low cost adsorbents for nickel removal from industrial waste water has been reviewed.

**ADSORBATE-Nickel (Ni):** Nickel is a silvery white, hard, malleable and ductile metal. It is a widespread distribution in the environment. It has an atomic number of 28 and the Maximum Contamination Limit (MCL) standard is 0.2 mg/l. Drinking water generally contains nickel at concentration less than 10 µg/l. Assuming a daily intake of 1.5 litre of water and a level of 5 to 10 µg nickel/ litre, the mean daily intake of the nickel from water for adults would be between 7.5 to 15 µg. Nickel is used in various forms for nickel plating, as a catalyst, as a mordant and in ceramic glazes etc. Again it is a micronutrient for most organisms but excessive quantities have toxic effects. Nickel and Nickel compounds belong to classic noxious agents encountered in industry but also known to affect non-occupationally exposed individuals. Inhalation exposure in occupational area is a primary route for nickel induced toxicity and may cause toxic effects in the respiratory tract and immune system. Electroplating and metal surface treatment process generates significant quantities of waste waters containing heavy metal from variety of applications. These include electroplating, electro less depositions, conversion-coating, anodizing-cleaning, milling, etching and printed circuit board (PCB) manufacturing. Petroleum refining which generates conversion catalysts contaminated with nickel,

vanadium and chromium (MukeshParmar,2013). Nickel is known haematotoxic, immunotoxic, neurotoxic, genotoxic, reproductive toxic, pulmonary toxic, nephrotoxic, hepatotoxic and carcinogenic agent.

- Higher chances of development of lung cancer, larynx cancer and prostate cancer
- Sickness and dizziness after exposure to nickel gas.
- Lung embolism
- Respiratory failure
- Birth defects
- Asthma and chronic bronchitis
- Allergic reaction such as skin rashes mainly from jewelry
- Heart disorders

## ADSORBENTS

**Characteristics of adsorbent:** The most important attributes of an adsorbent for any application are Adsorption Capacity, Selectivity, Regenerability, Kinetics, Compatibility and Cost.

**1.Adsorption capacity:** Adsorption capacity (or "loading") is the most important characteristics of an adsorbent. Simply stated, it is the amount of adsorbate taken up by thy adsorbent per unit mass (or volume) of the adsorbent. It depends on the fluid –phase concentration, the temperature and other conditions (especially the initial condition of the adsorbent).

**2.Selectivity:** Selectivity is related to capacity, the simplest is the ratio of the capacity of one component to that of another at a given fluid concentration .An ideal situation occurs when the major component is not much adsorbed (so it can be thought of as an inert "carrier"), which leads to a very large selectivity.

**3.Regenerability:** All cyclic adsorption applications rely on regenerability, so that the adsorbent can operate in sequential cycles with uniform performance. This means each adsorbate component (adsorptive or adsorbate) must be relatively weakly adsorbed (or physisorbed). The heat of adsorption provides a measure of the energy required for regeneration, and in that regard low values are desirable .regeneration might be accomplished by a thermal swing, pressure swing, chemical (e.g.,  By displacement, elution or supercritical extraction) or sometimes by a combination of those.

**4.Kinetics:** Mass transfer kinetics is a catch all term related to intra particle mass transfer resistance. It is important because it controls the cycle time of a fixed bed adsorption process .Fast kinetics provides a sharp breakthrough curve, while slow kinetics yields a distended breakthrough curve. The effect of a distended breakthrough curve can be overcome by adding adsorbent at the product and or by increasing the cycle time (which reduces the throughput per unit of adsorbent).

**5.Compatibility:** Compatibility covers various possible modes of chemical and physical attack that could reduce the life expectancy of the adsorbent, such as biological  fouling or attrition .For e.g., the adsorbent, binder and surface groups should be inert to carrier or solvent and should not irreversible react with the adsorbate(s) or contaminants.

**6.Cost:** Cost is the most subtle characteristics to understand because it may vary from week to week and sales rep to rep, even for the same exact material. Adsorbent should be cost effective.

**Preparation of various adsorbents:** In general, an adsorbent can be assumed a "low cost" if it requires a little bit processing, abundant in nature or if it is a by-product or a waste from industry. Natural material or certain waste from industrial or agricultural operation is one of the resources for low cost adsorbents. Generally; these materials are locally and easily available in large quantities. Therefore, they are inexpensive and have little economic value. Let us discuss about the preparation of low cost adsorbents obtained from agro and horticultural wastes and by-products used for the removal of nickel ions from wastewater.

**1.Coconut husk:** The coconut husk was cut into small pieces and blended, washed with distilled water to remove dirt and colour and air dried for 24 h to avoid thermic deactivation of the adsorbent surface. It was sieved to pass through a 2 mm stainless steel endecott sieve and a portion of this was stored in clean polyethylene containers labeled as unmodified adsorbent prior to analysis (O.K.Olayinka, 2009).

**2.Neem leaves:** The Neem leaves were dried for a period of three days. The Neem leaves were cleaned with distilled water and dried at room temperature.  The leaves were grounded with the help of grinding mill. The grounded Neem leaves were sieved and were of  particle size 0.25 to 0.50 mm. This was to allow for shorter diffusion path, thus

allowing the adsorbate (Neem leaves) to penetrate deeper into effluent more quickly, resulting in a higher rate of adsorption (Innocent OBOH, 2009).

**3.Bone charcoal:** The bone charcoal residue is a result of the pyrolysis process according to the following condition. The BC residue was maintained under an inert atmosphere to avoid any oxidation. It was crushed and sieved to give uniform particle size(~40 mesh size) for use in the different applications (Juan Carlos Moreno, 2010).

$$\text{Cow bones} \xrightarrow{\text{800 °C /5h (inert atmosphere)}} \text{BC residue + steam + oil + ammonia liquor}$$

**4.Coconut leaves:** Coconut leaves was washed with distilled water, dried and powdered. These powdered leaves were sieved with IS sieves (1000-600μ). Sieved samples was washed with distilled water and dried at room temperature 27℃ for 24 hours, and then samples was dried in hot air oven at a temperature 42℃ for 8 hours and later cooled in room temperature and preserved in air tight plastic container.

**Table.1.Physical constants of coconut leaves**

| Density | 0.117g/cm³ |
|---|---|
| Surface area | 0.23921cm²/g |
| Ph | 6.02 |

**5.Tea wastes:** Prior to the experiments, other soluble dirtness and coloured components wer soluble dirt's are removed from the tea wastes by washing with distilled water for much times until a colorless solution of tea waste was spectrometrically observed at room temperature. Decolourized and cleaned tea waste was dried to room temperature for few days and then used as adsorbents (EmineMalkoc, 2005).

**6.Rice husk:** Rice husk is agricultural waste mostly available in rural areas, they are collected and grinded in grinders then sieved and washed with distilled water repeatly for dirt and other particulate matter removal, then dried in hot oven at 100℃ for 24 hours, then either directly used as an adsorbent or treated with $H_2SO_4$ and then washed again with distilled water for removing acidity, washing upto totally acidity are removed and then dried at 100℃ for 12 hours then collected in a air tight plastic bags and then used as an adsorbent (MukeshParmar, 2013).

**ADSORPTION METHOD**

Adsorption is a process, similar to absorption, by which substance in a gas or liquid becomes attached to a solid. The substance can be a pollutant called an adsorbate, which is attached to the surface of a special solid. Adsorption occurs naturally, but industrialists have perfected adsorption methods to clean up hazardous waste or purify drinking water.

Tiny chemical particles suspended in another phase of matter, meaning in the air as a gas or in water as a liquid, are sometimes considered contaminants. These tiny particles can be separated from that phase, called the adsorbent, to enter a different phase. A material of another phase, like the solid carbon, preferentially targets these particles and bonds the adsorbate to its surface. The remaining air or liquid has been purified. This differs from adsorption where the particles never change phase, but enter pores of the solid along with the accompanying air or water. On the basis of type of forces of attraction existing between adsorbate and adsorbent, adsorption can be classified into two types:

**Physisorption or Physical adsorption:** When the force of attraction existing between adsorbate and adsorbent are weak vanderwaal forces of attraction, the process is called Physisorption or Physical adsorption. It takes place with formation of multilayer of adsorbate on adsorbent.

**Chemisorption or Chemical adsorption:** When the force of attraction existing between adsorbate and adsorbent are chemical forces of attraction or chemical bond, the process is called Chemisorption or Chemical adsorption. It takes place with formation of unilayer of adsorbate on adsorbent.

**1.Batch adsorption study:** Batch experiments were carried out at various $p^H$ (2-7), adsorbent dose (1-5 g/l) and stirring speed (180 rpm) for a contact time of 60 min. for each batch experiment, 100 ml of 100 mg/l both metal ions solution was used. After setting $p^H$ and adding desired amount of adsorbent the mixture was agitated on mechanical shaker for 60 min. after the mixture was filtered to separate the adsorbent from supernatant. The residual concentration of both ions was determined by flame atomic spectrometer. All experiments were replicated thrice for all the adsorbents and results were averaged. The removal percentage of Nickel was calculated for each run by the following expression:

$$R \% = (C_i - C_e) / C_i \qquad (1)$$

Where $C_i$ and $C_e$ are the initial and final concentration ions in the solution. The adsorption capacity of an adsorbent which is obtained from the mass balance on the sorbate in a system with solution volume V is often used to acquire the experimental adsorption isotherms. Under the experimental conditions, the adsorption capacities of all the adsorbents for each concentration of Ni(II) ions at equilibrium was calculated using equation (2)

$$q_e \ (mg \ g^{-1})\% = \{M \ (C_i - C_e) \ / \ M\} * V \qquad (2)$$

Where $C_i$ and $C_e$ are the initial and final concentration ions in the solution respectively. Vis the volume of solution (L) and M is the mass of adsorbent (g) used (H. ZavvarMousavi, 2011).

**2.Isothermic adsorption study:** Adsorption will continue until equilibrium will be established between the substance in solution and the same substance in the adsorbed state. At equilibrium a relationship exists between the concentration of the species in solution and the "concentration" of the same species in the adsorbed state (i.e., the amount of species adsorbed per unit mass of adsorbent). The adsorption equilibrium relationship at a given temperature is referred to as adsorption isotherm.

**Langmuir Isotherm:** The Langmuir isotherm has been used by various workers for the sorption of variety of compounds. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The linear form of Langmuir isotherm is given by the following equation:

$$1/q_c = 1/Q_o + 1/bQ_oC_c \qquad (3)$$

Where $q_c$ is the amount adsorbed (mg $g^{-1}$), $C_c$ the equilibrium concentration of the adsorbate (mgl$^{-1}$) and $Q_o$ and b are the Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively. When $1/q_e$ was plotted against $1/_{Cc}$, straight lines with slope $1/bQ_o$ were obtained, which show that the adsorption of Nickel ion. The Langmuir constants, b and $Q_o$, were calculated. The values of constants indicate favourable conditions for adsorption.

**Freundlich Isotherm:** The logarithmic form of Freundlich model is given by the following equation,

$$Log \ q_e = log \ K_F + 1/n \ log \ C_e \qquad (4)$$

Where $q_e$ is the amount adsorbed (mg $g^{-1}$), $C_e$ isthe equilibrium concentration of the adsorbate (mgl$^{-1}$) and $K_F$ and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The curve plotted between log $q_e$ and log $C_e$. Freundlich constants, $K_F$ and n, were calculated from the best fit lines in the curve and the values of these at different temperature are calculated (Innocent OBOH, 2009).

**3.Kinetic adsorption study:** The study of sorption kinetics describes the uptake rate of heavy metal ions, and evidently this rate controls the resident time of these ions at the solid liquid interface. Consequently it is important to establish the time dependency of such systems for various pollutant removal processes. Therefore, the required contact time for the sorption to be completed is important to give insight into a sorption process. This also provides information on the minimum time required for considerable adsorption to take place and the possible diffusion control mechanism between the adsorbed ion as it moves from the bulk solution towards the adsorbent surface. At the beginning stage of the adsorption process, the removal rate of the ions is higher. The faster beginning rate may be due to the availability of the uncovered surface area of the adsorbent initially. The adsorption kinetics depends on; (i) the surface area of the adsorbent, (ii) the nature and concentration of the surface groups (active sites), which are responsible for interaction with targeted ions. The kinetics of heavy metal ions sorption on the adsorbent was analyzed using kinetic models, these include: the pseudo-first order and pseudo-second order.

The adsorption rate constant proposed by Ho using pseudo first order reaction kinetic is shown below:

$$dQ_t \ / \ dt \qquad = k_1 \ (Q_e - Q_t) \qquad (5)$$

where $k_1$ is the adsorption rate constant for the first order adsorption, and $Q_1$ is the amount of heavy metal adsorbed at time t (mg/g). The integration of Eq. (5) gives the following expression:

$$ln \ (Q_e - Q_t) = -k_1t + C_1 \qquad (6)$$

where $C_1$ is the integration constant for first order reaction kinetic. The curve plotted between ln $(Q_e - Q_t)$ and time. Adsorption data was also evaluated according to the pseudo second order reaction kinetic proposed by Ho and McKay:

$$dQ_t \ / \ dt = k_2 \ (Q_e - Q_t)^2 \qquad (7)$$

where $k_2$ is the second order reaction constant. If Eq. (7) is integrated, the following expression is obtained:

$$1 / (Q_e - Q_t) = k_2 t + C_2 \qquad (8)$$

Where $C_2$ is the integration constant of the second order reaction kinetic. The curve plotted between $1 / (Q_e - Q_t)$ and time.

Rate constants were calculated from the slopes of the curves. The degree of goodness of the linear plot of these kinetic models con be judged from the value of the determination coefficient of the plot, which can also be regarded as a criterion in the determination of the adequacy of kinetic model (ReyadAAlDwariri, 2012).

**4.Column adsorption study:** The adsorbents are packed in a column like layers of bed. The fixed bed column made of Perspex tubes 2.0 cm internal diameter and 30 cm in height. The bed length was 30 cm. In a typical experiment the metal of a known concentration was pumped at a fixed flow rate to be filled with known bed height of adsorbent. The particle size of adsorbent was 1.0-3.0 mm. the $p^H$ of the solutions was maintained constant at 4.0. The temperature of stream feeding solution and of the column was controlled at 25 °C through a thermostatic bath.

After completing the process; the adsorbent contains the hazardous material. Therefore, appropriate actions must then be taken to treat the spent adsorbent at the end of a cycle. The adsorbent can be:

- Regenerated (I.e., the hazardous material may be removed by stripping)
- Disposed of (together with the pollutants it contains) in a landfill
- Destroyed (together with the pollutants it contains) in an incinerator

The above mentioned points are the main reason for selecting adsorption process.

**FACTORS AFFECTING ADSORPTION**

**1.Surface area of adsorbent:** Larger sizes imply a greater adsorption capacity.

**2.Particle size:** Size of the molecule with respect to size of the pores. Larger molecule may be too large to enter small pores. This may reduce adsorption independently of other causes. Smaller particle sizes reduce internal diffusion and mass transfer limitation to the penetration of the adsorbate inside the adsorbent (i.e. equilibrium is more easily achieved and nearly full adsorption capacity can be attained). However waste water drop across columns packed with powdered material is too high for use of this material in packed beds. Addition of powdered adsorbent must be followed by this removal.

**3.Contact time or Residence time:** Longer the time, the more complete adsorption will be achieved. However the equipment will be larger. The adsorption of metals such as Cu, Zn and Ni by wood ash is a rapid process and often reaches equilibrium within several hours. Ni(II) ions have sharp rise in percentage of removal with increasing contact time.

Solubility of solute (adsorbate) in liquid (waste water): Substance slightly soluble in water will be more easily removed from water (i.e. adsorbed) than substances with high solubility.

**4.Degree of ionization of the adsorbate:** More highly ionized molecules are adsorbed to a small degree than neutral molecules. The degree of ionization of a species is affected by the $P^H$ (for example, weak acid or weak base). This in turn affects adsorption.

**5.$P^H$:** The adsorptive capacity of metal cations increases with increasing $P^H$ of the sorption system, but not in a linear relationship. The percentage adsorption increases with $P^H$ to attain a maximum at $P^H$ 6 and thereafter it decreases with further increase in $P^H$ (MukeshParmar, 2013).

**6.Temperature:** Adsorption reactions are normally exothermic, so adsorption capacity increases with decrease of temperature. In the range of 15-40 °C, the maximum equilibrium adsorption capacity for Ni(II) ions by the wood ash was reached at temperature of 25 °C (MukeshParmar, 2013).

**7.Effect of Adsorbent Dosage:** The percent removal of heavy metals increases rapidly with increase in the dose of the adsorbents (MukeshParmar, 2013).

**8.Effect of initial concentration of metal:** The initial concentration provides an important driving force to overcome all mass transfer resistance of metal between the aqueous and solid phases. Decrease in resistance for the uptake of solute from solution with increase in metal concentration (MukeshParmar, 2013).

Effect of agitation rate: The adsorption removal efficiency increased weakly with increasing agitation rate (MukeshParmar, 2013).

## CONCLUSION

In recent years, environment has been polluted heavily because of discharging industrial effluent containing heavy metals. Environmental legislation has been used to control the quality of industrial discharge that contains toxic metals. To avoid environmental hazards, it is essential to remove metal contaminants from industrial effluents before discharging in water bodies. The toxic metals present in the effluent are non-biodegradable and generally toxic to living organisms. Conventional methods of precipitation and removal are increasingly getting expensive and not thoroughly efficient in all cases, so alternative strategy of adsorption has been envisaged for capturing of materials by low cost adsorbents. Overview of this review study explains that adsorption technique is a cost effective and technically feasible method. Replacement of expensive adsorbents by low cost, more effective and readily available waste by-products as adsorbents such as rice husk, coconut leaves, coconut husk, cow bone charcoal, tea wastes, neem leaves etc are very effective in removing nickel ions from contaminated waste water.

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