Catalytic Demetalization of Ni+2 Ions from Aqueous Solutions Using Two Types of Activated Carbon

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Abstract. Heavy metals are dangerous contaminants due to their toxic effects on all components of the environment as well as their high toxicity to humans when entering the food chain. The current study aims to investigate the potency of nickel ions demetalization in both practical and statistical parts. The practical portion included the use of two types of activated carbon, namely the ordinary granular activated carbon (GAC) and promoted granular activated carbon loaded with sulfur namely (S-GAC), to complete the demetalization process of nickel from aqueous solutions via batch mode, while the statistical aspect dealt with the representation of the data obtained by multiple regression model using a statistical package STATDISK program. The practical results showed the possibility of demetalization of nickel by GAC and S-GAC adsorbents. The percentage of demetalization efficiency is inversely proportional to the initial concentration of nickel while it was directly proportional to the pH, temperature, agitation speed, the dose of GAC and S-GAC adsorbents and the contact time. The maximum percentage demetalization efficiency reaches to 78.41% and 90.75% for GAC and S-GAC respectively. The results of statistical part show that identical with the practical results and the correlation coefficient R² values were (0.9988 and 0.9997) and p-values were (3.8x10⁻⁷ and 4.45x10⁻⁷) in case of GAC and S-GAC catalysts respectively.

Keywords: Nickel ions, catalytic, activated carbon, sulfur, STATDISK program

1. Introduction
The heavy metals are profusely found in nature, where they scud via the geochemical cycles to the surrounding [1]. The high concentrations of heavy metals in the aquatic environment are dangerous to living organisms due to the ability of these organisms to accumulate and concentrate the heavy metals in their bodies [2], which may cause imbalance in their vital functions in addition to transfer of these elements through the food chains of the human causing unhealthy damages [3,4]. The heavy metals are defined as those elements that are have density equal to five times the density of water i.e. 5 g.cm⁻³ or more [5] and have negative effects on the environment when over-used and affect the health of
humans, animals and plants [6]. All of these metals share with many of their natural properties, but their chemical reactions with other elements are different and this applies to their environmental effects [7]. Some of these metals, such as mercury (Hg), lead (Pb) and cadmium (Cd), their origin forms a threat to public health, while others like chromium (Cr), iron (Fe) and copper (Cu) are confined to workplaces where prolonged exposure occurs [8,9]. This is why it is less dangerous than other metals such as lead, which has increased in recent times and become very abundant in water, air and soil [10]. Many of heavy metals are essential for life but in very small amounts, so they are toxic if they exceed the allowable level and reach to high concentration in the body and then become able to interfere with the growth of cells and the digestive system [11]. The poisoning with heavy metal occurs when enter the human body as a biochemical compound, or enter the human body in high quantities i.e. above the allowable limits on a long period of time (cumulative toxicity) [12], or enters the human body at low concentrations over a long period of time leading to occupational disease, or enter the human body by way of short term with high concentration [13,14]. Human exposure to the harmful effect of these metals has increased due to the excessive and continuous increase in their use in daily life, as it has spread in most of the developed countries especially [15]. The processes of melting and purification of metals have the pollution to the water and air environments, although this was confined to specific places at first, but it is seemed to have the limitations with time [16].

There are various sources that cause pollution with heavy metals in the environment such as: (a) Releases from accumulation of elements impurities include energy from coal combustion and heat production, production of energy from fossil fuels, cement production, mining and other metal activities including the extraction and processing of raw oars and recycling of metals such as iron and steel, zinc and petroleum production [17]. (b) Releases from the extraction and intentional use of heavy elements which include extraction of mercury from metals, amalgamation process, production of chlorine – alkali – detergents, use of fluorescent lamps, metal tools, dental filler amalgam, manufacturing of products containing mercury like thermometers, electronic circuits, bio-pesticides and other products such as batteries, fireworks and laboratory chemicals [18]. (c) Releases from the waste treatment arising from the impurities and heavy - duty use containing these metals, including waste incineration (municipal, medical and hazardous waste) and recycling and storage [19]. (d) Releases discharge of industrial municipal and agriculture wastewater contaminated with liquid waste containing heavy metals such as residues of electroplating smelting industries and so on to different water bodies [20].

The removal of heavy metals from water can be accomplished through several techniques, the most important are implicate chemical precipitation, reverse osmosis, ion-exchange, filtration, flocculation, solvent extraction, electrochemical and membrane technologies etc. [21]. However, all of these techniques have their attendant advantages and restrictions in usages. Its advantage in general is the potential to remove toxic metals in uneven efficiencies between them [10], but the disadvantages of these techniques are expensive, not environment friendly and usually dependent on the concentration level of pollutants in the residue [16]. Often most of these processes are ineffective in much diluted or concentrated solutions as follow [18]. Therefore, the searches for new techniques are needed to eject toxic metals from aqueous solutions and diminish their concentrations in environment to accepted levels with suitable, efficient, cost effective, not expensive and eco-friendly remedies method for wastewater treatment [22]. In the last few decades, adsorption has been exhibited to be a substitution technique for minimizing thawed toxic metal ions from aqueous wastes [23]. Adsorption is considered as simple economic and simple techniques that does not require an initial treatment or special requirements. At the same time, it has a great removal efficiency to remove heavy metals [24]. One of the most important adsorbents used to remove heavy elements from wastewater is activated carbon due to its high surface area, great adsorption capacity and suitable porous structure [25]. On the other hand, activated carbon is associated with the contaminants because it does not interact with it and contains the groups of carboxyl, nitrogen, free radicals, and metal ions and ketones on its surface [26]. However, although activated carbon is effectively used to remove many types of contaminants from aqueous solutions for a long time, but the cost of raw materials (such as coal or wood), as well as loss of 10-15% of its weight as a result of each regeneration, and other reasons made the removal process
using activated carbon was expensive and not applicable [27]. The non-economic cost problem of activated carbon and other classical adsorbents has prompted researchers to find suitable and cost-effective alternatives such as industrial residues or agricultural residues [28-32]. Currently low-cost materials are increasingly concerned with their use as direct adsorbents or as a cheap raw material for the preparation of activated carbon to treat waste water contaminated with heavy metals [24,33], pesticides and fertilizers [34], dyes [35,36], organic chemicals [37], inorganic pollutants [31], radioactive waste [29] or even treated crude oil [38,39]. The two main aims of this paper are investigated the ability of two types of activated carbon ordinary (GAC) and exhausted loaded by sulfur (S-GAC) to use as adsorbents for demetalization process of nickel from aqueous solutions. Then, preparing a suitable statistical approach using multiple regression model and statistical package, STATDISK program, to represent the experimental data obtained. Also try to fill the shortage of current researches in dealing with the statistical aspect.

2. Experimental Work

2.1. Granular Activated Carbon (GAC)

The GAC used in the present work was purchased from local chemical laboratories; it was supplied from Unicarbo, Italians. The physio-chemical characteristic properties of GAC were explained in Table 1.

| Table 1. Characterization properties of GAC (Maddodi et. al., 2020) |
|---------------------------------------------------------------|
| **Chemical Composition** | **Physical Properties** |
| Element | wt. % | Property | Value |
| C | 84.15 | pH | 7.65 |
| O | 9.22 | Bulk Density, g/cm³ | 0.635 |
| Ca | 0.32 | Relative Density g/cm³ | 1.728 |
| Fe | 2.56 | Porosity | 0.6827 |
| K | 1.79 | Particle Size, mm | 0.75-1.00 |
| Mg | 0.10 | Pore Volume, cm³/g | 0.6235 |
| Mo | 0.31 | BET Surface Area, m²/g | 780.528 |
| Na | 0.86 | |
| P | 0.50 | |
| Si | 0.19 | |

2.2. Promoted Granular Activated Carbon (S-GAC)

The promoted GAC used in the present work was obtained from GAC residues of catalytic desulfurization of heavy and light naphtha fractions as described on (Abbas and Alalwan, 2019; Abbas and Ibrahim, 2019) and named as (S-GAC). The residues were collected and sorted according to its content of sulfur. The sulfur content was ranging between (5.88-11.34) ppm as measured by X-ray Fluorescence analysis. The activation of two activated carbon types (GAC and S-GAC) was achieved by heating it to 150 °C in atmospheric pressure over night, and then used them directly to test the removal process of nickel ions from laboratory prepared aqueous solutions without any further treatment.

2.3. Stock Solutions

The demetalization experiments were conducted using laboratory prepared aqueous solutions for avoiding the interference with other elements, substances and compounds that may be existence in real
wastewater. So, 500 mg/l stock solution of nickel (Ni) was prepared by dissolving 1318.5 mg of nickel sulfate (NiSO₄) in one liter of double distilled water. All aqueous solutions used in this paper were prepared via dilute the stock solution to the desired concentration using dilution formula: \( C_1V_1 = C_2V_2 \) where: \( C_1 \) and \( V_1 \) are the concentration (ppm) and volume (ml) of original stock solution prepared respectively, while \( C_2 \) and \( V_2 \) are the concentration (ppm) and volume (ml) of new aqueous solution used in experiment respectively. The nickel concentration in the treated solution was measured by Shimadzu AA-6200 atomic absorption spectrophotometer using calibration curve shown in Figure 1 below.

![AAS Calibration curve of Nickel Ions Concentration](image)

3. Methodology

3.1. Demetalization Experiments

The experiments of demetalization process of nickel (Ni) as heavy metal were conducted using two types of adsorbents each one alone, the first one is ordinary granular activated carbon and the other is granular activated carbon loaded with sulfur compound (which behave as promoter) named GAC and S-GAC respectively. All experiments were carried out by batch mode in an orbital water bath shaker (Innova4080, The New Brunswick Scientific Company) at various designing parameters. The experiments were conducted at atmospheric pressure in a laboratory unit of batch mode. The demetalization process was initiated with preparing a 100 ml of Ni²⁺ ions aqueous solutions at particular concentration in 150 ml Erlenmeyer flask. The pH of aqueous solution was adjusted using 0.1 N HCl or 0.1 N NaOH purchased from Sigma-Aldrich Co. then adding the desired amount of adsorbent and the flask content was heating to required temperature. When all operating conditions are prepared, the flask was shaking at the determined agitation speed for required period. The operating parameters of demetalization process were initial concentration of heavy metals varied between (1-100) ppm, PH of aqueous solutions varied between (1-8), agitation speed varied between (100-500±1) rpm, temperature varied between (25-50±0.5) °C, contact time varying between (1-4) h, dose of adsorbents varied between (0.1-5.0) g and the content of sulfur in case of S-GAC was varied between (5.88-11.34) ppm. The experiments were conducted triplicated to reduce the experimental error. The sample was dropped out, twice filtered with Whitmann® filter paper No.3 to ensure remove any impurities and finally analyse by atomic absorption spectrophotometer and determine the nickel concentration using calibration curve.

3.2. Determination of Nickel Content

The demetalization process efficiency was calculated by the following equation:
Where: \(\%R\): the percentage removal of \(\text{Ni}^{+2}\) ions from aqueous solution; \(C_i\): Initial concentration of heavy metal in the SSAS before demetalization, ppm and \(C_f\): Final Concentration of Heavy metals after desulfurization, ppm.

The demineralized concentration of heavy metals studied in this research was determined by Flame Atomic Absorption Spectrophotometer (Model Shimadzu AA-6200). The characteristic wavelength was 346.2 nm for nickel ions. To eliminate the intrusion with organic matter and to change metal associated with particulates to the free metal form that can be detection by atomic adsorption device; a cold digestion was used by adding HCl to samples to make 4N solution of HCl.

4. Results and Discussion

4.1. Effect of Initial concentration

The effect of the initial concentration of nickel ions on the removal efficiency was studied via a series of laboratory experiments within a concentration range varying from (1-100) ppm, when other operational conditions were kept constant at optimal values. The obtained practical results are represented in Figure 2. It is noted from the above figure that the removal efficiency decreases with the increase in the initial concentration value of nickel ions in the solution, whereas, the removal efficiency reduced from 78.41% to 16.93% and from 96.88% to 26.15% for both adsorbent substances GAC and S-GAC, respectively, with an increase in the nickel concentration from 1 to 100 ppm. The reason for this result is due to the fact that the adsorbent material possesses a constant surface area and any increase in concentration means an increase in the number of nickel ions for the same volume, and this leads to a strong competition between nickel ions at high concentrations, while gradually decreasing with a decrease in concentration. When the adsorbent pores are saturated with nickel ions, the ions number of free nickels in the solution will be greater in case of high concentrations thus the removal efficiency would be reduced. This result is agreed with [41].

4.2. Effect of Agitation Speed

Agitation speed is considered as an important design factor in determining the behaviour of adsorption it increases mass transfer and the diffusion of the substance. Within a range of 100-500 rpm, a set of experiments was conducted to identify the adsorption behaviour of nickel ions from aqueous solutions using (GAC and S-GAC) as adsorption media. It is noted from Figure 3 that the relationship between removal efficiency and agitation speed is a direct relationship up to 400 rpm, and then the removal efficiency becomes constant. The high removal efficiency with increasing agitation speed may be due to the fact that the high speed is responsible for breaking down the films layers formed on the surface of GAC and S-GAC that impede the adsorption process. By breaking these film layers, the resistance to the penetration of ions into gaps and pores (GAC and S-GAC) will become less, which increases the adsorption of nickel ions and reduces their number in the solution, which in turn leads to increased efficiency of adsorption. This result is agreed with [33].
4.3. Effect of pH
The pH value play an important role in adsorption process, the effect of this important parameter has been studied in detail on the adsorption efficiency of nickel ions from contaminated aqueous solutions within the three ranges of acid, neutral and basic pH. The direct proportional between the adsorption efficiency and the pH shown in Figure 4 can be explained by reducing competition between positive ions in the solution, as the rise in the value of the acidity of solution leads to an increase in negative hydroxide ions, which provides many effective sites on the surface of the adsorbent material. This will certainly lead to absorb nickel ions, thus increasing the adsorption efficiency. At low pH values, the protons will prevail in the solution, which in turn will generate large repulsive forces with nickel ions that carry the positive charge too, making the active sites a desired destination for two types of ions at the same time, thereby reducing the adsorption efficiency. This result is agreed with [28,42].

4.4. Effect of Adsorbent Dose
Figure 5 shows the relationship between the adsorbent dose and the corresponding adsorption efficiency of the nickel ions using both GAC and S-GAC as adsorbents media. The proportional relationship between the two variables can be attributed to the fact that the adsorbed substance contains a fixed surface area per unit mass of that substance. When the amount of absorbent material increases, the surface area exposed to the contaminated solution will increase due to the increase in mass, which increases the chance of nickel ions reaching the active sites and attaching to the functional groups, thus increasing the adsorption efficiency. Therefore, it is noted that the less absorbent material has lower adsorption efficiency. It is also noticed from Figure 5 that the removal efficiency reaches a certain limit and does not change after it despite the increase in the mass of the adsorbent material. The reason for this may be due to reaching a state of equilibrium, at which the material reaches the level of saturation and the material pores cannot receive new nickel molecules at current operational conditions. This result is agreed with [43].

Figure 2. Effect of Initial Concentration of Nickel Ions on the Percentage Removal

Figure 3. Effect of Agitation Speed on the Percentage Removal of Nickel Ions
4.5. Effect of Contact Time

Figure 6 shows the relationship between the adsorbent dose and the corresponding adsorption efficiency of the nickel ions using both GAC and S-GAC as adsorbents media. The proportional relationship between the two variables can be attributed to the fact that the adsorbed substance contains a fixed surface area per unit mass of that substance. When the amount of absorbent material increases, the surface area exposed to the contaminated solution will increase due to the increase in mass, which increases the chance of nickel ions reaching the active sites and attaching to the functional groups, thus increasing the adsorption efficiency. Therefore, it is noted that the less absorbent material has lower adsorption efficiency. It is also noticed from Figure 6 that the removal efficiency reaches a certain limit and does not change after it despite the increase in the mass of the adsorbent material. The reason for this may be due to reaching a state of equilibrium, at which the material reaches the level of saturation and the material pores cannot receive new nickel molecules at current operational conditions. This result is agreed with [43].

4.6. Effect of Temperature

Among the factors that directly affect the efficiency of the adsorption process and the ability of the adsorbent material is temperature, due to its main role in influencing the kinetic energy of the adsorbent molecules and the morphology of the adsorbent material. The effect of this factor on the adsorption efficiency of nickel ions from aqueous solutions was investigated using GAC and S-GAC as adsorbents by a series of laboratory experiments with a range between 25-50 °C while the other operational factors were rested at the optimum values. The apparent increase in the adsorption efficiency with temperature rise can be the result of the energy of the molecules, as the increase in temperature leads (as is known) to the increase in the kinetic energy of the particles of the polluted material spread in the solution, which increases its speed and thus allows the penetration of the film layers formed on the surface of the material, which increases the chance of it reaching the active sites on the surface of the adsorbent material. In addition to that, raising the temperature may lead to an expansion of the adsorption surface gaps, which would allow the absorption of a larger number of nickel particles and thus increase the efficiency of the treatment process, by increasing the susceptibility of the material to adsorb a larger amount of nickel ions from the contaminated solution. Figure 7 indicates that raising the temperature from 20 to 50 °C has improved the adsorption efficiency by 80 and 96 % for GAC and S-GAC. This result is agreed with [30,32].
Figure 6. Effect of Contact Time on the Percentage Removal of Nickel Ions

Figure 7. Effect of Temperature on the Percentage Removal of Nickel Ions

4.7. Effect of Adsorbent Media Type
Among the factors that directly affect the efficiency of the adsorption process and the ability of the adsorbent material is temperature, due to its main role in influencing the kinetic energy of the adsorbent molecules and the morphology of the adsorbent material. The effect of this factor on the adsorption efficiency of nickel ions from aqueous solutions was investigated using GAC and S-GAC as adsorbents by a series of laboratory experiments with a range between 25-50 °C while the other operational factors were rested at the optimum values. The apparent increase in the adsorption efficiency with temperature rise can be the result of the energy of the molecules, as the increase in temperature leads (as is known) to the increase in the kinetic energy of the particles of the polluted material spread in the solution, which increases its speed and thus allows the penetration of the film layers formed on the surface of the material, which increases the chance of it reaching the active sites on the surface of the adsorbent material. In addition to that, raising the temperature may lead to an expansion of the adsorption surface gaps, which would allow the absorption of a larger number of nickel particles and thus increase the efficiency of the treatment process, by increasing the susceptibility of the material to adsorb a larger amount of nickel ions from the contaminated solution. Figure 7 indicates that raising the temperature from 20 to 50 °C has improved the adsorption efficiency by 80 and 96 % for GAC and S-GAC. This result is agreed with [30,32].

4.8. Statistical Analysis
Statistical analysis was conducted for the data obtained from the laboratory testing using the atomic absorption spectrophotometer device for 156 samples of contaminated solutions at different operational conditions to identify the percentage of nickel removal using GAC and S-GAC. Each sample represents a practical experiment that was performed by varying 6 design factors in the case of GAC and 7 design factors in the case of S-GAC. These factors were the initial concentration of nickel (C), the acidic function of the solution (pH), agitation speed (u), temperature (T), contact time (t), absorbent dose (w) using GAC in addition to the amount of sulphur loaded (S) on the promoted activated carbon S-GAC as well as the percentage of nickel adsorption efficiency (% R). When input the data of the two adsorbents (GAC and S-GAC) into the STATDISK program and analysing it using the multiple regression function, two statistical models were resulted that describe the process of nickel removal from aqueous solutions using GAC and S-GAC. The value of correlation coefficient ($R^2$) was 0.9988 and 0.9997 while p-values were ($3.8 \times 10^{-7}$ and $4.45 \times 10^{-7}$) for both GAC and S-GAC, respectively. The values of the correlation coefficient between the practical values and the expected values for both (GAC and S-GAC) using the multiple regression analysis model were high [24,45]. Parameters for the independent variables are listed in Table 2, while Figures 8 and 9 represents the
match between the experimental and statistical data. Using these factors, the equations describing regression analysis can be represented as follows:

For GAC %R = -104.3685 - 0.6513766(C) - 5.244091(pH) + 0.054089(u) + 5.219156(T) - 0.4646887 (t) + 120.6199(w).

For S-GAC %R = -210.3699 - 1.027254(C) - 3.915985(pH) + 0.3690141(u) + 9.64171(T) - 1.204168 (t) + 95.65794(w) - 2.438626(S).

Table 2. The values of constants for GAC and S-GAC Statistical Equations According to STATDISK Program Analysis

|        | GAC          | S-GAC         |
|--------|--------------|---------------|
| Coeff b0: | -104.3685    | -210.3699     |
| Coeff b1: | -0.6513766   | -1.027254     |
| Coeff b2: | -5.244091    | -3.915985     |
| Coeff b3: | 0.054089     | 0.3690141     |
| Coeff b4: | 5.219156     | 9.64171       |
| Coeff b5: | -0.4646887   | -1.204168     |
| Coeff b6: | 120.6199     | 95.65794      |
| Coeff b7: |              | -2.438626     |
| R^2    | 0.9988148    | 0.9997622     |
| p-value | 3.802124e-7  | 4.451500e-7   |

Figure 8. The matching between the experimental and statistical data using GAC

Figure 9. The matching between the experimental and statistical data using S-GAC

4.9. Application of ZRL (Zero Residues Level) concept for the wastes

In order to complete the environmentally friendly treatment process and to achieve the ZRL principle of the waste, a study was conducted to investigate the possibility of disposing the remaining toxic absorbent material after the completion of the nickel adsorption process from aqueous solutions using GAC and S-GAC, due to the content of nickel, sulfur and carbon. A simple, fast and economical method was to convert those residues into a rodenticide, determine the half lethal dose (LD$_{50}$) of the waste and compare it with the half lethal dose mentioned in the literature [44]. The possibility of applying this approach using the same method used by [44] and on rattus rattus species has been investigated. The practical results obtained showed that it could be used these residues as a rodenticide due to the toxicity of the metals loaded on activated carbon. By this way, aqueous solutions contaminated with nickel ions can be removed using the activated carbon depleted from the catalytic desulfurization process and converted to a cheap, effective and economical rodenticide without any harmful residues to the environment. Table 3 shows the values of the half lethal dose for the two types of residues used, as well as in the literature.
Table 3. Lethal Dose of Prepared rodenticide

| Group           | Type of Feeding          | Calculated LD<sub>50</sub> of Male (mg/kg) | Calculated LD<sub>50</sub> of Female (mg/kg) | Standard LD<sub>50</sub> (mg/kg) |
|-----------------|--------------------------|-------------------------------------------|---------------------------------------------|---------------------------------|
| Control (CG)    | Rat Provender (Ordinary) | No-fatalities                             | No-fatalities                               | –                               |
| 1               | Rat Provender + GAC      | 15.542                                    | 11.976                                      | > 10,000 [46]                   |
| 2               | Rat Provender + Ni<sup>2+</sup>-GAC | 248.061                                | 210.442                                    | 200-264 [47]                   |
| 3               | Rat Provender + Ni<sup>2+</sup>-S-GAC | 48.253                                    | 37.167                                      | 46-39 [48]                     |

5. Conclusions
Given the amount of pollution from which the environment suffers from all its elements, it has become obligatory for all specialists in this regard to contribute to addressing environmental problems in new ways that do not require significant costs and do not lead to additional problems and at the same time are possible and applicable. The concept of zero residual level is a novel method presented by researchers in this study to address one of the persistent environmental problems, which is the problem of water sources pollution by adsorption technology to purify water and get rid of heavy metals using harmful residues that are exhausted and non-value and then turn them into useful materials so that it does not remain any kind of residues at the end of process. This research found, within its results, the possibility of reusing activated carbon (previously used to remove sulfur from crude oil as an adsorbent material) to recover nickel ions from polluted aqueous solutions with a high efficiency of 90.75% compared to the efficiency of the ordinary activated carbon that reached 78.41% at a concentration of 1 ppm of Ni<sup>2+</sup> and acidic function of 6. The ideal values for agitation speed, contact time, temperature, and adsorption media dose were 300 rpm, 180 minutes, 50 °C, and 1 g, respectively. The results obtained were closely related to that of the statistical model when analysed using the multiple regression analysis in STATDISK program. The residual waste after completed the adsorption process was could be used as an ideal raw material for preparing an effective cheap rodenticide, and this was shown by the results that were done on the laboratory rats of (Rattus rattus) species. By these results the current research shows a good ability to use the residues in beneficial, economic and environmentally friendly ways. Also, this study introduces a clear vision of the concept of zero residual level.

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