



Electrolytic Generation of Nickel Hydroxide and Nickel Oxide Nanoparticles for Advanced Applications

H. H. Shaarawy, H.S. Hussein, Mona A. Abdel-Fatah*,
Nabila H. Hussien, and S.I.Hawash

*Chemical Engineering & Pilot Plant Department, Engineering Research Division, National Research Center,
33 El-Bohouth St., Dokki, Cairo, Egypt, Post Code 12622*



CrossMark

Abstract

Nano nickel hydroxides and nano nickel compounds attract great attention because it is a significant industrial material of commercial importance and applications in nickel-metal hydride batteries, super capacitors, water treatment, etc. This investigation gives the results of electrolytic preparation of nickel hydroxide powder by anodic dissolution technique and conversion of this nickel hydroxide to nano nickel oxide via heat treatment. The obtained operating conditions for anodic dissolution of nickel substrate in saline solution were 75mA/cm², pH 6, 3g/l. sodium chloride, 20°C, electrode gap distance 3cm, electrode reverse polarity interval time 5min. at 150rpm stirring rate. The obtained nickel hydroxide powder completely converted to nano nickel oxide at 500°C for 6hr. Morphology, particle size and crystallographic patterns of prepared nickel hydroxide and nano nickel oxide were investigated by transmission electron microscope (TEM) and the scanning advanced electronic diffraction (SAED) pattern. It was found that average particle size of synthesized nano nickel hydroxide were of nano tube shapes with smooth surface and average diameters in the range of 2.16 – 3.32 nm. Obtained results affect the design of nickel hydroxide electrodes for charge storage applications. The obtained nano nickel oxide was tested for the removal of Methylene blue dye (MB) from its solutions via adsorption. For MB solution of 100mg/l. concentration the optimum conditions for complete removal were found to be: pH 11, 100mg/l. MB, 10g/l. nano nickel oxide dose, 20°C, stirring rate 150rpm, at contact time 90min. the results show that the adsorption capacity of MB on the nano nickel oxide surface was 25mg.g⁻¹, and with cleaning and drying then reuse of the nano nickel oxide more than 12 times of MB adsorption process without any significant change of adsorption capacity indication that nano nickel oxide is very good dye adsorbent.

Keywords: Electrolytic Generation, Methylene blue dye, Nickel Hydroxide, Nickel Oxide, Nanoparticles, Advanced Applications

1 - INTRODUCTION

Batteries and super capacitors have been developed as energy storage devices. High energy density can be generated through diffusion controlled reduction oxidation (redox) reactions in bulk electrode material [1]. Batteries have numerous applications at little and big scales, in small devices like portable electronics, and larger systems like stationary hybrid vehicles [2]. One of the most important materials for batteries is nickel hydroxide [Ni(OH)₂], which is a crystalline complex compound and its structure depends on preparation technique [3]. Both small and high capacity devices need

energy storing capacity [4, 5]. Thus high capacity applications like hybrid vehicles and stationary power require large energy storage capacity and long service life [6] besides its importance for corrosion and battery performance [7]. Most important two properties of batteries for applications are capacity density and reversible discharge capacity [2].

Nickel hydroxide generation can be done by different approaches, and nano particles nickel hydroxide of different crystallography can also be prepared [8]. Nickel hydroxide nano particles was prepared hydrothermally in the range of 3 –450nm

*Corresponding author e-mail: monaamin46@gmail.com

Receive Date: 06 July 2021, Revise Date: 15 July 2021, Accept Date: 15 July 2021

DOI: 10.21608/EJCHEM.2021.84356.4129

©2021 National Information and Documentation Center (NIDOC)

and it was found that: decreasing particle size to 20 nm increases the capacity per gram (CS) while capacity unit area (CA) remains constant and most reduction in particle size decreases both CS and CA which have implications in Ni(OH)₂ electrodes design and in charge storage applications [9]. Also Ni(OH)₂ is an active material to be used in an alkaline rechargeable battery as positive electrode [10]. Nickel hydroxides have strong peaks related to Faradaic oxidation/reduction of Ni(OH)₂ for battery material typically [11]. So like nanostructure material oxides NiO has considerable interest as lithium ion battery anode due to its environmental friendly nature, ease of synthesis and low cost [12].

Electrolytic activity of porous nickel electrodes investigation revealed that porous nickel electrodes showed electro-catalytically activity towards oxygen evolution reaction and efficiently removed phenols from alkaline solutions [13]. Replacing Mn₂/MnO₂ redox by nickel based cathode resulted 10 time areal capacity and lower cost as \$ 83/ KWhKg⁻¹ based on active material [14]. Also nickel hydrogen battery exhibits energy density of about 140 WhKg⁻¹ [14]. Nickel oxide nano-powder was synthesized by chemical precipitation by subsequent milling, heat treatment and water washing for the precursor compound (Ni(OH)₂-NiCO₃·H₂O) [15].

Nano-structured (Ni(OH)₂) was also prepared by a fast and facile procedure via Sono-chemical technique [16]. The synthesized Ni(OH)₂ electrode exhibited maximum specific capacitance of 1256 F/g at a current density of 200 mA/g in 1M KOH (aq.) and showed pseudo-capacitive behavior due to the presence of redox reaction with long term stability of 85% after 2000 cycles [16] which demonstrated that Ni(OH)₂ electrode is very promising and efficient for super-capacitor applications [16].

Also Ni nano-powder can be prepared by chemical reduction of Ni ions with hydrazine hydrate at pH ~12.5 then sonicated the solution to activate the reduction reaction which resulted Ni nano-powder of particle size from 12 to 14nm. Particle size can be reduced to 7nm by addition of polyvinyl-pyrrolidone to the synthesis [17].

Nano nickel compounds such as nano nickel hydroxide, and nano nickel oxide have great applications in water treatment, nano fuel

preparation, electronic industry (super capacitors and batteries), and flame retardant materials [18-21]. In this investigation the main aim is to develop a cost-effective green process to produce nano nickel hydroxide and nano nickel oxide through a cleaner production process including anodic dissolution of nickel sheets for generation of nano nickel hydroxide which will be converted to nano nickel oxide via heat treatment. Further target of our study is testing the produced nano nickel oxide in MB adsorption from its solutions and in future studies obtained nano nickel hydroxide will be tested in super capacitors production.

2. Experimental

2.1 Apparatus

Figure (1) represents the electrolytic cell used for anodic dissolution of nickel sheets to nano nickel hydroxide powder.

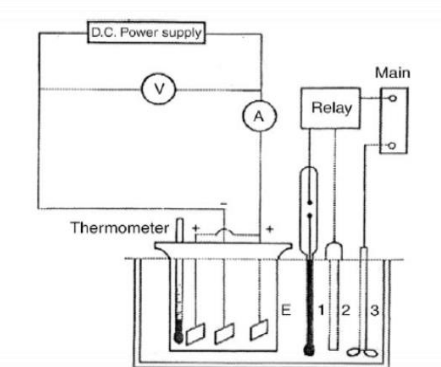


Figure (1) Electrolysis cell used for synthesis of nickel hydroxide

2.2 Materials & Procedures

2.2.1 Materials

Nitric and sulfuric acid were obtained from el Nasr pharmaceutical chemical Co., pure reagents for analysis. Nickel sheets of high analytical grade were used as anode and cathodes manufactured by El Naser Co. for chemicals.

2.2.2 Procedures

2.2.2.1 Anodic dissolution of Nickel Sheet

Figure (1) represents the electrolytic cell used for nickel sheet anodic dissolution and generation of nano nickel hydroxide powder. The cell is a 250 ml capacity Plexi-glass rectangular cell.

Three high analytical grade nickel sheets of dimensions 2 x 10 x 0.5 cm were used as one anode which is located in the middle pathway of two nickel

cathodes. D.C power supply of 50V, and 5A with digital display, voltage and current control with sensitivity of 0.1V and 0.1A, was used for sullyng of direct electric current. Temperature controller used for adjustment of the electrolysis process temperature within range of 20°C to 100°C.

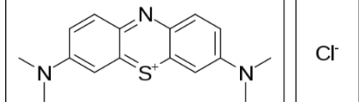
The electrolyte solution is stirred during the electrolysis process using magnetic stirrer within 0-500 rpm. Low concentration sodium chloride solution (3g/l) was used as electrolyte for nickel anodic dissolution process for generation of nano nickel hydroxide particles. The nickel substrates were polished via sand paper and soaked in acetone for 3min., after that they were subjected for alkaline degreasing to remove oils and fats adhered at their surfaces.

The alkaline solution containing 0.5M NaOH, 0.5M Na₂CO₃, and 10g/l EDTA, was used for degreasing by soaking for 15min. at 50°C. The degreased nickel substrate was rinsed with running water then acidified by 0.1M sulfuric acid. Once the electrodes submerged in the sodium chloride solution, D.C. current is adjusted at the desired value with stirring. At the end of the electrolysis time, the solution constitutes the nano nickel hydroxide particles that is soaked for about 24hr. rinsing with running water was carried out till the pH reached 7.

The mixture was filtered, dried and the resulted block was grinded. The synthesized nickel hydroxide powder is heated at 500°C for 6hr. to be converted to nano nickel oxide powder. Both of the obtained nano nickel hydroxide and nano nickel oxide particles were subjected to the analytical and physical characterization. Operating conditions such as effect of electrolyte pH, applied current density, electrolysis time, solution temperature, electrodes gap distance and sodium chloride concentration were investigated. The obtained nano nickel oxide particles were tested for adsorption of cationic dyes for instance MB solution of 100mg/l.

The nano nickel oxide particles adsorbent was applied for removal of the basic dye MB, which is a heterocyclic aromatic compound, dark green, and solid at room temperature. The chemical structure of the MB is shown in Table (1). The wavelength corresponding to the maximum absorbance was detected at 660 nm using single beam (UV-Vis) spectrophotometer as shown in Figure (2).

Table (1) chemical composition of MB [22]

Chemical and physical data	
Formula	C ₁₆ H ₁₈ ClN ₃ S
Molar Mass	319.85/mole
Molecular Structure	

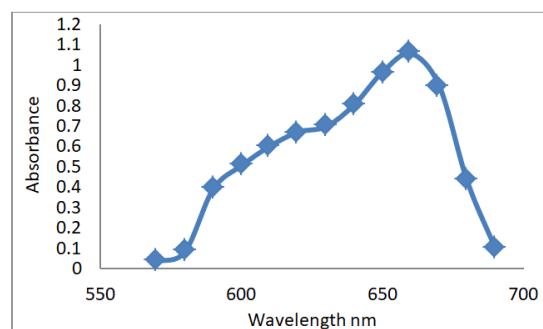
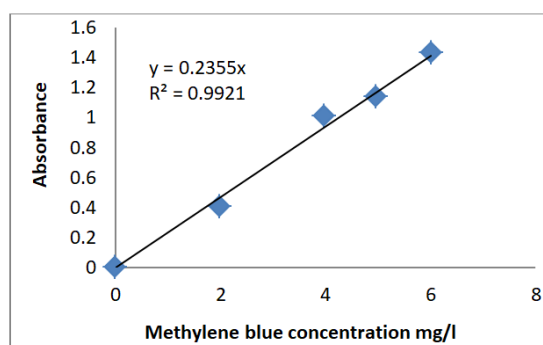


Figure (2) Variation of absorbance of MB dye (100mg/l) solution with wavelength

Figure (3) Variation of MB dye concentration with absorbance at (λ_{max} =660nm)

Activate

This wavelength was selected to measure the absorbance of residual concentration of MB, while Figure (3) shows the relation of MB concentration and the absorbance obtained at the optimum wavelength (660 nm). The following equation is used to measure the dye concentration remained:

$$Y=0.2355 *X \quad (1)$$

Where:

Y is absorbance and *X* is MB dye concentration

Adsorption capacity Equilibrium experiments were performed to determine the adsorption capacity of the adsorbent as following: 1 g of the nano nickel oxide was added to 100 ml of MB solution (100mg/l)

then stirring for 5min and subjected to filtration. After that, the absorbance of the filtrate was measured at 660 nm to determine the concentration of residual MB dye. The concentration and adsorption capacity of dye were calculated using the following equation:

$$\text{Adsorption Capacity } (q_e) = (C_i - C_f) \frac{V}{M} \quad (2)$$

$$\text{Removal \%} = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \quad (3)$$

Where:

q_e (mg/g) denote the equilibrium adsorption capacity, C_i is the initial concentration of MB (mg/l), C_f is the final concentration of the MB (mg/l), M is the mass of the nano nickel oxide adsorbent (g), and V is the volume of the dye solution (L).

2.3 Characterization

2.3.1 XRD diffraction

X-ray diffraction (XRD) was carried out using Bruker's D8 advanced X-ray diffract meter via $\text{CuK}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). Dynamic Light Scattering (Model no: HORIBA and Nano particle analyzer SZ100) was used to measure the particle size.

2.3.2 Transmission electron microscope test

The obtained nano-particles were characterized by means of a JEOL-JEM1200 transmission electron microscope (TEM). The TEM sample was prepared by adding a drop of the nano-solution on a 400 mesh copper grid coated by an amorphous carbon film and let the sample to dry in open air at room temperature. The average diameter of nano-particles was determined within the range of 100nm that was found in several chosen areas in enlarged micro-photographs. Moreover, the same electron microscope JEOL-JEM-1200 was used for the examination of the selected area electron diffraction patterns (SAED) tested particles

2.3.3 SEM-EDX Analysis

The surface morphology of the nano nickel hydroxide and nano nickel oxide particles were investigated via SEM-EDX analysis.

3. Results and Discussion

The preparation of nano nickel oxide through the anodic dissolution of nickel substrate have to pass through the generation of nano nickel hydroxide powder which will be then converted to nano nickel

oxide using heat treatment. Several operating conditions controlling the anodic dissolution of nickel substrate and the generation of nano nickel hydroxide powder such as: electrolyte pH, applied current density, electrolysis time, solution temp, NaCl concentration, and electrodes gap distance were investigated. In the following part investigation of the optimum conditions for the generation of nickel hydroxide powder were carried out.

3.1.1 Effect of pH

For studding the effect of electrolyte pH on the anodic dissolution of nickel substrate, the other operating conditions were fixed at: C.D. 75mA/cm^2 , electrolysis time 30min., NaCl 3gm/l, electrodes gap distance 3cm, stirring rate 150rpm at 20°C . Figure (4) shows the effect of the pH on the dissolution efficiency and the generation efficiency of nano nickel hydroxide powder.

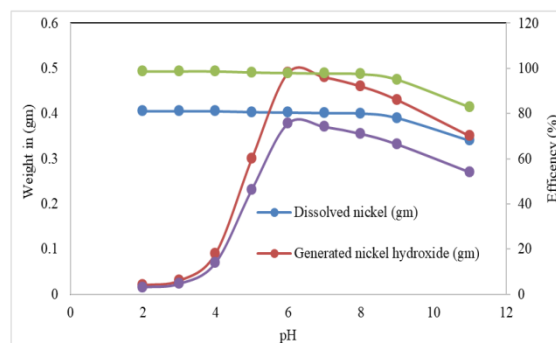


Figure (4) Effect of solution pH on dissolved nickel and nano nickel hydroxide formation during nickel anodic dissolution at operating conditions: C.D. 75mA/cm^2 , 20°C , 150rpm, electrodes gap distance 3cm, and NaCl 3g/l for electrolysis time 30min.

As it is clear from the Figure (4) that, as the pH increased from 2 to 6 the dissolved nickel is about 0.4gm and the Faradays dissolution efficiency is within the range of 97.9% after that as the pH increased the dissolved nickel decreased and also the dissolution efficiency which reached to 82% at pH 11 this may be attributed to the electrode passivation within this pH range from 8-11.

On the other hand, at low pH the dissolved nickel conversion efficiency to nickel hydroxide is low within the range of pH 2-4 which may be attributed to the strong acidic medium which keeping the dissolved nickel as nickel chloride. As the pH increases the nickel hydroxide generation efficiency increases reached its maximum value at pH 6 which

is about 76% then it started to decrease again due to the decreasing of the dissolved nickel due to electrode passivation. Based on the above pH value of 6 was taken as optimum.

3.1.2 Effect of applied current density

The effect of applied current density on dissolved nickel, anodic dissolution current efficiency, and conversion of dissolved nickel to nickel hydroxide powder, were respectively graphically represented in Figure (5) during the nickel anodic dissolution process. These were experimentally carried out at pH 6, sodium chloride Concentration 3g/l, electrolysis time 30mins, and electrodes gap distances 3cm, with stirring rate 150rpm at 20°C.

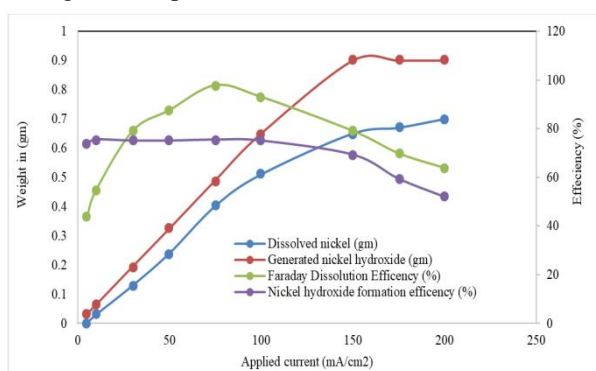


Figure (5) Effect of applied current on dissolved nickel and nano nickel hydroxide formation during nickel anodic dissolution at operating conditions: pH6, 20°C, 150rpm, gap distance 3cm, and NaCl 3g/l for electrolysis time 30min

The results indicate that as current density increases the dissolved nickel ions generated increases too, and the formed nickel hydroxide increases also till current density 150mA/cm², and after that although current density increases, formed nickel hydroxide efficiency is constant this may be attributed to the formation of adhered black powder layer at the electrode surfaces during dissolution which decreases the dissolved nickel. Based on the above results applied current density of 75mA/cm² was taken as optimum.

3.1.3 Effect of electrolysis time

Figure (6) represents the effect of electrolysis time on both nickel anodic dissolution process and nickel ion conversion to nano nickel hydroxide, respectively at applied current density 75mA/cm², pH 6, and NaCl concentration 3g/l, electrodes gap distance of 3cm and stirring rate 150rpm at 20°C.

The results show that as the electrolysis time increases the generated dissolved nickel ions and the formed nano nickel hydroxide increase, while both the anodic dissolution current efficiency and conversion to nano nickel hydroxide efficiency having higher values till electrolysis time 30min. then started to decreases this may be attributed to the formation of adherence of white layer on the surface of electrode which decreases the dissolution of nickel substrate. Based on the above 30min. was taken as optimum electrolysis time for nickel anodic dissolution process.

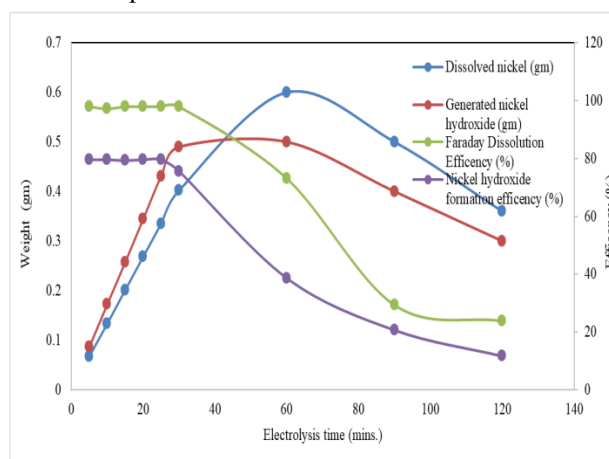


Figure (6) Effect of electrolysis time on dissolved nickel and nano nickel hydroxide formation during nickel anodic dissolution at operating conditions: pH6, C.D. 75mA/cm², 20°C, 150rpm, NaCl 3m/l and electrodes gap distance 3cm.

3.1.4 Effect of sodium chloride concentration

Figure (7) show the effect of sodium chloride concentration on generated dissolved nickel weight, anodic dissolution current efficiency, and the conversion of generated dissolved nickel ion to nano nickel hydroxide powder, respectively during the nickel anodic dissolution process, at the following operating conditions: pH 6, applied current density of 75 mA/cm², electrolysis time 30mins, electrodes gap distance 3cm, with stirring of 150rpm, at 20°C, results indicated that, with increasing NaCl concentration, the generated dissolved nickel weight, the anodic dissolution current efficiency, and the conversion of the generated dissolved nickel ion to nano nickel hydroxide powder increase reaching their maximum values at sodium chloride concentration 3g/l then no significance change obtained at higher concentration of NaCl. So 3g/l sodium chloride was taken as optimum electrolyte concentration during nickel anodic dissolution process

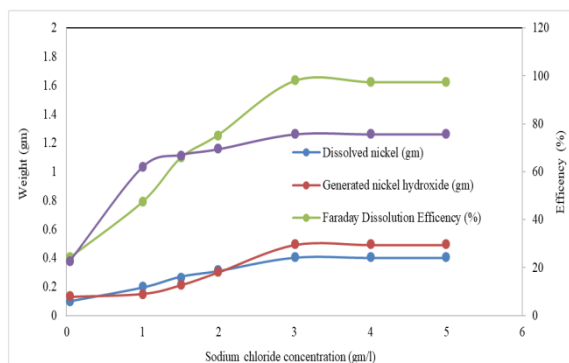


Figure (7) Effect of sodium chloride concentration on dissolved nickel and Nickel hydroxide formation during nickel anodic dissolution at operating conditions: pH6, C.D. $75\text{mA}/\text{cm}^2$, 20°C , 150rpm, and gap distance 3cm for electrolysis time 30min.

3.1.5 Effect of temperature

The effect of electrolyte temperature change during anodic dissolution of nickel in sodium chloride solution at operating conditions pH 6, C.D. $75\text{mA}/\text{cm}^2$, electrolysis time 30min. NaCl 3g/l, electrodes gap distance 3cm, and 150rpm was studied. Figure (8) shows that there is no effect of the electrolyte temperature increasing on the nickel substrate anodic dissolution efficiency and generation efficiency of nano nickel hydroxide efficiency, so from the economic point of view 20°C was taken as optimum.

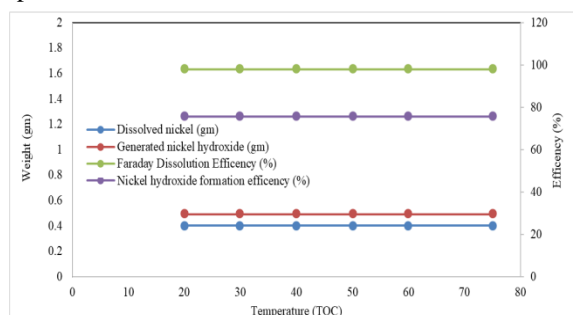


Figure (8) Effect of Electrolyte temperature on dissolved nickel and Nickel hydroxide formation during nickel anodic dissolution at operating conditions: pH6, C.D. $75\text{mA}/\text{cm}^2$, NaCl 3g/l., 150rpm, and gap distance 3cm for electrolysis time 30min.

3.1.6 Effect of Electrodes gap distance

Figure (9) indicates that at the operating conditions pH 6, electrolysis time 30min., sodium chloride concentration 3g/l., C.D. $75\text{mA}/\text{cm}^2$, 150rpm at 20°C , as the gap distance decreased less than 3cm no significance change occur but the observations shows that black power is obtained within the light green nickel hydroxide powder this may be attributed

to the high attack of the electric current and the exceeding of the nickel oxidation potential.

While at electrodes gap distance more than 3 cm there are decreasing in the dissolved nickel, formed nano nickel hydroxide powder, Faradays efficiency and nickel hydroxide generation efficiency, these may be due to the decreasing of the throwing power between electrodes, so 3cm as electrodes gap distance may be taken as optimum value.

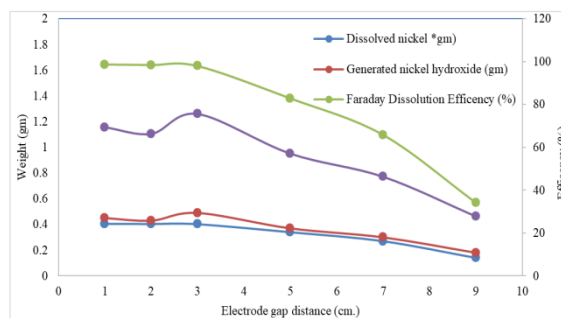


Figure (9) Effect of electrodes gap distance on dissolved nickel and Nickel hydroxide formation during nickel anodic dissolution at operating conditions: pH6, C.D. $75\text{mA}/\text{cm}^2$, 20°C , 150rpm, and sodium chloride 3g/l for electrolysis time 30min.

3.1.7 Effect of reverse polarity interval time

Based on the above obtained results the optimum conditions for the electrolytic generation of nano nickel hydroxide powder using the anodic dissolution of nickel metal substrate as a base for preparation of nano nickel oxide particles were; C.D. $75\text{mA}/\text{cm}^2$, pH 6, NaCl concentration 3gm/l, electrodes gap distance 3cm, electrolysis temperature 20°C , at stirring rate 150rpm. From the industrial point of view, we need continuous production of nano nickel hydroxide powder without need of electrode cleaning every 30min. so we are looking for cleaning process during the anodic dissolution of nickel without stopping the process.

Most efficient cleaning process is the reversing electrode polarity during the electrolysis process. So, study the effect of reverse electrodes polarity interval time on the dissolved nickel, nano nickel hydroxide generation, and there efficiencies was suggested. The results obtained were graphically represented in Figure (10) and shows that at reversing polarity at time interval 5min. maximum nickel dissolution efficiency and nano nickel hydroxide powder generation efficiency were obtained which they are 97% and 92% respectively while as the time intervals

increase the nickel hydroxide generation efficiency decreases, so reverse polarity interval time 5min. was taken as optimum.

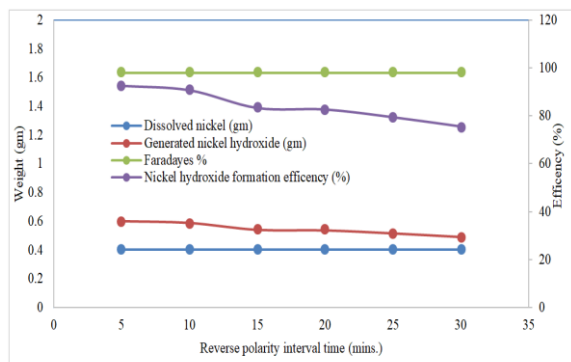


Fig.(10) Effect of reverse polarity interval time on dissolved nickel and nano nickel hydroxide formation during nickel anodic dissolution at operating conditions: pH6, C.D. 75mA/cm², 20°C, 150rpm, NaCl 3g/l and gap distance 3cm for electrolysis time 30min.

The investigation of the optimum conditions for nano nickel hydroxide electrolytic generation using nickel metal anodic dissolution in saline solutions indicates that C.D. of 75mA/cm², pH 6, sodium chloride concentration 3gm/l, 20°C, electrodes gap distance, stirring rate 150rpm at reverse polarity time interval 5min. will give the maximum nickel dissolution efficiency and nano nickel hydroxide powder generation efficiency. The obtained nickel hydroxide powder after washing filtration and drying is clanked for 6hr. at 500°C for conversion from nano nickel hydroxide powder to nano nickel oxide particles. The obtained nano nickel hydroxide and nickel oxide particles were characterized as follows:

3.2.1 SEM-EDX analysis

The morphology of nickel oxide was performed by scanning electron microscope (SEM-EDX). The EDX analysis reveals the peaks related to nickel and oxygen which confirm the formation of nickel oxide crystals as shown in Figure (11 a & b). Also from Figure (11 c & d), it is clear that, the crystalline texture and layered structure of nickel hydroxide and nickel oxide. Regarding the SEM results of nano nickel hydroxide Figure (11c) shows that large grain size with no sharp grain boundaries was present, while Figure (11d) illustrates smaller grain size of nano nickel oxide with sharp grain boundaries were formed.

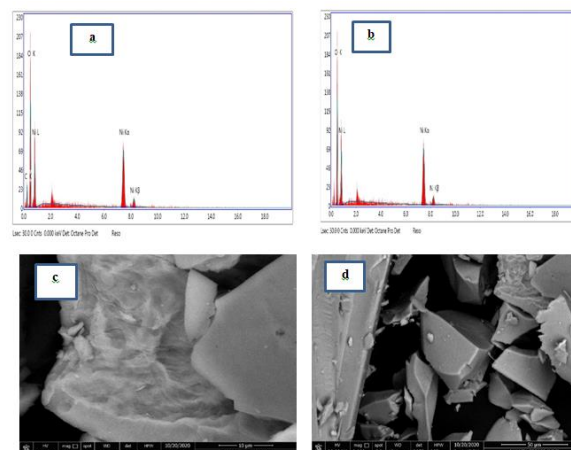


Figure (11 a, b, c& d) EDX-SEM images of Nano nickel hydroxides and nano nickel oxide

3.2.2 TEM analysis

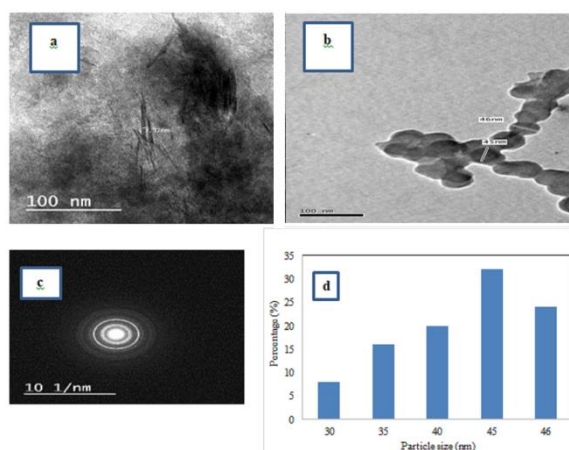


Figure (12 a, b, c and d) TEM image, SAED, and histogram of nano nickel hydroxide and nano nickel oxide particles

Figure (12 a & b) shows the TEM image and SAED of the obtained nano Nickel hydroxide powder and nano nickel oxide, respectively. It can be seen that, the Nickel hydroxide nano-particles are ranged in filament shape with width of 2 to 3 nm and length of 60nm with active surface area of its double face of 300nm and SAED analysis confirmed the crystalline structure of nano Nickel hydroxide. After heat treatment of the nano scale nickel hydroxide powder for 6hr. at 500°C, semi sphere particles of nano nickel oxide of main diameter of 45nm were formed. Figure (12c) represents the histogram of the heat generated nano nickel oxide powder. As it is clear from the figure about 76% of the obtained nano nickel oxide particles are of the range of 40nm, 45nm, and 46nm,

respectively with is matched the nano safety particle size which is more than 15nm.

3.2.3 XRD analysis

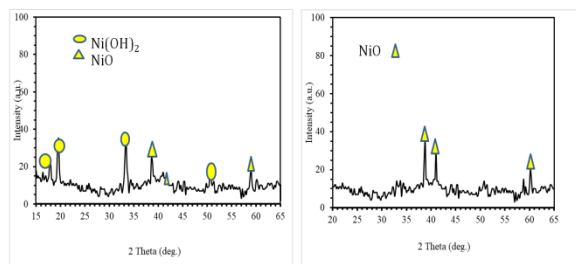


Figure (13 a and b) XRD of nano nickel hydroxide obtained by anodic dissolution at room temperature and nano nickel oxide obtained at 500°C treatment for 6hr

Figure (13a) shows the XRD patterns of a synthesized $\text{Ni}(\text{OH})_2$, and NiO respectively. In case of synthesized $\text{Ni}(\text{OH})_2$, all diffraction peaks can be readily indexed to hexagonal $\beta\text{-Ni}(\text{OH})_2$ with lattice constants $a = 3.130 \text{ \AA}$ and $c = 4.630 \text{ \AA}$, which agrees well with the well-known diffraction pattern (data from JCPDS file 74-2075). The diffraction peaks reveal strong and sharp, good crystal linity of the final products. No peaks of impurities were found, indicating pure $\beta\text{-Ni}(\text{OH})_2$ of hexagonal phase were successfully obtained. Moreover, Figure (13b) represents the total conversion of nickel hydroxide to nickel oxide led to the formation of peaks of nickel oxide that appear in this Figure [24-25].

3.3 Removal of MB dye from its solutions using nano- Nickel Oxide

Nano nickel hydroxide and nano nickel oxides have great applications in industry such as batteries, super capacitors, wastewater treatment. In this study we will test the efficiency of the obtained nano nickel oxide as adsorbent for removal of MB from its solutions as an example in wastewater treatment. Several operating conditions controlling the removal of MB from its solution such as solution pH, nano nickel oxide dose, solution temperature, contact time, and stirring rate. Synthetic solution of MB of concentration of 100mg/l was used.

3.3.1 Effect of MB solution pH

As shown in Figure (14) the adsorption of the dye with pH from 3 to 12 were studied keeping all other parameters constant (nano nickel oxide 10g/l, temperature 20°C, contact time 30min., stirring rate 150rpm, with MB 100mg/l). It was observed that: the

amount of dye absorbed per unit weight of adsorbent increased as increasing pH value. This is due to electrostatic force between the adsorbent and positively charged basic dyes which become less. This is in good agreement with the results reported before [22] as its clear pH 11 will be taken optimum.

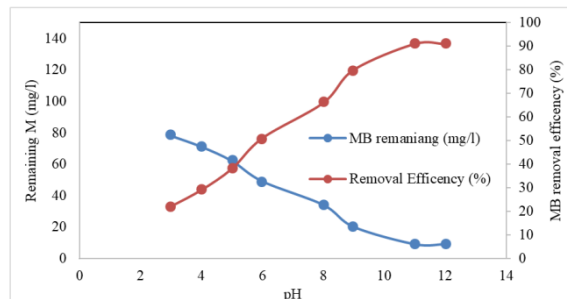


Figure (14) Effect of MB solution pH variation on the removal of MB from its solution using nano nickel oxide at 20°C, contact time 30min., stirring rate 150rpm, and nano nickel oxide 10g/l, at MB 100mg/l.

3.3.2 Effect of Nano nickel Oxide Dose

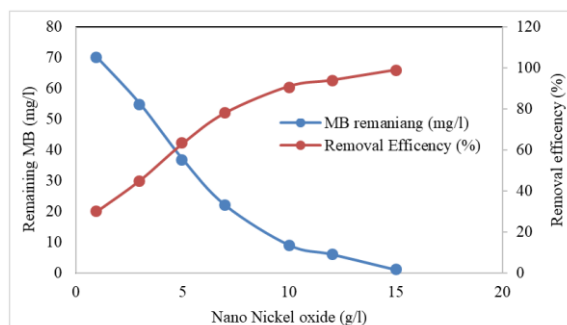


Figure (15) Effect of nano nickel oxide concentration on the removal of MB from its solution using nano nickel oxide at 20°C, contact time 30min., pH 11, stirring rate 150rpm, at MB 100mg/l.

The removal efficiency of MB from its solution of concentration 100mg/l with different doses of nano nickel oxide at the processing conditions mentioned in Figure (15) which are: 20°C, contact time 30min., pH 11, stirring rate 150rpm, at MB 100mg/l. It is clear from the Figure that as the dose of the nano nickel oxide increases the adsorption efficiency increases reaching its maximum (99%) at 15g/l, nano nickel oxide but from the economical view dose 10g/l nano nickel oxide with removal efficiency 91% was taken as optimum.

3.3.3 Effect of MB solution temperature

By increasing the temperature of MB solution from 20°C to 75°C, it is clear that increasing

temperature increases percent removal of MB from 91% to 99.6% at 60°C then it remains constant at more than 60°C which means that temperature almost has no great effect on nano nickel oxide adsorption capacity throughout this study as shown in Figure (16) also from the economical view the energy required to reach 99% removal will be very expensive so 20°C was taken as optimum.

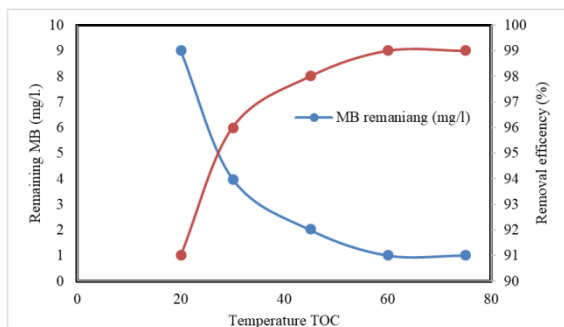


Figure (16) Effect of temperature variation on the removal of MB from its solution using nano nickel oxide at 10 g/l nano nickel oxide concentration, pH 11, stirring rate 150rpm, at MB 100mg/l for 30min.

3.4 Effect of stirring rate

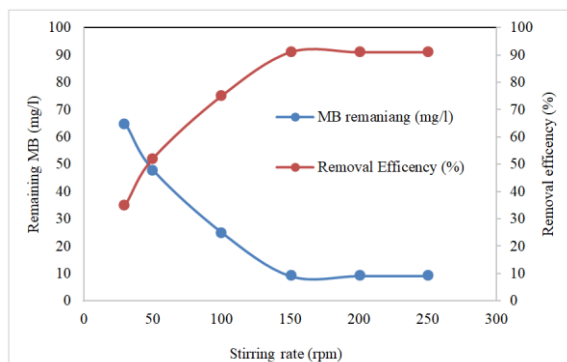


Figure (17) Effect of stirring rate on the removal of MB from its solution using nano nickel oxide at 10 g/l nano nickel oxide concentration, pH 11, temperature 20°C at MB 100mg/l for 30min.

Figure (17) Represents the effect of stirring rate on the adsorption efficiency of MB on nano nickel oxide particles at processing conditions 10 g/l nano nickel oxide concentration, pH 11, temperature 20°C at MB 100mg/l, for 30min. from the results it is clear that maximum adsorption efficiency obtained at stirring rate 150rpm and any increment in the stirring rate has no effect so 150rpm was taken as optimum stirring rate.

3.5 Effect of contact time

Percentage of MB removal was studied at different contact time intervals as shown in Figure (18) at operating conditions 20°C, 10 g/l nano nickel oxide, pH 11, stirring rate 150rpm, at MB 100mg/l, which illustrates that the maximum removal obtained (100%) at 90 min. where at 30min. 91% removal efficiency was obtained. As it is clear contact time of 90min was taken as optimum.

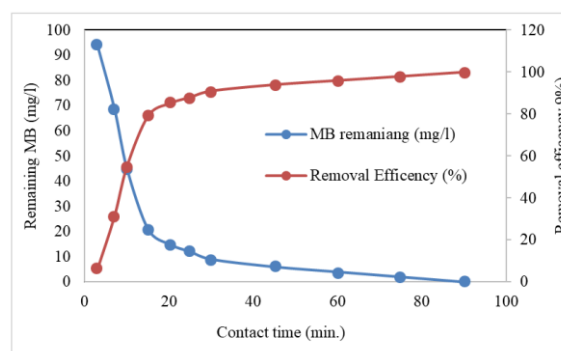


Figure (18) Effect of contact time the removal of MB from its solution using nano nickel oxide at 20°C, 10 g/l nano nickel oxide, pH 11, stirring rate 150rpm, at MB 100mg/l.

Based on the above the optimum conditions for removal of MB from its solutions (100mg/l.) using the obtained nano nickel oxide prepared throughout this study via the heat treatment of the electrolytic generated nickel hydroxide powder were pH 11, 100mg/l. MB, 10g/l. nano nickel oxide dose, 20°C, stirring rate 150rpm, at electrolysis time 90min.

3.6 Adsorption capacity

For obtaining the adsorption capacity of nano nickel oxide prepared according the proposed process in this study, a solution of 500mg/l MB was prepared and addition of 10g/l of nano nickel oxide used for the removal of MB from this solution at operating conditions pH 11, 20°C, stirring rate 150rpm.

The remaining MB concentration was measured with respect to contact time till the MB concentration is constant. Figure (19) show the results of the above mentioned removal conditions. Using the results of Figure (19) and calculations of equation (2) the adsorption capacity of the obtained nano nickel oxide for MB removal from its solution is 25mg.g⁻¹

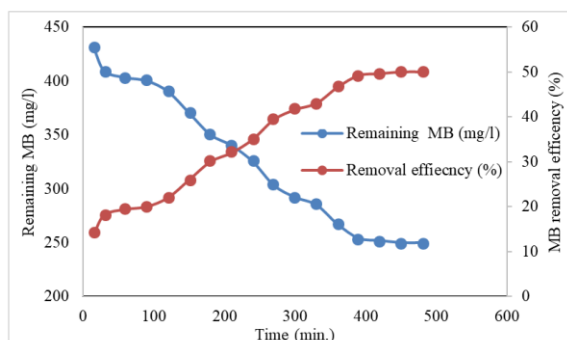


Figure (19) Effect of contact time on the removal of MB from its solution using nano nickel oxide at 20°C, 10 g/l. nano nickel oxide, pH 11, stirring rate 150rpm, at MB 500mg/l.

3.7 Recycling

In order to investigate the reusability of nano nickel oxide as an adsorbent for MB dye, after completing the adsorption process, the nano NiO particles recovered by filtration, washing with acetone and deionized water several times and drying at 100 °C for 2hr. Then, the dried nano powder was applied for future adsorption of MB. The recycled sample was used under the same operating conditions. The results show that more than 12 times of use of nano nickel oxide for removal of MB from its solution without no significant change of its adsorption capacity.

According to the present study anodic dissolution process for nickel sheets was carried out to generate nano nickel hydroxide powder which is then converted to nano nickel oxide via heat treatment for 6hr. at 500°C. The anodic dissolution process is a promising one which used in several previous studies [20-26]. In this study the obtained nano nickel oxide particles have very good adsorption capacity for the removal of MB from its solution which is 25mg.g⁻¹ without any need for making it as composite material as mentioned in et.al [27-32].

4. Conclusion

Nano nickel compounds (hydroxides and nickel oxide) were synthesized via anodic dissolution technique and conversion of nickel hydroxide into nano nickel oxide via heat treatment. The obtained operating conditions for anodic dissolution of nickel substrate in saline solution were 75mA/cm², pH 6, 3g/l. sodium chloride, 20°C, electrode gap distance 3cm. The obtained nickel hydroxide powder completely converted to nano nickel oxide at 500°C for 6hr. The obtained nano nickel oxide was tested

for the removal of MB from its solutions via adsorption. The adsorption capacity of MB on the nano nickel oxide surface was 25mg.g⁻¹, the adsorption capacity indicating that nano nickel oxide is very good dye adsorbant.

REFERENCES

1. Urso M, Torrisi G, Boninelli S, Bongiorno C, Priolo F, Mirabella S., Ni(OH)₂@Ni core-shell nano-chains as low-cost high-rate performance electrode for energy storage applications. *Scientific Reports* 9:7736 (2019). <https://doi.org/10.1038/s41598-019-44285-1>
2. Ash B, Paramguru R K and Mishra B K. Fundamental Investigation of Electrochemical Preparation of Battery Grade Nickel hydroxide. *Advanced Materials Research* 117, 15-20 (2010).
3. Subbaiah, T., Mallick S.C., Mishra K.G, Sanjay K., Das. R.P, Electrochemical precipitation of nickel hydroxide. *Journal of Power Sources* 112, 562–569 (2002).
4. Hu W-K, Gao X-P, Burchardt N. T, Nakstad N. K, J Power Sources, 160 (2006).
5. Fierro C., Zallen A., Koch J., Fetcenko M. A, J the Electrochem. Soc. 153 (3) (2006).
6. Kohler U., Antonius C, Bauerlein P., J Power Sources, 127 (2004).
7. Hall D. S, Lockwood D. J., Bock C, MacDougall, B R. Nickel hydroxides and related materials: a review of their structures, synthesis and properties, *Proc. R. Soc. A* 471: (2014). <http://dx.doi.org/10.1098/rspa.2014>
8. Sharel P. E, Liu D, Lazenby R A, Sloan J, Vidotti, M, Patrick R. Electrode position of Nickel Hydroxide Nanoparticles on Carbon Nanotube Electrodes: Correlation of Particle Crystallography with Electrocatalytic Properties. *J. Phys. Chem. C*, 27 (2016). <http://dx.doi.org/10.1021/acs.jpcc.5b12741>
9. Joseph H.L. Hadden, Mary P. Ryan, D. Jason Riley. Examining the charging behavior of nickel hydroxide nano-materials. *Electrochemistry Communications* 101, 47-51(2019).
10. YOUNG, Kwo, WANG, Lixin, MAYS, William SM, TR, REICHMAN, Benjamin, Macnichol Trail, Nickel Hydroxide Positive Electrode for Alkaline Rechargeable Battery. THE PATENT COOPERATION TREATY (PCT), WO 11 (2016).
11. Gogosti Y, .Penner R. M, energy storage in nano materials- capacitive, pseudo capacitive, or battery – life. *ACS Nano* 12, 2081-2083 (2018).
12. Khalil A, Lalia, B S and Hashaikeh R. Nickel oxide nanocrystals as a lithium-ion battery anode: structure-performance relationship. *J Mater. Sci*, 51:6624–6638 (2016).
13. Sechi E, Vacca A, Mascia M, Palmas S., Nickel-Based Non-porous Electrodes for Water Treatment. *Chemical Engineering Transactions*. 47, 97- 102 (2016).
14. Chen W, Jin Y, Zhao J, Liu N, Cuia, Y, Nickel-Hydrogen Batteries for Large-Scale Energy Storage, *PNAS*, 115, 11694–11699 (2018).
15. Saraei K, Moghaddam J, Preparation of NiO nanoparticles from Ni(OH)₂NiCO₃.H₂O precursor by mechanical activation, *International Journal of Minerals, Metallurgy and Materials* 21, (2014) .

16. Numan A, Duraisamy N, Omar F S, Gopi D, Ramesh K., Ramesh S., Sono-chemical synthesis of nano-structured nickel hydroxide as an electrode material for improved electrochemical energy storage application. *Progress in Natural Science: Materials International* (2017).
17. Tientong J, Garcia S, Thurber C R, Golden T D, Synthesis of Nickel and Nickel Hydroxide Nanopowders by Simplified Chemical Reduction. *Journal of Nanotechnology* (2014).
18. Amer Al-Nafiey, Mohammed H. K. Al-Mamoori, Saif Mohammed Alshrefi, Ali K. shakir, and Rafea Tuama Ahmed, "One step to synthesis (rGO/Ni NPs) nanocomposite and using to adsorption dyes from aqueous solution", *Materials Today: Proceedings* 19, 94–101 (2019).
19. C. Srinidhi and A Madhusudhan, "A Diesel Engine Performance Investigation Fuelled with Nickel Oxide Nano Fuel-methyl Ester", *INTERNATIONAL JOURNAL of RENEWABLE ENERGY RESEARCH* C.Srinidhi and A.Madhusudhan, 7, No.2, (2017).
20. Anne-Lise Brisse, Philippe Stevens, Gwenaëlle Toussaint, Olivier Crosnier and Thierry Brousse, "Ni(OH)₂ and NiO Based Composites: Battery Type Electrode Materials for Hybrid Supercapacitor Devices", *Materials* 11, 1178 (2018), <https://doi.org/10.3390/ma11071178>
21. S.R. Yousefi, D. Ghanbari, M. Salavati-Niasari, "Hydrothermal Synthesis of Nickel Hydroxide Nanostructures and Flame Retardant Poly Vinyl Alcohol and Cellulose Acetate Nanocomposites", *J. Nanostruct.*, 6(1): 80-85, Winter (2016) <https://doi.org/10.7508/jns.2016.01.013> .
22. Shaarawy H H, Hussein H S, Abdel Kader E, Hussien, Nabila H and Hawash S I, Adsorption performance of coated bentonite via graphene oxide, *Bulletin of the National Research Centre*, 44:53(2020). <https://doi.org/10.1186/s42269-020-00299-8>.
23. Hussein H.S., Shaarawy H.H., Hussien Nabila H., Abdel kader E., Hawash S.I., Synthesis of nano graphene for saving energy in water desalination", *Cleaner Engineering and Technology* 4,100162 (2021).
24. Patil V, Pawar S., Chougule M., Godse P , Sakhare R , Sen S. , Joshi P, Effect of Annealing on Structural, Morphological, Electrical and Optical Studies of Nickel Oxide Thin Films, *Journal of Surface Engineered Materials and Advanced Technology*, 1, 35-41 (2011).
25. Aghazadeh M., Rashidi A., Ganjali M. R., Maragheh M. G., Nickel oxide Nano-Rods/Plates as a High Performance Electrode Materials for Super capacitors; Electro-synthesis and Evolution of Charge Storage Ability, *Int. J. Electrochem. Sci.*, 11, 11002 –11015, (2016).
26. Abdel-Fatah M. A., Hawash S. I., Shaarawy H.H., Cost-effective Clean Electrochemical Preparation of Ferric Chloride and its Applications, *Egypt. J. Chem.* 64, No. 7 pp. 3841 - 3851 (2021).
27. Albokheet WA, Gouda M. and Al-Faiyz Y. Removal of Methylene Blue Dye Using Nickel Oxide/ Carboxymethyl Cellulose Nano composite: Kinetic, Equilibrium and Thermodynamic Studies. *Journal of Textile Science & Fashion Technology* 8 (2),1-10 ,12, (2021).
28. Abdel-Fatah, M.A., Hussein, N.H., Hawash, S.I., Shaarawy, H.H. Investigation of using sidr leave extracts in nano-silver preparation, *ARNP Journal of Engineering and Applied Sciences*, 2016, 11(19), pp. 11649–11654
29. Abdel-Fatah, M.A., Elsayed, M.M., Al Bazed, G.A., Hawash, S.I. Sewage water treatment plant using diffused air system, *ARNP Journal of Engineering and Applied Sciences*, 2016, 11(17), pp. 10501–10506
30. Amin, A., Al Bazed, G., Abdel-Fatah, M.A., Experimental study and mathematical model of coagulation / sedimentation units for treatment of food processing wastewater, *Ain Shams Engineering Journal*, 2021, 12(1), pp. 195–203
31. Abdel-Fatah, M.A., Shaarawy, H.H., Hawash, S.I. Integrated treatment of municipal wastewater using advanced electro-membrane filtration system, *SN Applied Sciences*, 2019, 1(10), 1153
32. Abdel-Fatah, M.A., Khater, E.M.H., Hafez, A.I., Shaaban, A.F., Performance of fouled NF membrane as used for textile dyeing wastewater, *Membrane and Water Treatment*, 2020, 11(2), pp. 111–121