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Co-biosorption potential of *Acacia nilotica* bark in removing Ni and aminoazobenzene from contaminated wastewater

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ABSTRACT

In this biosorption study, the potential of *Acacia nilotica* bark in simultaneous removal of Ni and aminoazobenzene was investigated. For this purpose, the impact of different experimental conditions on the co-biosorption potential of *Acacia nilotica* bark was studied. In result, the maximum biosorption of Ni and dye was in the acidic range pH, that is, 6 and 4, with sorbent dosage of 1 and 0.8 g after 40 min of the experiment when both were at 4 ppm, respectively. In case of adsorption isotherms, both mono- and multi-layer adsorption occurred simultaneously in the case of Ni as clear from the R^2 values of isotherms (R^2 for Langmuir = 0.999) and (R^2 for Freundlich = 0.941). In case of dye, uniform monolayer adsorption was predominant (R^2 for Langmuir = 0.980) as compared to the multi-layered adsorption. The maximum amount of monolayer adsorption of Ni and dye onto the biosorbent was 0.60 and 0.348 mg g^{-1}, respectively. From the kinetics model, chemisorption was predominant in the case of both Ni and dye adsorption on biosorbent. In conclusion, the bark of *Acacia nilotica* has great potential for Ni and dye removal from co-contaminated wastewater.

Keywords: Dye; Heavy metal; Freundlich; Langmuir; Kinetics; Biosorption

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1. Introduction

Through a variety of sources such as rapid industrialization and urbanization, various pollutants such as toxic heavy metals and dyes are released into the environment [1,2]. Due to the toxic, persistent, and non-biodegradable nature of these pollutants and unrestricted discharge into the environment, it has been a great threat to human health due to its detrimental effect on the soil water continuum [3,4]. Their discharge into the aquatic environment and drinking water supplies is a major health hazard not only for aquatic life but also for human health due to their bioaccumulation potential in living cells and subsequent carcinogenic effects. Moreover, the legal limitations for the levels of different heavy metals and dyes in the effluents necessitate the need for wastewater treatment containing these poisonous metals [5].

The main sources of heavy metals such as nickel (Ni) and dyes include effluents from textiles, electroplating, smelting, paint pigments, batteries, mining operations, and the agriculture sector [6]. At very low concentrations, Ni is very toxic and may cause lung cancer, skin dermatitis, kidney damage, edema, pulmonary fibrosis, and gastrointestinal disorders [7–9]. The safe limit for Ni in drinking water set by the US Environmental Protection Agency and the World Health Organization is 0.5 and 0.07 ppm, respectively [10]. Above all discussion necessitates devising certain strategies with the potential to remove these contaminants from the environment.

4-Aminoazobenzene has been used in inks for inkjet printers, vital staining in microscopy, yellow pigments, yellow-colored smoke in pyrotechnics, and other chemicals such as styrene resins, lacquers, oil stains, insecticides, waxes, and varnishes. It is highly carcinogenic for living organisms, causing liver tumors [11,12]. It is produced as an intermediate during the synthesis of various dyes such as acid yellow, solid yellow, indulines, and chrysoidine and is known as aniline yellow or 4-phenylazoaniline.

Various physicochemical strategies such as ion exchange, evaporation, chemical oxidation, and precipitation, and membrane filtration have been employed [13–17]. However, these strategies are costly, energy-intensive, secondary pollution potential, or low efficiency [18,19]. Therefore, searching for a low-cost and environment-friendly technique is the need of the hour.

Biosorption is one such simple strategy, which employs low-cost organic materials for the removal of toxic materials in contaminated waters and is highly selective and efficient with no detrimental effect on the environment [20,21]. It has been employed worldwide for the removal of various pollutants from wastewater and found to be an efficient and sustainable strategy [22,23]. In addition, it offers an alternative to the existing approaches being used for the removal of the various pollutants from wastewater without harming the environment [24]. Various low-cost plant materials have been found suitable for the efficient removal of various metals from the contaminated waters [19,22,25–32].

Recently, there has been an increasing trend in the use of non-living plant biomass as potential biosorbents for Ni(II) removal from wastewaters [33,34]. The biosorption potential of the material being used as a biosorbent depends upon experimental conditions such as pH, temperature, biomass amount, particle size, initial metal concentration in the solution, contact time, etc. [35–41]. According to Fomina and Gadd [20], various mechanisms (absorption, adsorption, ion exchange, surface complexation, and precipitation) are involved during biosorption. Various studies have found that pretreatment of waste biomass with an acid improves the biosorption capacity of the material being used. For example, Gupta and Jain [43] treated *A. vera* waste using various acids and recorded the strong metal adsorption capacity of Na_2CO_3-modified *A. vera* leaf waste. Similarly, Vázquez et al. [44] pretreated *Pinus pinaster* bark with formaldehyde and sulfuric acid, which ultimately enhanced the biosorption capacity. *Acacia nilotica* L. is a fast-growing, multipurpose tree legume. Its bark and leaves are abundantly available and can be used for the biosorption of heavy metals and dyes from contaminated waters [45,46].

Recently, there has been great emphasis on devising certain strategies to remove multiple contaminants simultaneously, for example, co-contamination of heavy metals and dyes in textile effluent. The concentration of Ni in various industrial effluents may reach up to 10 mg L^{-1} [47]. Similarly, the concentration of dyes in colored effluents from textile and other industries may reach up to 20 to 500 mg L^{-1} [48]. Up to our knowledge, no study has investigated the potential of *Acacia nilotica* bark in the simultaneous removal of Ni and aminoazobenzene. Therefore, this research work was conducted to study the co-biosorption potential of *Acacia nilotica* bark for Ni and dye from synthetic contaminated water, to optimize different parameters such as pH, contact time, the quantity of the sorbent, sorbate concentration and Ni and dye ratios, and to analyze the biosorption effectiveness through isothermal and kinetic models.

2. Materials and methods

2.1. Biosorbent

The bark of *Acacia nilotica* L. was selected as a biosorbent for the adsorption of nickel (Ni) and dye (aminoazobenzene) from the aqueous media. The biosorbent was pretreated as described in the following section.

2.2. Pretreatment of biosorbent

Firstly, the biosorbent was physically cleaned and then almost 200 g of it was heated in water (2 L) for 25 min to remove out the water-soluble contaminants and dirt particles. Afterward, the mixture was cool at room temperature and filtered. The wet biosorbent was dried out at 500°C in an electrical oven and was ground in an electrical grinder. The ground biosorbent was soaked in HNO_3 solution (2.5 M); this mixture was shaken for 2 h and then filtered at room temperature. Later on, the biosorbent was washed with deionized water 3–4 times until it was free from all the acid contents. Finally, the remaining biosorbent was dried overnight in an electrical oven at about 80°C, ground in an electrical grinder, and passed through a sieve with mesh size 100 mm. This pretreated biosorbent was preserved in a glass bottle, labeled, and placed in a vapor, smoke, and dirt-free environment.

2.3. Preparation of solutions

To prepare a 1 M HNO_3 solution, 6.45 mL concentrated HNO_3 was carefully poured into 100 mL deionized water. For 0.1 M disodium ethylenediaminetetraacetic acid (EDTA) solution, 18.61 g disodium EDTA was dissolved in 500 mL deionized water. For washing glassware, the chromic acid solution was prepared by mixing potassium dichromate (20 g) with sulfuric acid (5 mL). After dissolution, the volume of the solution was made up to 300 mL with sulfuric acid.

Stock solutions (1,000 ppm) of Ni and aminoazobenzene were prepared by dissolving 1.759 g nickel nitrate [$Ni(NO_3)_2$; 99.1%] and 1.010 g aminoazobenzene ($C_6H_5N{=}NC_6H_4NH_2$; 99%), respectively. The working solutions (2, 4, 6, 8, 10, and 12 ppm) of Ni and aminoazobenzene were prepared by diluting the stock solution using the following equation:

$$C_1V_1 = C_2V_2 \tag{1}$$

Standard stock solutions of Ni and aminoazobenzene were prepared in dilute HNO_3 and deionized water. For each sorption study, freshly prepared solutions of Ni and dye from the stock solution were prepared.

2.4. Sorption studies

A series of batch sorption experiments were conducted by taking a certain amount of biosorbent in clean iodine flasks (25 mL) containing Ni and dye solution at a specified concentration. The flask containing the mixture was shaken (140 rpm) at room temperature for 45 min. Later on, the mixture was filtered by using pretreated filter papers. The amount of Ni and dye in the filtrate was determined by using an atomic absorption spectrometer (PerkinElmer, Shelton, CT, USA, AAnalyst 800) and UV-Visible spectrophotometer (UV-1700 Shimadzu, Kyoto, Japan), respectively. The sorption percentage of metal and dye and quantity sorbed (ppm of metal and dye/g of the sorbent) was calculated by using the following equations:

$$\text{Sorption}\left(\%\right) = \frac{C_i - C_f}{C_i} \times 100 \tag{2}$$

$$\text{Sorption quantity} = \frac{\left(C_i - C_f\right)}{W} \times V \tag{3}$$

where C_i is metal and dye concentration (ppm) in solution before sorption; C_f is metal and dye concentration (ppm) in solution after sorption; V is solution volume (mL) and W is biosorbent weight (mg).

Later on, various parameters like the amount of biosorbent, pH, contact time, the concentration of sorbates (Ni and dye), and metal dye ratio were optimized in a series of batch experiments. The details about each experiment are given in the following sections.

2.4.1. pH

A batch experiment was conducted under varying pH (1, 2, 3, 4, 5, 6, and 7) of the reaction mixture (metal + dye + biosorbent) to find out the optimum pH for maximum adsorption of Ni and dye. The pH of the reaction mixture was set up using 1 M HNO_3 solution and maintained with ammonium hydroxide (NH_4OH) solution by using a pH meter (inoLab®-WTB GmbH; Weilheim, Germany). Briefly, 25 mL of Ni and dye solution (5 ppm each) with 0.5 g biosorbent individually at room temperature were shaken at an electrical shaker (Fisher Scientific Haake Bath Water Shaker SWB 20, Germany) for 45 min at each pH, separately. After finding the optimum pH, the pH was maintained in the subsequent adsorption studies using HCl or NaOH. In addition, there was no remarkable change in the initial pH monitored during the adsorption experiments.

2.4.2. Amount of biosorbent

After finding out the optimum pH for maximum sorption of Ni (pH = 6) and dye (pH = 4), another batch experiment was conducted to find out the optimum amount of biosorbent under its varying amounts for maximum sorption of Ni and dye. The various amounts of biosorbent tested separately for Ni and dye were 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 g, which were used by taking 25 mL each Ni (5 ppm) and dye (5 ppm) separately at pH 6 and 4, respectively. At room temperature, the reaction mixtures were mixed on a shaker for 45 min.

2.4.3. Contact time

After finding out pH (6 for Ni and 4 for dye) and amount of biosorbent (0.5 g), another batch experiment was conducted to find the optimum contact time for the maximum sorption of Ni and dye on the biosorbent. Different contact times such as 10, 20, 30, 40, 50, and 60 min separately for Ni and dye were investigated. The reaction mixture included 25 mL of each Ni (5 ppm) and dye (5 ppm) solution separately and the sorption percentage of Ni and dye on biosorbent was investigated at pH 6 and 4, respectively. The biosorbent in both Ni and dye was applied at 0.5 g. The reaction mixture containing Ni and dye at specified pH and amount of biosorbent was shaken for 10–60 min. To find out the minimum time required for the maximum sorption, the filtrate was subjected to analysis of Ni and dye using atomic absorption spectrometer and UV-Visible spectrophotometer, respectively after each reaction time.

2.4.4. Metal and dye concentration

After finding out the optimum pH (6 for Ni and 4 for dye), amount of biosorbent (0.5 g), and contact time (45 min.), the effect of various concentrations (2, 4, 6, 8, 10, and 12 ppm) of metal and dye on the maximum sorption of Ni and dye on biosorbent was tested in another batch experiment. For this purpose, the reaction mixture containing 0.5 g biosorbent added in 25 mL of each concentration of Ni and dye separately at pH 6 and 4, respectively was shaken for 45 min.

2.4.5. Metal and dye ratios

To investigate any interaction effect of Ni and dye on each other's sorption percentage, Ni and dye solutions, each at 5 ppm was mixed in different ratios (1:1, 1:3, and 3:1) based on volume. The reaction mixtures of different ratios of Ni and dye with biosorbent (0.5 g) were shaken for 45 min.

In all the batch experiments, after the reaction time, the reaction mixture was filtered through pretreated filter paper. The amount and sorption percentage of Ni and dye sorbed on biosorbent were calculated by determining the concentration of Ni and dye in the filtrates by using an atomic absorption spectrometer (iCE 3000 Sequence – Thermo Scientific, USA) equipped with a cathode lamp and UV-Visible spectrophotometer.

2.5. Mathematical modeling

2.5.1. Isothermal studies

The adsorption isotherm is a useful parameter to describe the distribution pattern of adsorbate molecules between the liquid and the solid phase at equilibrium [49]. In the present study, the Langmuir and Freundlich isotherms were used to analyze the adsorption data. Langmuir [50] assumes a surface with homogeneous binding sites, equivalent sorption energies, and no interactions between adsorbed species. The Langmuir isotherm is expressed by the following mathematical relation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{q_{\max}K_L} \tag{4}$$

where C_e = equilibrium concentration of Ni or dye (mg L^{-1}), q_e = quantity of Ni or dye adsorbed onto the adsorbent at equilibrium (mg g^{-1}), $q_{\max}$ = maximum monolayer adsorption capacity of adsorbent (mg g^{-1}) and K_L = Langmuir adsorption constant (L mg^{-1}). The plot of C_e/q_e against C_e gives a straight line with a slope and intercept of $1/q_{\max}$ and $1/q_{\max}K_L$ respectively. K_L is an important tool in the calculation of the dimensionless equilibrium parameters (R_L) that explains the favorability of the adsorption process; R_L is calculated using the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \tag{5}$$

The Freundlich isotherm [51] assumes an empirical model not limited to monolayer coverage alone but also describes multilayer adsorption. It is expressed mathematically as in Eq. (6):

$$\log q_e = \frac{1}{n}\log C_e + \log K_f \tag{6}$$

where q_e = quantity of Ni or dye adsorbed at equilibrium (mg g^{-1}), C_e = concentration (mg L^{-1}) of Ni or dye in solution at equilibrium; K_f and n are Freundlich constants incorporating the factors affecting the adsorption capacity and adsorption intensity, respectively. The plots of logq_e against logC_e give a linear graph with slope $1/n$ and intercept logK_f from which n and K_f can be calculated respectively.

2.5.2. Kinetics model

The kinetics models are helpful in the elucidation of the possible dye adsorption mechanism as well as possible rates controlling steps during adsorption [52]. The kinetics of the adsorption systems were studied using the pseudo-first-order and pseudo-second-order models.

The pseudo-first-order kinetic model of Lagergren [53] is given by the following equation:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{7}$$

where q_e = quantity adsorbed at equilibrium (mg g^{-1}) and q_t = quantity absorbed at time t (mg g^{-1}). k_1 = rate constant for the pseudo-first-order sorption (min^{-1}). A linear graph with a negative slope is expected from the plot of ln(q_e – q_t) against t at different concentrations, k_1 and q_{cal} can then be obtained from the slope and intercept, respectively.

The pseudo-second-order kinetic model [54], is presented in the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1(t)}{q_e} \tag{8}$$

where k_2 = rate constant of the pseudo-second-order kinetic equation in g mg^{-1} min^{-1}, q_e = maximum sorption capacity in mg g^{-1} and q_t (mg g^{-1}) = amount of sorption at time t. Linear graphs are obtained from a plot of t/q_t against t from which q_e and k_2 can be calculated from the slope and intercepts.

2.6. Quality control

2.6.1. Materials

The chemicals used during the study such as nitric acid (HNO_3), sulfuric acid (H_2SO_4), potassium dichromate ($K_2Cr_2O_7$), disodium EDTA ($C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$), nickel nitrate ($Ni(NO_3)_2$), aminoazobenzene ($C_6H_5N{=}NC_6H_4NH_2$), and ammonium hydroxide (NH_4OH) were of the Merck, Germany. The dye used in the experiment was an azo dye used in printing and dyeing leather, paper, and textile. The molecular structure of aminoazobenzene is shown in Fig. 1. The deionized H_2O used in all the research work was bought from GM Scientific (Peshawar, Pakistan) with pH = 6.85 and density = 0.998 g cm^{-3}.

2.6.2. Washing and storage of glassware

The glassware used during the experiment was washed with the chromic acid solution. Each flask was filled with H_2O and 1 mL of chromic acid solution was added to it. Then the flasks and glassware were kept for one day in the fumes, smoke, and dirt-free environment. After 24 h, the flasks and other glassware were washed with tap water 3–4 times and finally rinsed with deionized water. Finally, flasks and other glassware were dried at about 70°C in an electrical oven for 60 min and then preserved in the vapors, smoke, and dirt-free environment.

2.6.3. Pretreatment of filter papers

The filter paper sheets were cut into small pieces as required for filtration. Later, the small pieces were soaked in disodium EDTA solution (0.1 M) for five min. After soaking, the small pieces of filter papers were rinsed with deionized water 3–4 times so that the filter papers were free from all the chemicals. Finally, the filter papers were dried at room temperature in a smoke and dirt-free environment and stored in a clean jar.

3. Results and discussion

Adsorption with carbon materials has become an effective approach due to its simplicity in design and operation, ability to adsorb a wide range of contaminants such as heavy metals and dyes and fast adsorption kinetics. An effective adsorbent should have characteristics such as adsorb a wide range of contaminants, easily available at a commercial scale, economical, and environment friendly. The adsorbent used in the present study was the biosorbent, that is, the bark of *Acacia nilotica* L., a tree commonly found in almost all the countries and it was tested for its ability to adsorb Ni and dye from artificially contaminated water. The results obtained during various batch experiments for the sorption of Ni and dye (aminoazobenzene) on biosorbent (*Acacia nilotica* L.) from the aqueous media are presented and discussed in the following sections:

3.1. Effect of pH

The pH of the solution determines the surface charge of the adsorbent and the state of adsorbate in the solution. The results obtained during the optimization of pH for maximum adsorption of dye and Ni are presented in Fig. 2. From the results, it was clear that the maximum adsorption of dye and Ni onto the biosorbent was at different pH values. The optimum pH for maximum adsorption of dye and Ni onto the biosorbent was in the acidic range, that is, 4 and 6, respectively. Rapid adsorption of dye on biosorbent was observed between pH 2 and 4 and the maximum adsorption (87.6%) was observed at pH 4. Adsorption was rapidly decreased as the pH increased from 4 to 7. In the case of Ni, a rapid increase in adsorption was observed as the pH was increased from 4 to 6 and the maximum adsorption (97.8%) was observed at pH 6. As the pH was increased from 6 to 7, the adsorption was decreased.

The solubility of heavy metals declines at pH greater than 7 due to the precipitation of heavy metals by hydroxides; hence, the aqueous medium with basic pH for Ni adsorption was not tested. Also, the biosorbent surface with abundantly available negatively charged groups is essential for the maximum adsorption of heavy metals [40]. At low pH, the hydrogen ions contest with the heavy metal ions, and consequently, active sites become protonated, which restricts the adsorption of heavy metal ions on biosorbent surfaces [36]. On the other hand, as the pH increases from 1 to 7, more and more negatively charged groups on the surface of the biosorbent are developed, thereby enhancing the adsorption of heavy metal ions on the surface of the biosorbent. Subsequent batch experiments were conducted at the respective optimum pH for Ni and dye, that is, 6 and 4, respectively.

3.2. Effect of the adsorbent dosage

The dose of sorbent was varied from 0.2 to 1.2 g to investigate its effect on the sorption of Ni and dye on biosorbent. Each sorption batch experiment was conducted at the respective pH for Ni (pH = 6) and dye (pH = 4). The results showed that the adsorption of Ni and dye was increased with the increasing concentration of biosorbent (Fig. 3). However, the increase in adsorption was sharp in the case of dye compared to Ni when the adsorbent dose was increased from 0.6 to 0.8 g. The maximum Ni (99%) and dye (79%) adsorption was observed when the adsorbent dosage was 1 and 0.8 g.

Earlier, it has been found that adsorption percentage is increased with increasing the dose of adsorbent as adsorption sites are increased with an increasing quantity of adsorbent [38,40]. At a lower concentration of biosorbent, the effective removal can be associated with the reduced particle size, which offers additional surface area on biosorbent [39]. The abrupt increase in dye adsorption may be due to the breakage of larger biomass particles of the adsorbent into smaller ones increases the affinity of exposed minute cracks towards metal and dye, thereby resulting in enhanced adsorption as observed in the present

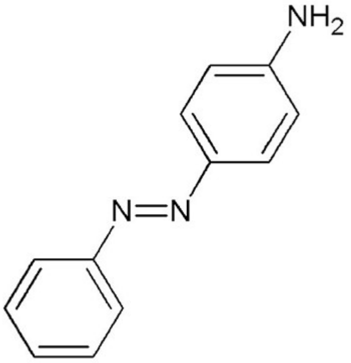

Fig. 1. The structure of amino azo benzene.

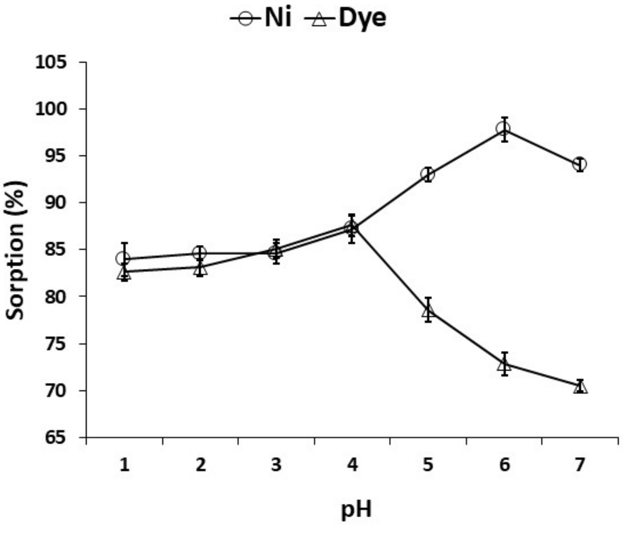

Fig. 2. Effect of pH on biosorption potential of *Acacia nilotica* bark for Ni and dye.

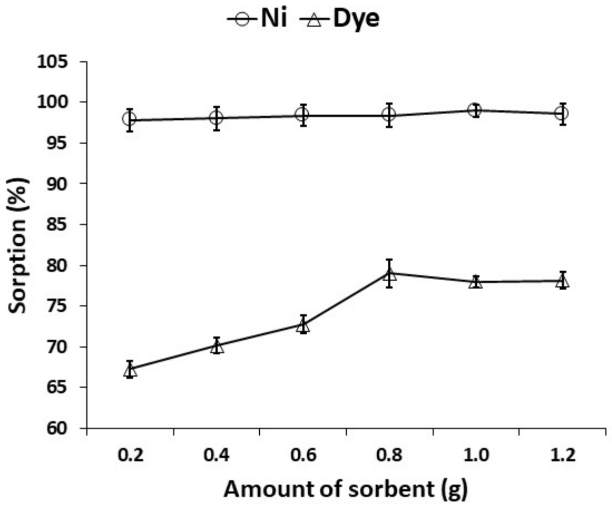

Fig. 3. Effect of amount of sorbent on biosorption potential of *Acacia nilotica* bark for Ni and dye.

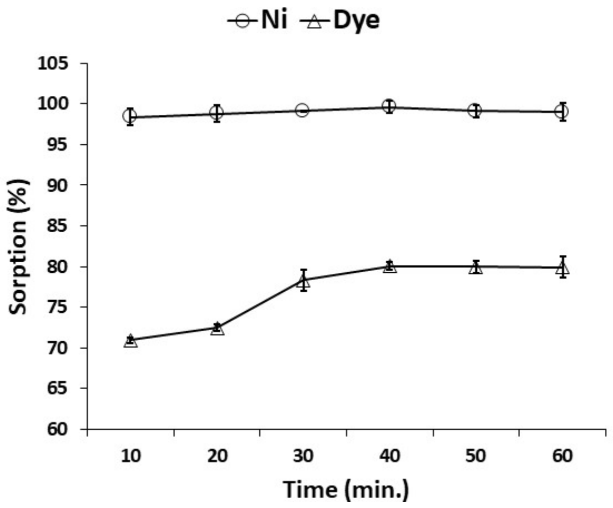

Fig. 4. Effect of contact time on biosorption potential of *Acacia nilotica* bark for Ni and dye.

study. In subsequent batch experiments, the adsorbent was applied at 0.8 and 1.0 g for dye and Ni at pH 4 and 6, respectively.

3.3. Effect of contact time

After finding out the optimum pH and adsorbent dosage for optimum adsorption of Ni and dye, another batch experiment was conducted to find out the optimum time for the maximum adsorption of Ni and dye. The contact time varied from 10 to 60 min. From the results presented in Fig. 4, it was found that adsorption increased with increasing the reaction time. An abrupt increase in adsorption was observed after 20 min in the case of dye. The maximum adsorption of Ni (99.6%) and dye (80.1%) on the biosorbent were observed after 40 min of the experiment. The increase in adsorption of Ni and dye with increasing reaction/contact time and later on decrease in adsorption might be due to the higher availability of negative sites at the beginning and later these negative surfaces were occupied which resulted in less increase in adsorption of Ni [55].

3.4. Effect of metal and dye concentration

To find out the maximum concentration of Ni and dye that can adsorb on 0.8 and 1.0 g adsorbent with pH 6 and 4, respectively during 40 min. of reaction/contact time, another batch experiment was conducted. The concentration of Ni and dye was varied from 2 to 12 ppm. From Fig. 5 it is clear that the adsorption was increased with the increasing concentration of Ni and dye, and later on, decreased at higher concentrations. In addition, the adsorbent had a wide range of adsorption for the metal, that is, Ni instead of the dye. The maximum adsorption of Ni and dye was observed when both were at 4 ppm during respective experiments. The initial increase and later decrease in the adsorption of both Ni and dye might be due to the overload of the adsorption sites in the adsorbent. Therefore, a restrictive number of adsorption sites is accessible for sorption at a greater concentration of metal and dye.

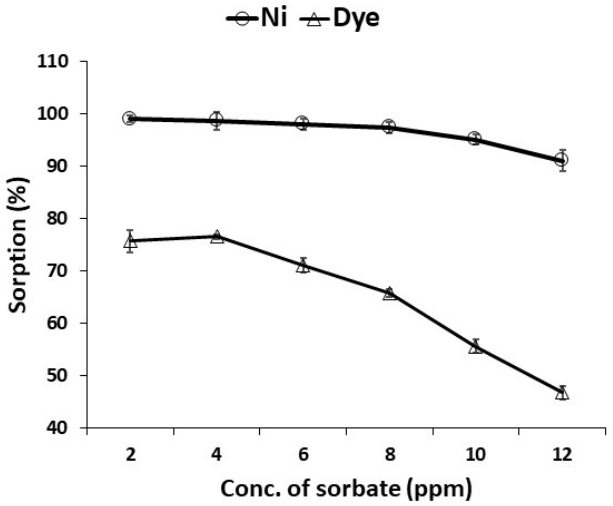

Fig. 5. Effect of metal and dye concentration on biosorption potential of *Acacia nilotica* bark for Ni and dye.

3.5. Effect of different ratios of metal and dye

After optimization of pH of the solution, the time of contact, the quantity of sorbent, and the number of sorbates for maximum adsorption of Ni and dye, the primary goal of the present research work was to study any competitive effect of Ni and dye on each other during sorption on the adsorbent. In this regard, Ni and dye were mixed in different ratios, that is, 1:1, 1:3, and 3:1 v/v. In results, it was found that there was no effect of mixing Ni and dye in different ratios on the adsorption of Ni (Fig. 6). However, the adsorption of dye was significantly changed under different mixing ratios. The maximum adsorption

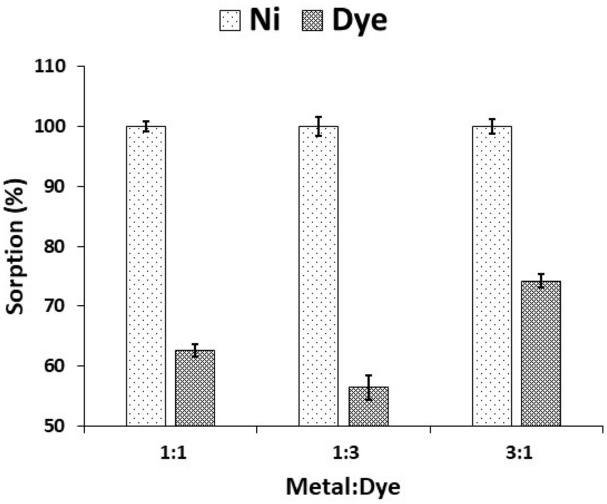

Fig. 6. Effect of metal and dye ratio on biosorption potential of *Acacia nilotica* bark for Ni and dye.

Table 1
List of calculated parameters from the Langmuir and Freundlich adsorption isotherm models for the adsorption of Ni and dye (amino azo benzene) onto *Acacia nilotica*

	Ni^{+2}	Dye
Langmuir isotherm		
q_{max} (mg g^{-1})	0.600	0.348
R_L (min^{-1})	0.061	0.677
R^2	0.999	0.980
Freundlich isotherm		
$1/n$	0.426	0.494
n	2.346	2.026
K_f	0.821	0.422
R^2	0.941	0.870

(74.2%) of dye was observed when Ni and dye were mixed in 3:1 while that of the minimum (56.4%) was observed when Ni and dye were mixed in 1:3. No effect of mixing Ni and dye in different on the adsorption of Ni might be due to its availability in the ionic form (Ni^{2+}) in solution. It may also be due to the smaller size of the Ni ions compared to dye which resulted in higher adsorption on the biosorbent at all ratios. In the case of dye availability in the solution form, it was found that the maximum detachment was observed when the metal and dye were mixed at a 3:1 ratio. The minimum detachment in solution form was observed when metal and dye were mixed at a 1:3 ratio, which reveals that dye adsorption was dependent on the quantity of dye available in the solution form.

3.6. Adsorption isotherm

The results obtained from the applied adsorption isotherms are presented in Table 1. From the presented data, it is clear that the values of R_L calculated for Ni and dye adsorption were less than 1 while that of the values of n was greater than 1 which suggests that the Ni and dye adsorption was favorable. In the present study, both mono- and multi-layer adsorption simultaneously occurred in the case of Ni as clear from the R^2 values (R^2 for Langmuir = 0.999) and (R^2 for Freundlich = 0.941) isotherms (Figs. 7 and 8). However, the monolayer was predominant compared to multilayer adsorption, thereby suggesting that adsorption was on a uniform site of the adsorbent. Similar results were recorded by Sánchez-Nava et al. [41] and Inyinbor et al. [56]. Similarly, 0.22 mmol g^{-1} adsorption was recorded with the application of *Acacia nilotica* leaves in real wastewater contaminated with Cr [46]. Salem and Awwad [8] used modified loquat bark (MLB) for biosorption of Ni in electroplating wastewater with 12.48 mg Ni L^{-1}. The application of MLB resulted in the maximum biosorption, that is, 27.548 mg Ni(II) g^{-1} that is quite high as compared to that observed in the present study. The reason might be the simultaneous adsorption of Ni and dye on the adsorption sites of the biosorbent used. In case of dye, uniform monolayer adsorption was predominant (R^2 for Langmuir = 0.980) as compared to the multi-layered adsorption (Figs. 7 and 8). However, multi-layer

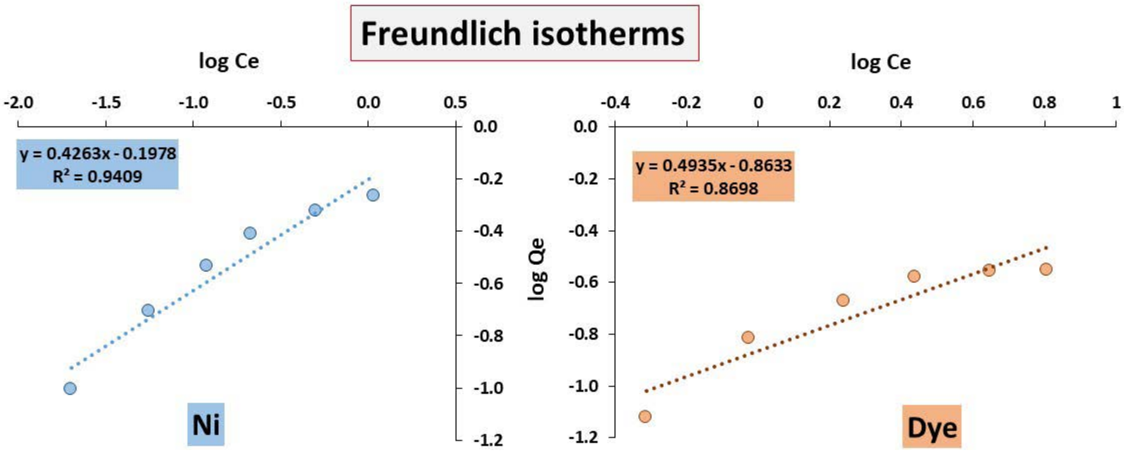

Fig. 7. Freundlich isotherms for metal and dye biosorption.

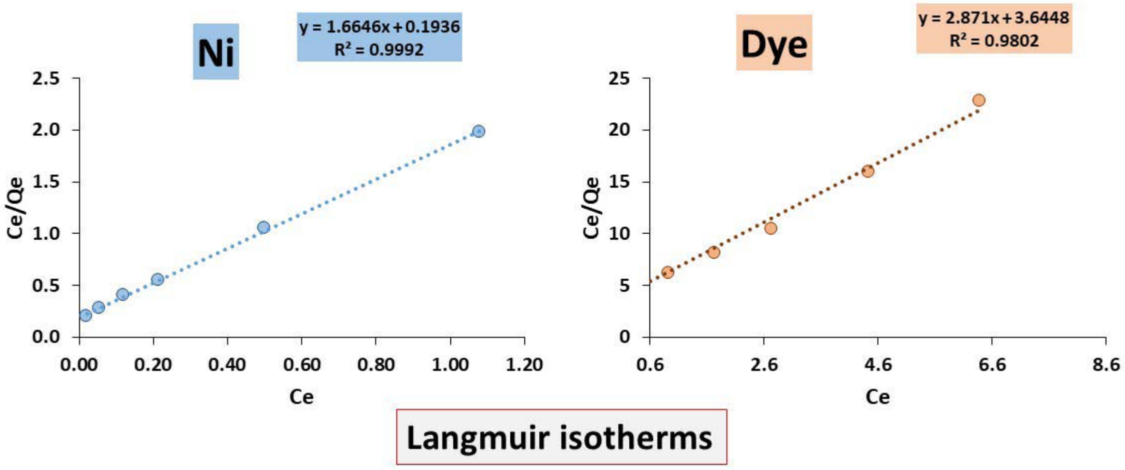

Fig. 8. Langmuir isotherms for metal and dye biosorption.

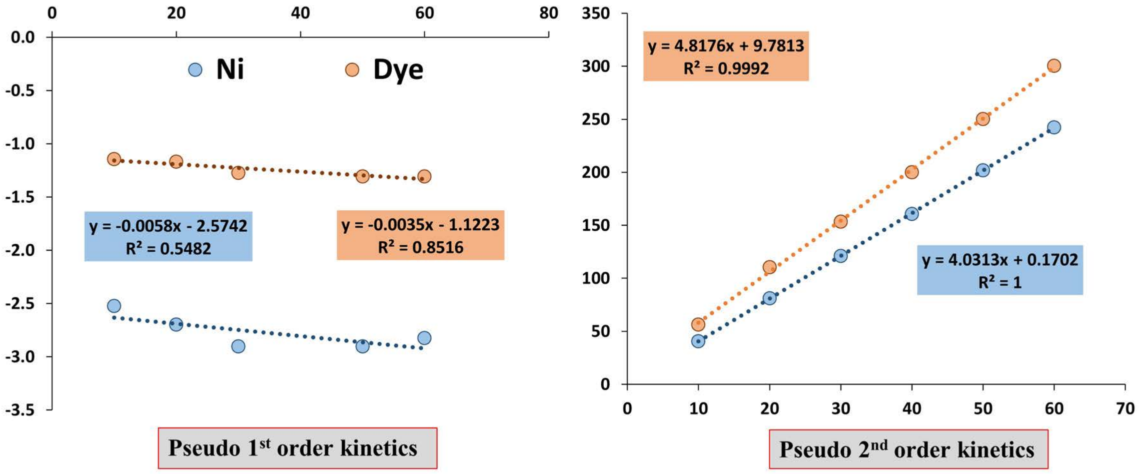

Fig. 9. Kinetics for metal and dye biosorption.

adsorption also played an important role in dye adsorption onto the biosorbent (R^2 for Freundlich = 0.870). The maximum amount of monolayer adsorption of Ni and dye onto the biosorbent was 0.60 and 0.348 mg g^{-1}, respectively. These results are following Hameed et al. [37]. Under real contaminated wastewater conditions, various factors such as the presence of other heavy metals and other ions may occupy the adsorption sites, and ultimately a decrease in the adsorption potential of the biosorbent used may be observed. Therefore, it is suggested to test the biosorption potential of *Acacia nilotica* bark using real wastewater effluent collected from a textile or tanning industry so that the observed results may be verified and recommended for the treatment of industrial wastewater.

3.7. Sorption dynamics

The results obtained after the application of pseudo-first and second-order kinetics are presented in Fig. 9 and Table 2. From the data, it is clear that the second-order rate constant in case of both Ni and dye was more than that of the first-order kinetics. Based on the results obtained from the present batch experiment, the results could be further applied to full scale or continuous process, probably using a fixed column. Therefore, chemisorption was predominant in the case of both Ni and dye adsorption on biosorbent.

Table 2
List of parameters obtained from pseudo-first-order and pseudo-second-order kinetic model parameters for the adsorption of Ni and dye (amino azo benzene) onto *Acacia nilotica*

	Ni^{+2}	Dye
Pseudo-first-order kinetics		
k_1 (min^{-1})	0.0247	0.0459
R^2	0.8425	0.9932
Pseudo-second-order kinetics		
k_2 (min^{-1})	4.1136	4.7024
R^2	0.9999	0.9987

It is also clear from the higher R^2 values for Ni (R^2 = 0.9999) and dye (R^2 = 0.9987). The initial adsorption rate of both Ni and dye was increased with increasing concentrations of biosorbent, which is in line with the findings of Malik [35].

4. Conclusions

From the results, optimum adsorption of Ni was observed at pH = 6 with contact time = 40 min. when 1.0 g adsorbent (*Acacia nilotica*) was used. In the case of dye, the maximum adsorption was observed at pH = 4.0 when 0.8 g adsorbent was used for 40 min. There was no significant effect of metal:dye ratio on adsorption of Ni but adsorption of dye was more when metal:dye ratio was 3:1, respectively. Both mono- and multi-layer adsorption simultaneously occurred in the case of Ni adsorption as clear from Langmuir and Freundlich isotherms. In case of dye, uniform monolayer adsorption was predominant as compared to the multi-layered adsorption. Also, the adsorption of both Ni and dye was through chemisorption. In conclusion, the bark of *Acacia nilotica* has significant potential for Ni and dye removal from co-contaminated wastewater.

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