Removal of nickel ions and methylene blue dyes from aqueous solutions using alkaline algae biomass

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Abstract—The sorption of nickel (II) and methylene blue dye (MB) from aqueous solution by alkaline treated algae biomass was investigated. 0.05 M NaOH resulted in increasing the removal efficiency of algae biomass from 77.48 to 97.43% and from 79.71 to 97.53 % for Ni (II) and MB, respectively. Pseudo first order, pseudo second order and intra-particle diffusion kinetic models were tested, good coefficients of determination (R²) were attained from pseudo second order kinetic model for both contaminants; therefore, chemical adsorption was the mechanism that governed the sorption process by alkaline treated algae. The data were best fitted to Langmuir isotherm model and a maximum sorption capacity achieved were 2.889 mg/g for Ni (II) and 6.406 mg/g for MB. The separation factor shows irreversible isotherm type due to R_1 < 1 for both contaminants. Alkali pretreatment of algae mixture could be an effective and low cost strategy for enhancing Ni (II) and MB sorption from aqueous solution.

Keywords— Biosorption, Algae biomass, Coefficient of determination, Methylene blue, Nickel (II).

1. Introduction

Water pollution is a major environmental problem faced by modern society that leads to ecological disequilibrium and health hazards [10]. Metals are known to be toxic and released into the environment in amounts that pose a danger to ecosystem, including mercury, cadmium, nickel, chromium, zinc, lead, selenium, silver and copper [9]. A significant threat to public health and the environment resulted from the exposure to these heavy metals, due to their toxicity, persistence in nature, and bioaccumulation in the food chain [16]. On the other hand, dyes is one of the significant classes of the pollutants, when enter the water it is no longer good and sometimes difficult to treat as they have a synthetic origin and a complex molecular structure which makes them more stable and difficult to be biodegraded [26]. Some of the conventional methods employed to reduce the pollutant content in the discharges include ion exchange, lime precipitation, electrolytic methods, membrane process, biodegradation, photocatalytic, photolytic, advanced oxidative degradation and adsorption onto activated carbon. All these methods are generally expensive [18, 8]. Biosorption can be defined as the ability of biological materials (algae, bacteria, fungi and yeast) to accumulate contaminants from wastewater through metabolically mediated or physico-chemical pathways of uptake. Recently biosorption technique by using algal biomass is proven to be economical and beneficial to the environment. Compared to conventional treatment, biosorption have many advantages including high efficiency, low cost, no additional nutrient requirement, biological and/or chemical sludge can be minimized, regeneration of biomass, and metal recovery is possible [1]. many problems have been observed by using untreated biomass as adsorbents like low adsorption capacity, high chemical oxygen demand (COD) and biological oxygen demand (BOD) as well as total organic carbon (TOC) as a result of releasing soluble organic compounds restricted in the biomass; so, the adsorbents need to be treated or modified before being used as adsorbent [24]. Several physical/chemical treatments had been used to enhance the uptake of organic and inorganic contaminant by algal biomass that provide additional binding sites by changing the cell wall properties of algae biomass. Algal biomass physical treatments like freezing, drying, heating, boiling, and crushing usually lead to improve the level of adsorbate biosorption. In general, algae chemically modified exhibit higher biosorption capacities than unmodified forms. The most common algal pretreatments are formaldehyde, NaoH, HCl, glutaraldehyde, and CaCl2 [33]. The
treatment with alkaline is noticed as one of the widely active chemical treatment techniques for surface modification in order to improve its adsorption properties [26]. A few researchers have attempted to modify biomass chemically prior to its application for biosorption [21]. Bulgariu and Bulgariu, 2016 showed that alkaline treated algae waste biomass can be used effectively for large scale treatment of wastewater [7]. Kumar and Bandyopadhyay, 2006 treated rice husk adsorbent with HCl, NaOH, NaHCO3, and C3H5ClO to increase sorption capacity toward cadmium ions, the NaHCO3 gives the highest removal efficiency among other used solutions [18]. Pirbazari et al., 2014 showed that alkali treated Foumanat tea waste has high efficiency of in removing methylene blue dye from aqueous solution.[26]

The aim of this study was to quantify the efficacy of alkaline (NaOH) pretreatment on the ability of mixed algae to sorb Ni (II) and MB dye and to investigate the time and concentration of treated material on the removal efficiency.

2. Materials and methods

2.1 Material

The algae biomass was collected from the artificial irrigation canal near college of engineering in Baghdad University. 0.5 kg of collected algae were analyses for their genus and species and percentage weight by using microscope in biological department, Ibn Al-Haitham college, university of Baghdad. The results showed that there were three divisions were dominated in this sample, the Chrysophyta algae was the highest percentage, and these results were listed in Table. 1. The collected materials were washed many times with water to remove the adhering dirt, impurities, and other unwanted materials finally two times with distilled water to ensure clearness. The washed algae were left under sun for three days to dry and then dried in oven at 60°C for 3 h to ensure that the sample dried completely. The dried algae ground and sieved into 177µm. Pretreatment of the algae biomass was carried out as follows: A thirty grams of dry biomass (177µm) was treated with 500 ml of (0.05, 0.1 and 0.5 M) NaOH at 25°C for 1hr and then agitated on a shaker (ISO 9001, model: LSI-3016A, NO.B110416002, Korea) for 60 min at 50 rpm. After centrifugation, the biomass washed several times with distilled water until pH 7.0 was reached, and then dried at 60 °C for 4 hours in the oven (model: F62700, Barnstead Thermolyne, Germany). Fig. 1 shows algae biomass pictures treated with different concentration of NaOH.

| Table 1: Division, genus, species and weighting percentage of collected algae. |
|------------------|------------------|------------------|
| Division         | Genus            | Species          | %    |
|------------------|------------------|------------------|
| Chrysophyta      | Navicular        | Many species     | 80%  |
|                  | Cymbella         |                  |      |
|                  | Nitzschia        |                  |      |
|                  | Pinularia        |                  |      |
| Cyanophyta       | Anabaena         | 2 species        | 5%   |
|                  | Oscillatoria     | 3 species        |      |
|                  | phormidium       |                  |      |
| Chlorophyta      | Spirogera        | 1 species        | 14%  |
|                  | Chlamydomonas    |                  |      |
|                  | Cosmarim         |                  |      |
|                  | Chlorella        |                  |      |
|                  | Scenedesmus      |                  |      |
| Microscopic      |                  |                  | 1%   |
| animals          |                  |                  |      |

2.2 Organic and inorganic contaminants preparation

Synthetic aqueous stock solution 1000 mg/l of methylene blue was prepared by dissolving 1.0 g of MB in 1L of distilled water, and the concentration of MB used (50 mg/l) were obtained by dilution of the stock solution [29]. While for nickel aqueous stock solution 1000 mg/l was prepared by dissolving 4.955 g of Nickel nitrate hexahydrate in 1L of distilled water, and the required concentration (35 mg/l) were gained by dilution of the stock solution. The pH of solution was adjusted by adding 0.1 M HCL or 0.1 M NaOH to get the desired value. Dissolved metal and dye concentrations in solution were determined by a flame atomic absorption spectrophotometer AAS (Model: 210 VGP, USA), and UV visible spectrophotometer (Cary-100 conc., Varian, USA), respectively. The characteristic
wavelength used in analysis is 232.0 nm for nickel ion and 662 nm for methylene blue. The biosorption capacity and removal efficiency were calculated as follows [3]:

\[ q_e = \frac{(C_i-C_e)W}{m} \]  
\[ \% \text{ Removal efficiency} = \frac{(C_i-C_e) * 100}{C_i} \]

Where \( C_i \) and \( C_e \) are the initial and equilibrium contaminants concentration in the solution (mg/l), \( V \) the volume of solution in (L), and \( m \) the quantity of biomass applied in (g).

2.3 Method

The experiment on the effects of pH was conducted by mix-up 0.5 g adsorbent dosage (non-treated algae) with 50 ppm of MB and 35 mg/l solution at different pH (1-8), then the flasks were shaken at 200 rpm for 2 hr. To examine the differences in removal efficiency between alkaline treated and free algae with time, the experiment was conducted by mixing 35 mg/l with 8 g/l biomass dosage for Ni (II) and 50 mg/l with 6g/l for MB at 200 rpm for 120 min. Different concentrations of treated solution were used to study the effect of increasing alkaline concentration on the removal efficiency.

3. Kinetic and isotherm models

The solution pH was adjusted to 5 for MB and 6 for Ni (II) ions. These values corresponded to the maximum sorption of test contaminants by untreated biomass in batch system. The cells were harvested at different time period and the MB and Ni (II) ion content in the filtrate was determined. The data for the time course of pollutants sorption were fitted to pseudo first order, pseudo second order and intra-particle diffusion models. In order to determine the adsorption isotherm of algae biomass for MB and Ni (II) adsorption, the sorption studies were carried out at 25°C [5]. Experimental isotherm is suitable for selection of the most appropriate sorbent, for describing adsorption capacity to enable calculation of the feasibility of this process for a given application, and for determination of requirements sorbent dosage. Furthermore, the isotherm plays a vital role in the design of sorption systems and predictive modeling procedures for analysis [18]. The Langmuir adsorption has been widely used adsorption isotherm for the adsorption of a solute from a liquid solution as cited in [13]. Langmuir equation relates the coverage of molecules on a solid surface at a fixed temperature. The Langmuir model assumes a monolayer adsorption of solutes onto a surface comprised of identical sites with homogeneous biosorption energy [2, 6].

\[ \frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \]  
\[ R_L = \frac{1}{1 + \frac{b C_0}{1}} \]

Where:

\( q_e \) is the sorbed contaminants on the biomass (mg.g\(^{-1}\)), \( q_m \) is the maximum sorption capacity for monolayer coverage (mg.g\(^{-1}\)), \( b \) is the constant related to the affinity of the binding site (L.mg\(^{-1}\)), \( C_e \) is contaminants concentration in the solution at equilibrium (mg.L\(^{-1}\)), and \( R_L \) is the separation factor.

Freundlich equation is derived to model the multilayer sorption and for the sorption on heterogeneous surfaces with a non-uniform distribution of biosorption heat over the surface [6]. The Freundlich isotherm theory states that the ratio of the amount of solute adsorbed onto a particular mass of sorbent to the concentration of the solute in the solution is not constant at different concentrations [32]. The heterogeneity of the surface and multilayer biosorption to the binding sites positioned on the surface of the biomass are considered in the Freundlich isotherm which is an empirical expression and expressed as follows [2]:

\[ \log q_e = \log K + \frac{1}{n} \log C_e \]

Where \( K \) = adsorption capacity constant (mg.g\(^{-1}\)), \( 1/n \) = adsorption intensity constant. Both \( K \) and \( n \) are constants, being indicative of the extent of adsorption and the degree of non-linearity between solution and concentration, respectively. \( 1/n < 1 \) indicates normal biosorption, while a \( 1/n > 1 \) indicates cooperative adsorption [30].

4. Results

4.1 pH effect

The pH is a significant issue affecting the removal of contaminant from aqueous solutions [22], affect the function groups on the adsorbent surface, and determine the solubility of dyes in the aqueous medium [11, 27]. The effect of solution pH on the sorption of Ni (II) ions and MB dye was examined by adjusting the pH in the range (1-8) as shown in Fig. 2. The initial pH values were investigated lower than 9.0 since insoluble nickel hydroxide starts precipitation from the solution at higher pH values [20], making true sorption studies impossible. The minimum removal efficiency was detected at low pH [pH= 1.0], the reason behind this behavior may be due to at high H\(^+\) concentration the adsorbent surface becomes more positively charged such that the attraction between adsorbents and both pollutants is reduced [25]. The binding sites, at pH close to 5 are negatively charged due to presence of carboxylic, hydroxyl and amino groups. The removal percentage of methylene blue (MB) reaches maximum at pH 5, no significant altered beyond pH 5 was observed because at higher pH, the surface of adsorbent particles may be negatively charged which enhances the positively charged dye cations through electrostatics forces of attraction [13]. The observed values also agree well with the result obtained by [28]. In opposite for nickel ions biosorption increasing pH (1.0-6.0), the surface area becomes more negatively charged thus facilitating greater
metal removal by algal biomass, due to the absence of hydrogen ions and this leading to increase the ability of establishing links between metal cations and algae biomass [33], and then at pH (7.0-8.0), the percentage removal decreases due to the formation of anionic hydroxide complexes [17, 12].

Figure 2: Effect of pH solution on removal efficiency of organic and inorganic pollutants at initial conditions (m=0.5 g/100 ml, Ci= 35 mg/l for Ni (II) & 50 mg/l for methylene blue, speed= 200 rpm, and time=120 min)

4.2 Effect of contact time and kinetics modelling

Fig. 3 represent the kinetic removal of MB dye and Ni (II) by virgin and alkali algae biomass. At each time interval, alkaline-pretreated algae sorbed more contaminants than the unmodified one. The sorption of MB and Ni (II) by modified algae attained the equilibrium within 15 min, while for virgin algae the equilibrium achieved at 60 min. Sodium hydroxide treatment of lignocellulosic materials can cause swelling which leads to an increase in internal surface area, a decrease in the degree of polymerization, a decrease in crystallinity, separation of structural linkage between lignin and carbohydrates, increase in the amount of galactouronic acid groups after hydrolysis of O- methyl ester groups, removes natural fats and waxes from the cellulose fiber surfaces thus revealing chemically reactive functional groups like –OH, and disruption of the lignin structure [23; 24]. NaOH increase the electrostatic interactions of metal ion cations, and provides optimum conditions for ion- exchange [33]. Kinetic data of MB dye and Ni (II) sorption fitted very well (high coefficient of determination) by pseudo-second order model (Fig. 4) rather than pseudo first order and intra-particle diffusion models (Fig. not shown) and tabulated in Table. 2.

Figure 3: Time course of Ni (II) (A) sorption by alkaline treated and free algae at (35 mg/l as initial concentration, 8 g/l biomass concentration, pH=6.0) & MB (B) sorption at (50 mg/l as initial concentration, 6 g/l biomass concentration, pH=5.0)
Figure 4: Pseudo-second order kinetic model for Ni (II) and MB dye

Table 2: Kinetics characterization of MB dye and Ni (II) biosorption onto alkaline treated algae biomass.

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Mathematical equation</th>
<th>Notation</th>
<th>Parameters values</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo- first order</td>
<td>( \ln (q_e - q_t) = \ln q_e - k_1 t )</td>
<td>( q_e ) is the amount of both contaminants retained on weight unit of biosorbent at equilibrium; ( q_t ) is the contaminant uptake capacity (mg/g) at any time ( t ); ( k_1 ) is the pseudo-first order constant rate (1/min).</td>
<td>( R^2 = 0.654 )</td>
<td>[19]</td>
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<td></td>
<td></td>
<td></td>
<td>( K_1 = 0.0182 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( q_e = 0.139 )</td>
<td></td>
</tr>
<tr>
<td>Pseudo-second order</td>
<td>( t ) ( q_t ) = ( \frac{1}{k_2 q_e^2} + \frac{t}{q_e} )</td>
<td>( k_2 ) is the observed rate constant of pseudo-second-order kinetic model (g/mg. min).</td>
<td>( R^2 = 0.9992 )</td>
<td>[15]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( K_2 = -1.303 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( q_e = 4.199 )</td>
<td></td>
</tr>
<tr>
<td>Intra-particle</td>
<td>( q_t = k_p t^{1/2} + C )</td>
<td>( k_p ) is the rate constant of intra-particle diffusion (mg/g min(^{1/2})), ( C ) is the value of intercept which gives an idea about the boundary layer thickness.</td>
<td>( R^2 = 0.4396 )</td>
<td>[31]</td>
</tr>
<tr>
<td>diffusion model</td>
<td></td>
<td></td>
<td>( K_p = -0.0197 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( C = 4.3922 )</td>
<td></td>
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</tbody>
</table>

4.3 Effect of NaOH concentration and equilibrium modelling

It has been found that the treatment with NaOH creates additional basic sites for binding cations species [14]. The adsorption efficiency increase by using base modify material due to the negatively charged hydroxyl anions [4]. NaOH also improves chemical and mechanical properties of cellulose material like structural durability, natural ion-exchange capacity and reactivity [24]. A decrease in removal efficiency was observed as shown in Fig. 5, when the concentration of NaOH increased from 0.05 to 0.5 MA. The reason behind this observation was due to the destruction of biomass [24]. Isotherm data of MB dye and Ni (II) sorption fitted very well with Langmuir isotherm model (high coefficient of determination) rather than Freundlich model as shown in Fig. 6 and Table 3.

**Figure 5**: Effect of NaOH modify concentration on the removal efficiency for Ni (II) (A) at (35 mg/l as initial concentration, 8 g/ l biomass concentration, pH=6.0, 177 µm particle size, and 120 min) & MB (B) sorption at (50 mg/l as initial concentration, 6 g/l biomass concentration, pH=5.0, 177 µm particle size, and 120 min)

**Figure 6**: Langmuir isotherm model for Ni (II) (A) and MB (B) biosorption.

**Table 2**: Kinetics characterization of MB dye and Ni (II) biosorption onto alkaline treated algae biomass.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$q_m$</td>
<td>$b$</td>
</tr>
<tr>
<td>Ni (II)</td>
<td>2.889</td>
<td>-2.68</td>
</tr>
<tr>
<td>MB</td>
<td>6.406</td>
<td>-2.61</td>
</tr>
</tbody>
</table>

**Conclusions**

The present study may help in developing an efficient and economically feasible technology for removing organic and inorganic from aqueous solution. it shows that the alkaline algae biomass mixture could remove as much as 97.43 and 97.53% of Ni (II) and MB, respectively from solution containing 35 mg/l for Ni (II) and 50 mg/l for MB. The treated algae biomass attained equilibrium in 15 min, which is short time compared to non-treated (virgin) algae that achieved equilibrium in 60 min. Increasing the concentration of treated solution from 0.05 to 0.5 M did not improve the removal efficiency, infect the removal percentage decrease as NaOH concentration increased. The Langmuir represent the data very well with $R^2$ equal to 0.9981 and 0.9994 for Ni (II) and MB, respectively so it is a monolayer process. The parameter $1/n$ was less than 1 that indicates normal biosorption process. The data fitted with pseudo second order that assumed the rate limiting step may be chemical sorption.

**References**


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