Technologies for elimination of chemical hazards

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Removal of methylene blue and nickel(II) ions in simulated and real wastewater using activated carbon beads derived from *Litsea glutinosa* seeds

***My Uyen Dao*[1,2,3], *Alexander S. Sirotkin*[1], *Hong Hanh Cong*[4], *Van Thuan Le*[2,3]✉, *and Hien Y Hoang*✉**

[1]Department of Industrial Biotechnology, Kazan National Research Technological University,
Kazan, Russia
[2]Center for Advanced Chemistry, Institute of Research & Development, Duy Tan University,
Danang, Vietnam, levanthuan3@duytan.edu.vn
[3]Faculty of Natural Sciences, Duy Tan University, Danang, Vietnam
[4]Institute of Materials Science, Vietnam Academy of Science and Technology, Hanoi, Vietnam
[5]Ho Chi Minh City University of Natural Resources and Environment, Ho Chi Minh city, Vietnam,
e-mail: hhy@hcmunre.edu.vn

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Abstract – The paper presents results of studying removal of typical industrial pollutants – methylene blue (MB) dye and Ni(II) ions from simulated contaminated aqueous solutions and real waste water samples using activated carbon beads (ACBs) obtained from natural seeds of *Litsea glutinosa* and modified by chemical activation with $NaHCO_3$. The adsorption performance of as-synthesized adsorbent toward methylene blue and Ni(II) ions in simulated solutions in different conditions was evaluated to find out the optimum adsorption conditions. The obtained results established that the MB adsorption reached the highest efficiency at the temperature of 35°C, contact time of 10 h, the adsorbent dosage of 6 g/L, and pH = 7; while the Ni(II) ions removal was optimized at the adsorbent dosage of 8 g/L, pH = 5, the temperature of 35°C, and contact time of 10 h. Furthermore, ACBs were also applied for treating real textile and plating wastewater samples with a removal efficiency of more than 80%. The results of the study revealed that ACBs could be used as a promising adsorbent for the removal of dyes and heavy metal ions from industrial wastewater.

Keywords: adsorption, activated carbon beads, methylene blue, Ni(II) ions, *Litsea glutinosa.*

Технологии ликвидации источников химической опасности

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Удаление метиленового синего и ионов никеля(II) из модельных растворов и реальных сточных вод с помощью гранул активированного угля, полученных из семян *Litsea glutinosa*

***М. У. Дао*[1,2,3], *А. С. Сироткин*[1], *Х. Х. Конг*[4], *В. Т. Ле*[2,3]✉, *Х. И. Хоанг*[5]✉**

[1]Кафедра промышленной биотехнологии, Казанский национальный исследовательский технологический университет, г. Казань, Россия
[2]Центр современной химии, Научно-исследовательский институт, Дуй Тан Университет, г. Дананг, Вьетнам, levanthuan3@duytan.edu.vn
[3]Факультет естественных наук, Дуй Тан Университет, г. Дананг, Вьетнам
[4]Институт науки о материалах, Вьетнамская академия наук и технологий, г. Ханой, Вьетнам
[5]Хошимин университет природных ресурсов и окружающей среды, г. Хошимин, Вьетнам,
e-mail: hhy@hcmunre.edu.vn

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Аннотация – Представлены результаты применения сорбента в виде гранулированного активированного угля, полученного из природных семян *Litsea glutinosa* путем химической активации с помощью $NaHCO_3$, для очистки модельных и реальных растворов сточных вод от двух типов промышленных загрязнителей – красителя метиленового синего (МС) и ионов никеля(II). Для определения оптимальных условий адсорбции оценены адсорбционные характеристики адсорбента в исходном состоянии по отношению к МС и ионам Ni(II) в модельных водных растворах при различных условиях. Полученные результаты показали, что адсорбция МС достигает максимальной эффективности при температуре 35°C при времени контакта 10 ч, дозировке адсорбента 6 г/л и pH = 7; в то время как удаление ионов Ni(II) было оптимальным при дозировке адсорбента 8 г/л, pH = 5, температуре 35°C и времени контакта 10 ч. Кроме того, сорбент был также применен для очистки реальных образцов сточных вод, получаемых в производстве текстильных материалов и гальванических покрытий, с достижением эффективности удаления более 80%. Результаты исследования показывают, что данный сорбционный материал может быть использован в качестве перспективного адсорбента для удаления красителей и ионов тяжелых металлов из промышленных сточных вод.

Ключевые слова: адсорбция, активированные углеродные гранулы, метиленовый синий, ионы Ni(II), *Litsea glutinosa.*

INTRODUCTION

Water pollution has increasingly become a serious problem in recent years [1]. The presence of various organic dyes and heavy metal ions in effluents discharged from plating, textile, galvanic, and battery industries can have a significant detrimental impact on the environment [2]. These pollutants are not only highly toxic but also non-biodegradable substances that accumulate in the human body and can cause many serious diseases such as dermatitis, headache, nausea, anemia, diarrhea, damage of lungs, and kidney, dysfunction of cardiovascular, and central nervous systems, etc. [3]. Consequently, wastewater contaminated with dyes and heavy metal ions must be treated before its release into the environment. Among wastewater treatment approaches, adsorption is the most commonly used technology for removing both dyes and heavy metals ions, due to its high efficiency, easiness of operation, low cost, and availability of various raw resources of natural origin [4, 5]. In general, there are many known adsorbing materials, such as silica gel, alumina, activated carbon, zeolites, etc. [6–10].

Activated carbon (AC) is characterized by large specific surface area, well-developed porosity, a possibility of modification with various surface functional groups, accordingly, it has been widely used to treat wastewater [11]. Nowadays, the

ACs obtained from biomass, lignocellulosic precursors are continuously being developed to become alternative material for the expensive commercial AC. Although AC in powder form has been shown its effectiveness in wastewater treatment, it is difficult to separate and recycle powdered AC after adsorption, which results in adsorbent loss and secondary pollution. Meanwhile, use of activated carbon beads (ACBs) with useful properties, such as easiness of separation from aqueous solution, high mechanical strength, and excellent durability, makes it possible to overcome the shortcomings of the known AC powder.

Litsea glutinosa (LG) is an evergreen plant from the laurel family found in southern China, the Indian subcontinent, Australia, and Southeast Asian countries [12]. The parts of the tree such as trunks, roots, and leaves are typically used for producing paper pulp, rope manufacture, and traditional medicine. Moreover, LG seeds are inedible and have been utilized to make candles and soaps [13]. According to our previous studies [14, 15], LG seeds, which contained 17.4% cellulose, 27.6% lignin, and 25.5% hemicellulose, could be used as precursors for preparing ACBs to remove dyes.

In the present study, the LG seeds were used to prepare AC in bead form via carbonization. Batch experiments were performed to evaluate the effects of such parameters as dosage, contact time, solution pH, ionic strength, and temperature, on the efficiency of adsorption of methylene blue (MB) and nickel(II) ions onto ACBs. Optimum experimental conditions for adsorption were evaluated with a view to apply the adsorbent for industrial wastewater treatment.

EXPERIMENTAL

Synthesis of ACBs

The ACBs synthesis was performed in several steps. Firstly, LG seeds (5–8 mm in diameter) were collected as a raw material in the forests of Central Vietnam. Next, the collected seeds were washed from dust and dirt, and dried at 50°C for 3 days. Then, the seeds were impregnated with 5% $NaHCO_3$ solution at 50°C for 24 h, followed by carbonization in a furnace at 450°C for 1 h. Finally, the obtained ACBs were sequentially washed with 1% HCl and distilled water up to neutral pH value.

The point of zero charge (pH_{zpc}) of ACBs was determined by the salt addition method [16]. In this method, 0.02 g of ACBs were added to 10 mL of 0.01 M solution of NaCl with its initial pH adjusted to 2–9 by pouring 0.1 M NaOH and 0.1 M HCl. After 48 h, the value of final pH was measured carefully and the point from plot of ΔpH (the difference between the final pH and the initial pH) against initial pH values was taken to be pH_{zpc}.

Batch adsorption modeling

The uptake efficiency of MB and Ni(II) ions from aqueous solution by ACBs was determined using a batch technique. The model MB and Ni(II) solutions were prepared by dissolving calculated amounts of pure $C_{16}H_{18}ClN_3S$ (CAS number 122965-43-9, 98.5%, Sigma Aldrich, USA) and $NiSO_4 \cdot 7H_2O$ (98%, Sigma Aldrich, USA) in distilled water. The freshly synthesized adsorbent was added into 50-mL Erlenmeyer flask with 25 mL of adsorbate solution of pre-defined initial concentrations. The mixture was shaken with a shaking speed of 100 rpm for 10 h. Thereby, the residual concentration of MB was directly measured by UV-Vis spectrophotometry (Cary 60, Agilent Technologies, USA) at a maximum absorption wavelength of 665 nm; while the Ni(II) ion concentration was determined by measuring its content in a solution pre-concentrated with dimethylglyoxime at a wavelength of 470 nm. The removal efficiency percentage of MB and Ni(II) adsorbed on ACBs was calculated by following equation:

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

where C_0 and C_e (mg/L) are initial and equilibrium concentrations of adsorbate solution, respectively.

Application: To evaluate the application ability of the prepared adsorbent in practice, ABCs were tested for their adsorption activity in real industrial wastewater containing MB and Ni(II) ions. The adsorption experiments were carried out under the optimized conditions. The wastewater samples were taken from local textile and plating factor in Hoa Khanh Industry Zone (Danang city, Vietnam).

RESULTS AND DISCUSSION

Effect of contact time

Preliminary experiments were performed in order to investigate the effect of contact time on the removal performance of MB and Ni(II) onto ACBs, and obtained results are illustrated in Fig. 1.

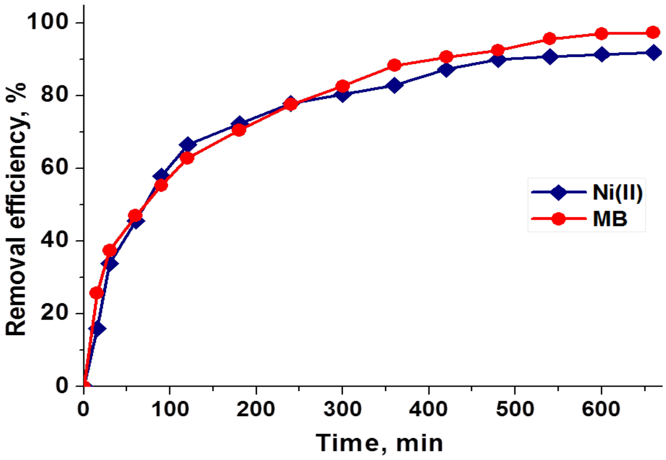

Fig. 1. Effect of contact time on adsorption of MB and Ni(II) ions by ACBs.
Experimental conditions: C_o = 20 mg/L, T = 25°C, t = 10 h, pH = 6 for MB, pH = 4 for Ni(II).

It is noteworthy that the adsorption of Ni(II) ions and MB took place quickly, and the uptake rate reached approximately 65% within the first 120 min of reaction time and then gradually increased with time. This phenomenon can be attributed to the abundant availability of the adsorption sites, which were progressively saturated during adsorption time [17]. After 10 h, an equilibrium uptake of MB and Ni(II) was attained, and the uptake efficiency didn’t show any change as the time increased. An operating time of 10 h, therefore, was selected for the entire equilibrium test.

Effect of adsorbent dosage

The influence of different adsorbent dosages on MB and Ni(II) removal by ACBs is described in Fig. 2. It is obvious that in the adsorbent weight range from 4 g/L to 12 g/L, the uptake efficiency of ACBs increased from 85.7 to 92.2% for MB, and from 74.1 to 93.4% for Ni(II) ions. The results can be explained by the presence of activated sites on the ACBs surface with improved availability [18]. However, the MB removal efficiency increased only 1.1 times (from 85.7 to 93.5%) while the adsorbent dosage was tripled (from 4 to 12 g/L). Similarly, the removal percentage of Ni(II) rapidly increased when the ABCs dosage raised to 8 g/L, and then negligibly reduced with further increasing the adsorbent dosage (Fig. 2). This may be attributed to fully consumption of the adsorption sites, resulting in a reduction in the total adsorption surface area available to Ni(II) ions. Thus, the use of 6 g/L and 8 g/L adsorbent dosage was considered as the optimal for removing MB and Ni(II) ions, respectively.

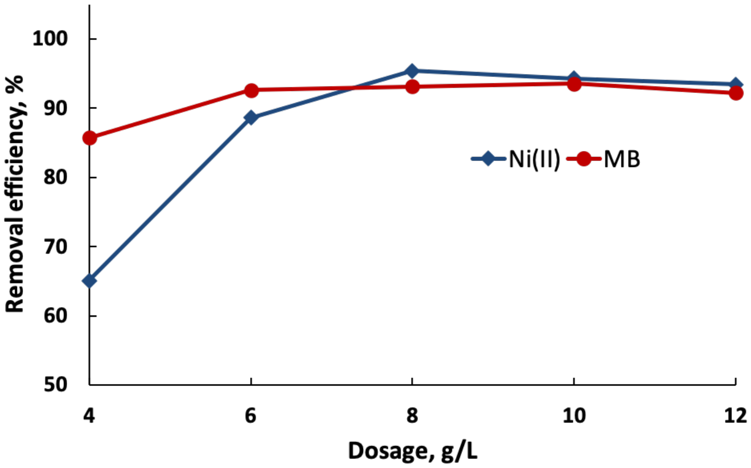

Fig. 2. Effect of adsorbent dosage on adsorption of MB and Ni(II) ions by ACBs.
Experimental conditions: C_o= 20 mg/L; T = 25°C; t = 10 h; pH = 6 for MB, pH = 4 for Ni(II).

Effect of pH

Besides the above effects, the uptake efficiency of MB and Ni(II) by ACBs was also affected by pH solution. Fig. 3 depicts the adsorption performance of ACBs in removing of MB and Ni(II) ions at various levels of pH. The study of Ni(II) adsorption was not conducted at pH higher than 8 in order to avoid the precipitation of $Ni(OH)_2$ [19].

The result from Fig. 3 demonstrated that the adsorption efficiency of MB and Ni(II) onto ACBs maximally reached 97% at pH = 8 and 92% at pH = 11, respectively. The percentage of MB and Ni(II) removal considerably rose with increasing the pH up to 5 (for Ni(II)), and up to 7 (for MB), and then insignificantly varied with higher value of pH. Therefore, the optimum pH values for MB and Ni(II) adsorption were selected to be 5 and 7, respectively, for further experimental studies. These values are close to real wastewater.

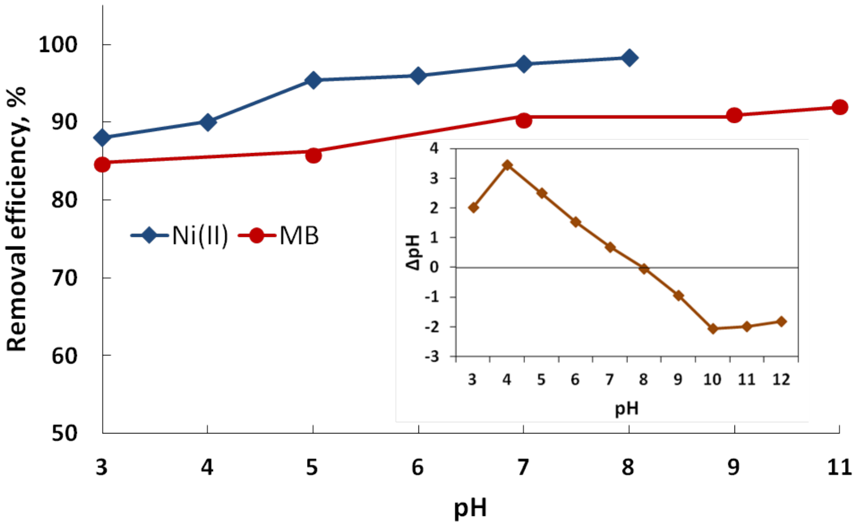

Fig. 3. Effect of pH solution on adsorption of MB and Ni(II) ions by ACBs.
Experimental conditions: C_o= 20 mg/L; T = 25°C; t = 10 h; dosage = 6 g/L for MB; 8 g/L for Ni(II).

The pH solution effect on adsorption efficiency of ACBs can be also explained by the point of zero charged, which was defined as 8 (see insert in Fig. 3). When the pH of solution is below 8, the studied adsorbent is positively charged. Vice-versa, when pH is above this value, the material is negatively charged, and tends to adsorb cation better [20]. Thus, increasing the solution pH results to enhance electrostatic interaction between charges on ACBs surface and MB molecules or Ni(II) ion. In addition, under acidic condition, the existence of H^+ ions can compete with dye cations adsorbing on the active sites of ACBs, leading to low adsorption uptake. A similar trend is observed in Yu-Kuang's research focused on MB removal by AC [21].

Effect ionic strength

The evaluation of ionic strength effect on MB and Ni(II) adsorption was carried out by adding an amount of NaCl with concentration varied in the range 0.05 – 1M at pH = 7 for MB and pH = 5 for Ni(II). The obtained result is presented in Fig. 4, indicating that less than 70% of MB removal efficiency was reached with increasing of NaCl concentration up to 1 M, confirming interaction of the co-existed cations in ACBs' adsorption. The reason which leads to the low uptake of MB can be due to competition between Na^+ ion and MB molecules on the ACBs surface.

As illustrated in Fig. 4, a similar trend was observed in the case of ion Ni(II) uptake. With the high concentration of NaCl (> 0.5M), the Ni(II) removal was dropped sharply and reached appropriately 40%. Therefore, it can be concluded that the ionic strength has a stronger negative effect on the Ni(II) adsorption compared to MB adsorption. This may be assigned to adsorption mechanism of these adsorbed substances. Since MB is a heterocyclic aromatic chemical compound, therefore, during the adsorption process, in addition to the impact of hydrogen bonding and electrostatic interactions as well as ion exchange, the MB adsorption can be also enhanced owing to π-π bonding interaction between aromatic ring structure of MB and ACBs [22]. This mechanism is completely absent during Ni(II) absorption.

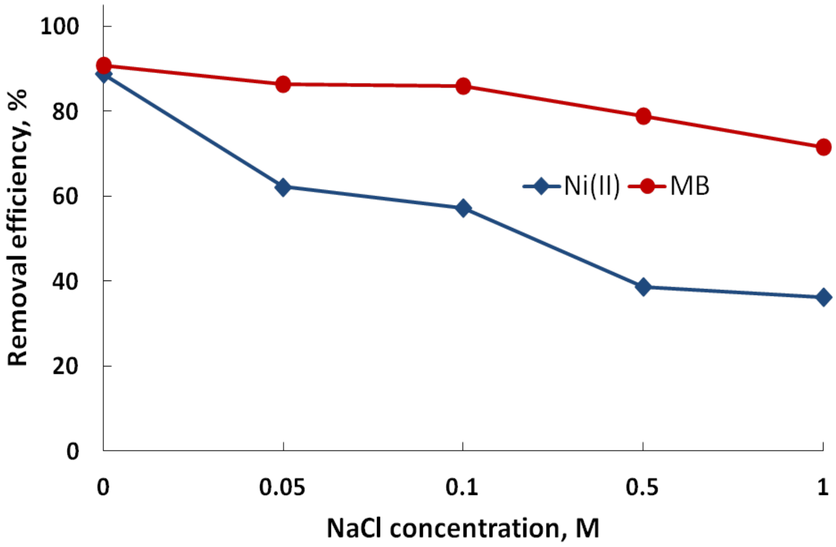

Fig. 4. Effect of NaCl concentration on adsorption of MB and Ni(II) ions by ACBs. Experimental conditions: C_o= 20 mg/L; T = 25°C; t = 10 h; pH = 7 for MB, pH = 5 for Ni(II).

Effect of temperature

Temperature is considered to be one of the important variables directly affecting the adsorption process. Thus, the effect of temperature on MB and Ni(II) ion removal uptake was studied at concentrations of 20 mg/L of adsorbed substances in the range 25 – 45°C (see in Fig. 5). It is obvious that the adsorption efficiency of both MB and Ni(II) ion increased with increasing temperature. This means that the adsorption process of MB and Ni(II) onto ACBs is an endothermic natural process. The high uptake of MB and Ni(II) ions at higher temperatures can be involved with increasing the movability of ion, thereby accelerating the migration of MB molecules or Ni(II) ions towards the internal pores of the ACBs carbon matrix. These obtained results are consistent with many reports [21, 23].

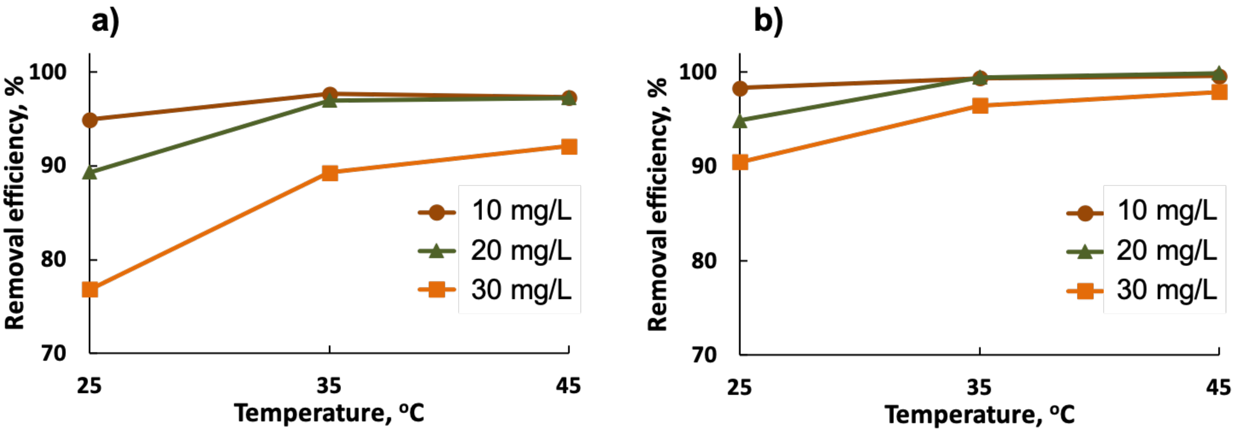

Fig. 5. Effect of temperature on adsorption of MB (a) and Ni(II) ions (b) by ACBs. Experimental conditions: C_o= 20 mg/L; t = 10 h; pH = 7 for MB, pH = 5 for Ni(II).

Application for wastewater treatment

Herein, industrial wastewater samples taken from textile and plating factories with the initial concentration of MB and ion Ni(II) of 85.14 and 48.03 mg/L, respectively, were used to evaluate the adsorptive capacity of ACBs in practice. As described in Fig. 6, a mixture which contained ACBs and 25 mL of the real wastewater was stirred for 10 h at the established optimum conditions (for textile wastewater sample: temperature 35°C, pH = 7, adsorbent dosage 6 g/L; for plating wastewater sample: temperature 35°C, pH = 5, adsorbent dosage 8 g/L).

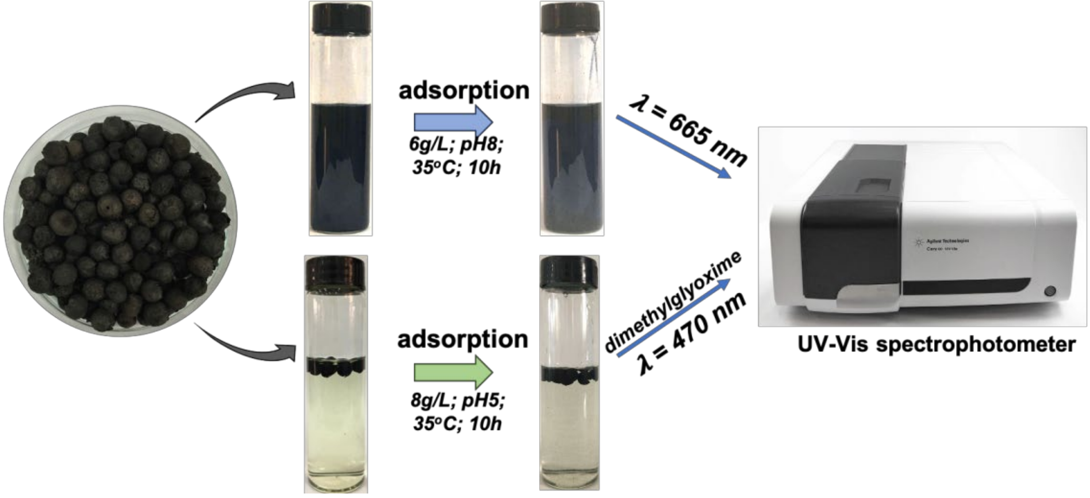

Fig. 6. Application ACBs for treatment of real industrial wastewater samples.

According to the obtained result demonstrated in Fig. 7, after 10 h of contact time, the MB and Ni(II) ion concentrations were determined as 9.43 and 10.45 mg/L, respectively, which equated to 87.72 and 80.36% removal efficiency. This can confirm the appliability of as-synthesized adsorbent for wastewater treatment.

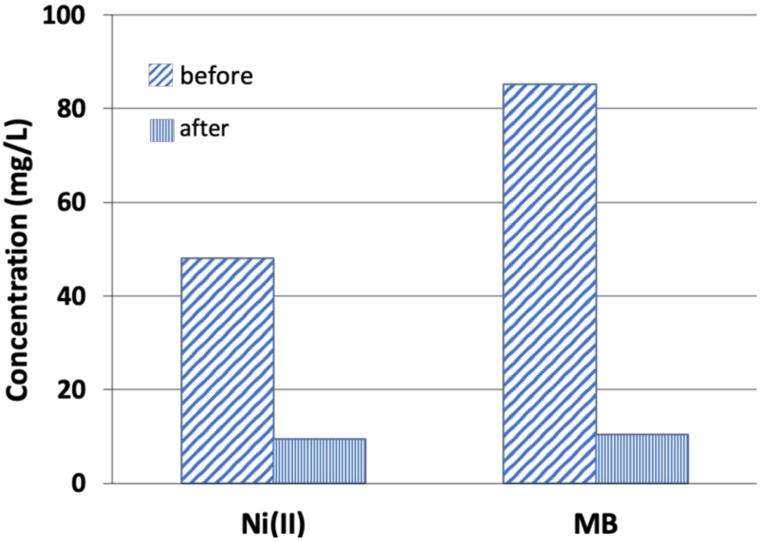

Fig. 7. Removal efficiency of MB and Ni(II) ion from textile and plating wastewater samples.

CONCLUSIONS

Activated carbon beads were successfully synthesized by carbonization and applied for removing methylene blue and Ni(II) ions from aqueous solutions. This study investigated the dependence of MB and Ni(II) removal efficiencies on adsorption factors, and pointed out the optimal conditions for the adsorption. The optimum condition for the removal of these hazardous substances was found to be contact time of 10 h, 35°C, pH = 5, 8 g/L of dosage, for Ni(II) ions, and pH = 7, and 6 g/L of dosage for MB. The high removal efficiency of MB and Ni(II) ions from textile and plating wastewaters has been shown which indicates that the novel adsorbent can be a promising material for treating contaminated wastewater.

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