Contents lists available at ScienceDirect

Process Safety and Environmental Protection

journal homepage: www.elsevier.com/locate/psep

# Preparation of Nickel hydroxide nanoplates modified activated carbon for Malachite Green removal from solutions: Kinetic, thermodynamic, isotherm and antibacterial studies

*Farzin Nekouei* [a,**], *Hanieh Kargarzadeh* [b], *Shahram Nekouei* [a], *Inderjeet Tyagi* [c], *Shilpi Agarwal* [d], *Vinod Kumar Gupta* [c,d,*]

[a] *Young Researchers and Elite Club, Science and Research Branch, Islamic Azad University, Tehran, Iran*
[b] *Faculty of Science and Technology, School of Chemical Sciences and Food Technology, Polymer Research Center (PORCE), Universiti Kebangsan Malaysia (UKM), 43600 Bangi, Selangor, Malaysia*
[c] *Chemistry Department, Indian Institute of Technology Roorkee, Roorkee 247667, India*
[d] *Department of Applied Chemistry, University of Johannesburg, Johannesburg, South Africa*

ARTICLE INFO

*Article history:*
Received 15 October 2015
Received in revised form 18 January 2016
Accepted 20 February 2016
Available online 11 March 2016

*Keywords:*
Nickel hydroxide nanoplates,
Activated carbon
Adsorption
Malachite Green
Liquid phase
Antibacterial study

ABSTRACT

An extremely small size novel adsorbent, nickel hydroxide nanoplate loaded on activated carbon ($Ni(OH)_2$-NP-AC) was synthesized using a simple, low cost and highly efficient method. The developed adsorbent was used for the removal of hazardous MG dye from the aqueous solution. To evaluate the importance of $Ni(OH)_2$ nanoplates on the adsorption and removal process, the contact time of virgin AC and $Ni(OH)_2$-NP-AC were compared (under the same conditions) that the results showed $Ni(OH)_2$ nanoplate had a crucial role in the removal or adsorption process. The surface unique textural and morphological properties such as high surface area (>960 $m^2\ g^{-1}$) and low pore size (<3.5 nm) made it possible for efficient and rapid removal of MG. Subsequently, the impact of various influential variables such as pH, adsorbent dosage, initial dye concentration, contact time and temperature were examined and optimized. The adsorption kinetic and equilibrium data of MG were found well fitted and found to be in good agreement with pseudo-second-order and Langmuir models, respectively. Finally, antibacterial activity of the synthesized nanoplates was evaluated by testing against some Gram-negative and Gram-positive bacteria. The results of this antibacterial testing indicated that the synthesized nanoplates showed effective bactericidal activity.


## 1. Introduction

One of main environmental pollution or hazard is the industrial effluents containing highly color dyes with significant amount of organic solids (Crini, 2006). The presence of such toxic contaminants in aqueous body leads to generation of several detrimental and hazardous impacts on the aquatic life due to their mutagenic and carcinogenic effects. The dyes discharging in environment are produced by textile, paper and printing activities. So, increasing demand and shortage of clean water sources due to the rapid development of industrialization, population growth and long-term droughts have become an issue worldwide. With this growing demand, various practical strategies and solutions have been adopted

* *Corresponding author at:* Indian Institute of Technology Roorkee, Chemistry Department, Roorkee 247667, Uttarakhand, India. Tel.: +91 1332285801; fax: +91 133227356.
** *Corresponding author.* Tel.: +39 081674281/+39 3273378505.
E-mail addresses: F.nekouei@hotmail.com, Farzin.nekouei@unina.it (F. Nekouei), vinodfcy@gmail.com, vinodfcy@iitr.ac.in (V. Kumar Gupta).
http://dx.doi.org/10.1016/j.psep.2016.02.011

to yield more viable water resources (Chong et al., 2010). The discharge of highly colored waste is not only aesthetically displeasing, but it also impedes light penetration, thus upsetting biological processes within a stream. In addition, many dyes are toxic to some organisms and may cause direct destruction of aquatic communities (Mohammadi et al., 2011).

Various methods have been proposed for removal of dyes from wastewaters such as coagulation and flocculation (Panswed and Wongchaisuwan, 1986), oxidation or ozonation (Malik and Saha, 2003; Koch et al., 2002), membrane separation (Ciardelli et al., 2000), adsorption (Sadegh et al., 2015a,b; El-Bindary et al., 2014). Among these methods, adsorption is a reliable method due to its simplicity, high efficiency and low cost (Wei et al., 2014).

Malachite Green (MG) has numerous industrial applications namely dyeing of silk, leather, plastics, paper and others and their appearance leads to detrimental effect on flora and fauna ecosystem following inhalation and/or ingestion (Ghaedi et al., 2014; Culp and Beland, 1996) and produce toxicity to respiratory system and reduced fertility in humans (Srivastava et al., 2004). MG with complex chemical structure is resistant to light and oxidizing agents and the efficiency removal of MG by biological treatment and chemical precipitation is low (DoganUluozlu et al., 2008).

Nanotechnology is one of the fast developing technologies with demanding products in various fields, due to their tiny size ($10^{-9}$ m) and large surface area (White et al., 2006). The research on nanoparticles has attracted wide attention during the last decade thanks to their unusual and size dependent and has been used in different fields (Taylor et al., 2013; Boisseau and Loubaton, 2011). Recently, nanoparticles have been used for modification of activated carbon as promising and effective new sorbents for removal of dyes form solutions because of their large surface area (Nekouei et al., 2015; Gupta et al., 2015; Vitela-Rodriguez and Rangel-Mendez, 2013; Asfaram et al., 2015).

Nickel hydroxide compounds stimulated a large interest in industrial and technical applications, for example as the active materials in electrochemical cycling and as a photocatalyst to remove organic dyes (Zhang et al., 2013). Furthermore, the feasibility of $Ni(OH)_2$ and NiO nanomaterials for their application in water treatment is also reported and evaluated (Song and Gao, 2008).

In this work, the $Ni(OH)_2$ nanoplate loaded on activated carbon was used for the removal of malachite green dye from aqueous phase. Moreover, for the first time the role of $Ni(OH)_2$ nanoplates on the adsorption of MG was discussed by comparing the result of contact time for virgin AC and $Ni(OH)_2$-NP-AC. Different analytical parameters affecting the adsorption like pH, initial dye concentration, temperature, contact time, and adsorbent dose were evaluated. The adsorption kinetic and equilibrium data of MG on this adsorbent were tested and discussed by different models. Furthermore, different thermodynamic parameters were calculated. Finally, antibacterial activity of the synthesized nanoplates loaded on activated carbon was evaluated.

## 2. Experimental

### 2.1. *Materials and chemicals*

All chemicals used were analytical grade and solutions were prepared with distilled water. Malachite Green (Table S1 in the Supporting Information) with chemical formula of $C_{52}H_{54}N_4O_{12}$ (Sigma-Aldrich sdn Bhd, Malaysia) with $\lambda_{Max} = 617$ nm was used for the preparation of the solutions of MG in desired concentrations. The working solutions were prepared by diluting the stock solution with distilled water. Nickel chloride ($NiCl_2$), ammonium ($NH_3$), ammonium chloride ($NH_4Cl$) and 4-(1,1,3,3-tetramethylbutyl)phenyl-polyethylene glycol (Triton X-100 or TX-100) were purchased from Sigma-Aldrich Co.

#### 2.1.1. *Precipitation method for preparation of $Ni(OH)_2$ nanoplates*

Nanoplates were synthesized by precipitation method using $NiCl_2$ as initial chemical and ammonium as precipitation agent. 0.3 g of $NiCl_2$ was dissolved in 50 mL distilled water in a 100 mL flask. Then, after adding 1 mL of 0.02 M Triton X-100, 9 mL $NH_3$ 4 M and 1 mL $NH_4Cl$ 1 M were added slowly under magnetic stirring at 50 °C (pH ≤ 11). The green suspension remained under a constant and strong stirring for 45 min. Subsequently, the suspension was filtered and washed several times by a mixture of distilled water and ethanol to remove impurities. Finally, the obtained precipitation was dried in an ambient condition, vacuum oven: 0.1 MPa, for 7 h before being characterized. Scheme S1 (Supporting information) reveals a possible formation mechanism for PbO nanosheet networks.

#### 2.1.2. *Preparation of $Ni(OH)_2$-NPs-AC*

The precursor materials were mixed as explained in Section 2.1.1. 5 g of AC was added to the suspension of $Ni(OH)_2$ in an ultrasonic bath, until the uniform and green suspension was obtained. The mixture was maintained at room temperature over a night (ca. 10 h) after adjusting the pH at 11. After filtering the alkaline solution, $Ni(OH)_2$-NPs-AC was washed several times with distilled water and dried in ambient condition and used as such for further experiments.

#### 2.1.3. *Role of $Ni(OH)_2$ nanoplates*

The $Ni(OH)_2$ nanoplates loaded on AC can confer some crucial properties to the AC. The three of the most important of those are (1) It results in the enhancement of the surface area and increasing the number of active sites leading to improve the adsorption capacity and efficiency; (2) it decreases adsorption time and causes very rapid adsorption of MG, only by using a very low amount of adsorbent dose i.e. 0.035, maximum 99.8% of the adsorption in 20 min for 20 mg $L^{-1}$ of MG; (3) Improving the antibacterial activity of AC (see Section 3.10). Therefore, it is needed to coat $Ni(OH)_2$ nanoplates onto the AC to perform an efficient and maximum adsorption. To further confirm the remarkable role of $Ni(OH)_2$ nanoplates on the adsorption of MG, we performed a couple of studies under the same conditions of $Ni(OH)_2$-NPs-AC for the virgin AC (20 mg $L^{-1}$ of MG, 0.035 g of AC, 323.15 K) in the pH range of 4 to 9. The results showed that the maximum removal (94.1%) was achieved around 165 h at pH 8. With regard the fact that one of the most important parameters in designing a low cost wastewater treatment system is equilibrium time (Taghizadeh et al., 2013); Hence, the role of $Ni(OH)_2$ nanoplates is crucial to save time and cost as well as increasing the efficiency of adsorption (99.8% > 94.1%).