Carbohydrate Polymers 86 (2011) 1533–1541

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Adsorption of Crystal Violet from aqueous solution onto NaOH-modified rice husk

Sagnik Chakraborty, Shamik Chowdhury*, Papita Das Saha

Department of Biotechnology, National Institute of Technology-Durgapur, Mahatma Gandhi Avenue, Durgapur (WB) 713209, India

ARTICLE INFO

Article history:
Received 4 March 2011
Received in revised form 10 June 2011
Accepted 21 June 2011
Available online 29 June 2011

Keywords:
Adsorption
NaOH-modified rice husk
Crystal Violet
Equilibrium
Kinetics
Thermodynamics

ABSTRACT

In this study, equilibrium, kinetics and thermodynamics of Crystal Violet (CV) adsorption onto NaOH-modified rice husk (NMRH) was investigated. Experiments were carried out as function of contact time, initial solution pH (2–10), adsorbent dose (0.5–5 g) and temperature (293, 303 and 313 K). The adsorption was favoured at higher pHs and lower temperatures. Adsorption data were well described by the Freundlich model, although they could be modelled by the Langmuir model as well. The adsorption process followed the pseudo-second order kinetic model. The mass transfer model based on intraparticle diffusion was applied to the experimental data to examine the mechanisms of the rate controlling step. It was found that intraparticle diffusion was not the sole rate controlling step. The activation energy (E_a) of the system was calculated as 50.51 kJ mol^{-1}. Thermodynamic parameters suggest that the adsorption is a typical chemical process, spontaneous, and exothermic in nature.

1. Introduction

In recent years, environmental contamination by synthetic dyes is a serious problem due to their negative ecotoxicological effects and bioaccumulation in wildlife (Saha, Chowdhury, Gupta, & Kumar, 2010). The contamination of water due to synthetic dye molecules causes damage to the environment and has adverse effects on public health (Akar, Özcan, Akar, Özcan, & Kaynak, 2009; Kiran, Ilhan, Caner, Iscen, & Yildiz, 2009). Besides, dyes are one of the sources of esthetic pollution and eutrophication (Tsai, Chang, Ing, & Chang, 2004). Industries such as textile, leather, paper, paint, acrylic, cosmetics, plastics, pharmaceutical, etc., use dyes in order to colour their products and also consume substantial volumes of water. As a result, they generate a considerable amount of coloured wastewater. It is estimated that approximately 12% of synthetic dyes are lost during manufacturing and processing operations and 20% of these lost dyes enter the industrial wastewaters (Chowdhury, Mishra, Saha, & Kushwaha, 2011). Techniques such as coagulation, chemical precipitation, membrane filtration, solvent extraction, reverse osmosis, photocatalytic degradation, sonochemical degradation, micellar enhanced ultrafiltration, cation exchange membranes, electrochemical degradation, integrated chemical–biological degradation, integrated iron(III) photoassisted-biological treatment, solar photo-Fenton and biological processes, and adsorption have been tested and evaluated for the treatment of dye bearing effluents (Rafatullah, Sulaiman, Hashim, & Ahmad, 2010). Among them, adsorption has been recognized as a promising technique due to its ease of operation, simplicity of design, high efficiency and comparable low cost of application in decoloration process (Chowdhury & Saha, 2010; Saha et al., 2010). A number of natural materials or the wastes/by-products of industries, which cost less and can be used as such or after some minor treatment have been tested and used for removal of dyes from aqueous solutions. In this connection, special attention have been given to agricultural wastes like orange peel, banana pith, banana peel, plum kernels, apple pomace, wheat straw, sawdust, coir pith, sugarcane bagasse, tea leaves, bamboo dust, etc. (Gupta & Suhas, 2009).

Rice husk, the hard, protective, outer shell of the rice grain is abundantly available as a by-product of the rice milling industries and creates potential environmental problems (Foo & Hameed, 2009; Li et al., 2011). The annual generation of rice husk is estimated to be around 120 million tonnes, accounting about one-fifth of the annual gross rice production throughout the world (Foo & Hameed, 2009). Any possible usage of that will yield economic as well as environmental dividends.

In nature, rice husk is tough, insoluble in water, woody, has chemical stability, high mechanical strength and is characterized by its abrasive inherent resistance behavior and silica–cellulose structural arrangement. It mainly consists of cellulose (32%), hemicelluloses (21%), lignin (21%), silica (20%) and crude proteins

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* Corresponding author. Tel.: +91 9831387640; fax: +91 3432547375.
E-mail address: chowdhuryshamik@gmail.com (S. Chowdhury).

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doi:10.1016/j.carbpol.2011.06.058

Nomenclature

A	Arrhenius constant
C_a	equilibrium dye concentration on the adsorbent ($\mathrm{mg\,L^{-1}}$)
C_e	equilibrium dye concentration in solution ($\mathrm{mg\,L^{-1}}$)
C_i	initial dye concentration ($\mathrm{mg\,L^{-1}}$)
E	mean free energy ($\mathrm{kJ\,mol^{-1}}$)
E_a	activation energy ($\mathrm{kJ\,mol^{-1}}$)
ΔG°	Gibbs free energy change ($\mathrm{kJ\,mol^{-1}}$)
ΔH°	enthalpy of reaction ($\mathrm{kJ\,mol^{-1}}$)
I	intraparticle diffusion model constant
K_C	distribution coefficient for adsorption
K_F	Freundlich constant ($\mathrm{mg\,g^{-1}}$) ($\mathrm{L\,g^{-1}}$)$^{1/n}$
K_L	Langmuir constant ($\mathrm{L\,mg^{-1}}$)
k	rate constant
k_i	intraparticle diffusion rate constant ($\mathrm{mg\,g^{-1}\,min^{-0.5}}$)
k_1	pseudo-first-order rate constant ($\mathrm{min^{-1}}$)
k_2	pseudo-second-order rate constant ($\mathrm{g\,mg^{-1}\,min^{-1}}$)
m	mass of adsorbent (g)
n	Freundlich adsorption isotherm constant
q_e	equilibrium dye concentration on adsorbent ($\mathrm{mg\,g^{-1}}$)
q_m	maximum adsorption capacity ($\mathrm{mg\,g^{-1}}$)
q_t	amount of dye adsorbed at time t ($\mathrm{mg\,g^{-1}}$)
R	universal gas constant ($8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$)
R^2	correlation coefficient
ΔS°	entropy of reaction ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
T	temperature (K)
V	volume of the solution (L)
β	D–R isotherm constant ($\mathrm{mmol^2\,J^{-2}}$)
ε	Polanyi potential ($\mathrm{J\,mmol^{-1}}$) $= RT\ln(1+1/C_e)$

(3%) (Chuah, Jumasiah, Azni, Katayon, & Thomas Choong, 2005; Ndazi, Karlsson, Tesha, & Nyahumwa, 2007). Cellulose is a polydisperse linear homopolymer consisting of regio-enantioselective β-1,4 glycosidic linked D-glucose units (Fig. 1a) (Ngah, Teong, & Hanafiah, 2011). The polymer contains three reactive hydroxyl groups at C-2, C-3 and C-6 atoms representing a favourable characteristic of rice husk to be a potential adsorbent material. However, the polymer is relatively inert as the three hydroxyl groups of each cellulose unit responsible for most of the interactions with organic and inorganic substances are involved in extensive inter- and intramolecular hydrogen bonding (Fig. 1b) (Mulinari et al., 2010). In addition, both lignin and silica constitutes a major obstacle in using rice husk as an adsorbent material. This is mainly because lignin acts as a cementing matrix between cellulose fibrils and hemicellulose molecules while silica is present on the outer surface of rice husks in the form of silicon-cellulose membrane (Ndazi et al., 2007; Yoshida, Ohnishi, & Kitaishi, 1962) and acts as a natural protective layer against termites and microorganisms attack on the paddy (Ndazi et al., 2007). As such, both lignin and silica can reduce the binding between accessible functional groups on rice husks' surfaces and adsorbate ions/molecules. Furthermore, the inner surface of rice husk is smooth and contains wax and natural fats that provide good shelter for the grain but the presence of these impurities also affects the adsorption properties of rice husk chemically and physically (Chowdhury et al., 2011). Therefore, rice husk need to be modified or treated before being applied for decontamination of dyes.

Alkali treatment is viewed as one of the widely employed chemical treatment techniques for surface modification of rice husk for the purpose of improving its adsorption properties. Treatment of rice husk with aqueous sodium hydroxide (NaOH) solutions breaks the covalent association between lignocellulose components, hydrolysing hemicellulose and de-polymerising lignin (Vadiveloo, Nurfariza, & Fadel, 2009). This treatment has a substantial influence on morphological, molecular and supramolecular properties of cellulose, causing changes in crystallinity, pore structure, accessibility, stiffness, unit cell structure and orientation of fibrils in cellulosic fibres (Siroky, Blackburn, Bechtold, Taylor, & White, 2011). NaOH also improves mechanical and chemical properties of cellulose such as structural durability, reactivity and natural ion-exchange capacity. Treatment with NaOH removes natural fats and waxes from the cellulose fiber surfaces thus revealing chemically reactive functional groups like –OH (Ndazi et al., 2007). Our previous findings indicated that NaOH-modified rice husk (NMRH) could be employed as an effective adsorbent for the removal of malachite green (Chowdhury et al., 2011) and safranin (Chowdhury, Mishra, Kushwaha, & Saha, 2010) from aqueous solutions. Hence a further attempt of the feasibility of applying NMRH for the removal of Crystal Violet dye from aqueous solution was explored in the present study.

Crystal Violet (CV), also known as genetian violet is a triarylmethane dye, extensively used as a purple dye in textile industry for dyeing of cotton and silk. It also finds application in the manufacture of paints and printing inks (Mittal, Mittal, Malviya, Kaur, & Gupta, 2010; Senthilkumaar, Kalaamani, & Subburaam et al., 2006). In the medical community, it is used as a biological stain and is the active ingredient in Gram's stain. In animal and veterinary medicine, it is employed as a bacteriostatic agent (Mittal et al., 2010). The dye is also used as an external skin disinfectant in humans. It is used as an additive to poultry feed to inhibit propagation of mold, intestinal parasites and fungus (Kumar & Ahmad, 2011). CV is a protein dye and hence it is used as an enhancer for bloody fingerprints. CV is carcinogenic and has been classified as a recalcitrant molecule since it is poorly metabolized by microbes, is non-biodegradable, and can persist in a variety of environments. The dye is responsible for causing moderate eye irritation, causing painful sensitization to light. It can also cause permanent injury to the cornea and conjunctiva since the product contains a cationic dye. It is highly toxic to mammalian cells and if absorbed in harmful amounts through the skin, it can cause skin irritation and digestive tract irritation. In extreme cases it may also lead to respiratory and kidney failures (Ahmad, 2009; Mittal et al., 2010; Saeed, Sharif, & Iqbal, 2010).

Therefore, the objective of this investigation was to explore the potential of NMRH as a low cost adsorbent for the removal of CV from aqueous solutions. The effects of initial solution pH, adsorbent dose, contact time and temperature on CV adsorption rate have been investigated. Adsorption kinetics, isotherms and thermodynamics were also evaluated and reported.

2. Materials and methods

2.1. Preparation and characterization of NMRH adsorbent

Native rice husk was obtained from a nearby rice mill of Durgapur, West Bengal, India. It was washed with distilled water and dried at 353 ± 1 K for 3 h in an oven drier. The rice husk was then modified according to the method described in our previous work (Chowdhury et al., 2011).

Textural characterization of the adsorbent material was carried out by Quantachrome NOVA 2200C (Quantachrome Corporation, USA) surface area and pore size analyzer. A gas mixture of 22.9 mol% nitrogen and 77.1 mol% helium was used for this purpose. The

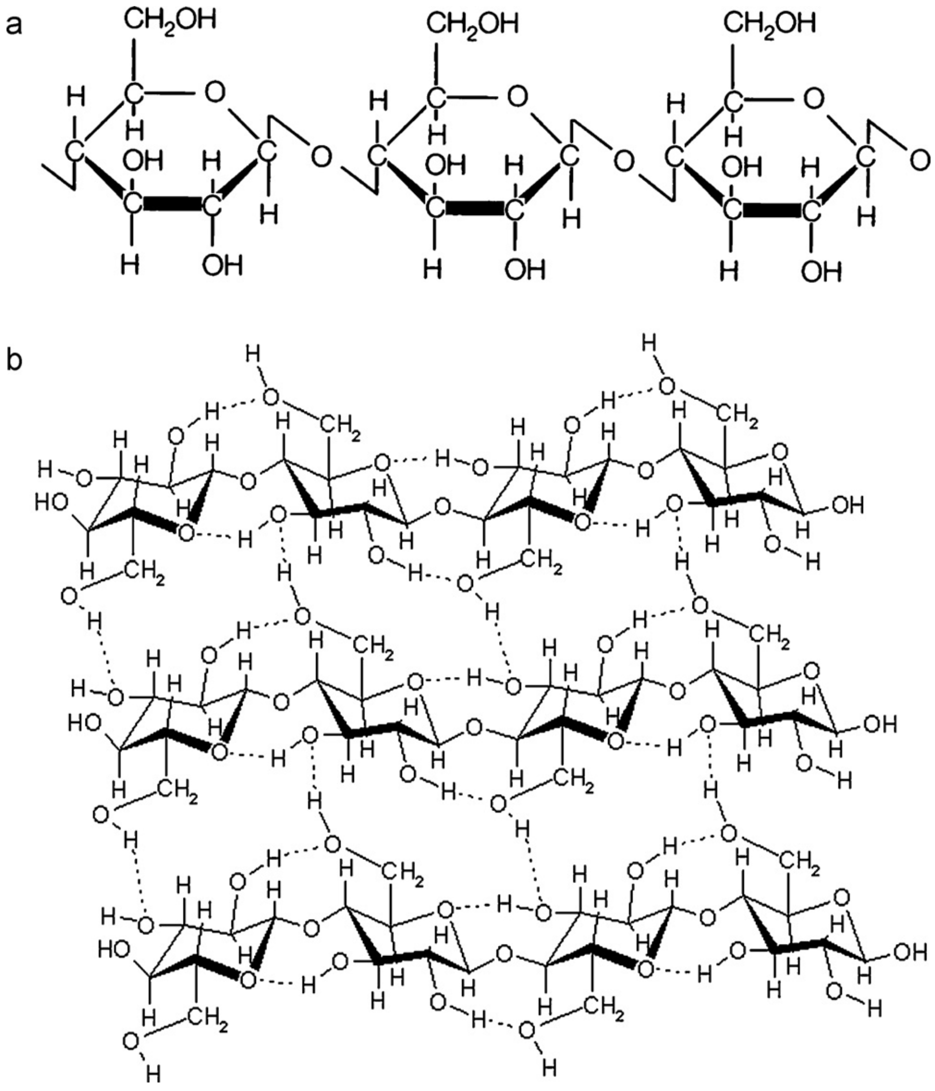

Fig. 1. (a) Structure of cellulose and (b) hydrogen bond system of cellulose.

Brunauer, Emmett, Teller (BET) specific surface area and pore diameter of the adsorbent were then determined. In order to examine the macromolecular structure of the adsorbent, X-ray diffraction (XRD) analysis of the adsorbent material was carried out using Miniflex X-ray diffractometer equipment with a CuKα radiation source (used at 30 kV and 15 mA, diffraction angle ranged from 60° to 10° with a scan speed of 5°/min). In addition, scanning electron microscopy (SEM) was used to study the surface morphology of the adsorbent. SEM studies were carried out using a scanning electron microscope (Model Hitachi S-3000N) at an electron acceleration voltage of 20 kV. Prior to scanning, the adsorbent was coated with a thin layer of gold using a sputter coater to make it conductive.

2.2. *Adsorbate*

Crystal Violet (CV) used in this study was of commercial quality (CI 42,555, MF: $C_{25}H_{30}N_3Cl$, MW: 408, λ_{max}: 580 nm) and was used without further purification. Stock solution (1000 mg L^{-1}) was prepared by dissolving accurately weighed quantity of the dye in double-distilled water. Experimental dye solution of different concentrations was prepared by diluting the stock solution with suitable volume of double-distilled water. The initial solution pH was adjusted using 0.1 M HCl and 0.1 M NaOH solutions.

2.3. *Adsorption studies*

Batch adsorption studies were carried out in 250 mL glass-stopperred, Erlenmeyer flasks with 100 mL of working volume, with a concentration of 50 mg L^{-1}. A weighed amount (1 g) of adsorbent was added to the solution. The flasks were agitated at a constant speed of 150 rpm for 3 h in an incubator shaker (Model Innova 42, New Brunswick Scientific, Canada) at 303 ± 1 K. The influence of initial solution pH (2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0), adsorbent dose (0.5, 1, 2, 3, 4, 5 g), contact time (5, 10, 15, 30, 45, 60, 90, 120, 150, 180 min) and temperature (293, 303, 313 K) were evaluated during the present study. Samples were collected from the flasks at predetermined time intervals for analyzing the residual dye concentration in the solution. The residual amount of dye in each flask was investigated using UV/VIS spectrophotometer (Model Hitachi – 2800). The amount of dye adsorbed per unit adsorbent (mg dye per g adsorbent) was calculated according to a mass balance on the dye concentration using Eq. (1):

$$q_e = \frac{(C_i - C_e)V}{m} \tag{1}$$

The percent removal (%) of dye was calculated using the following equation:

$$\text{removal}\,(\%) = \frac{C_i - C_e}{C_i} \times 100 \tag{2}$$

In order to ensure the reproducibility of the results, all the adsorption experiments were performed in triplicate, and the average values were used in data analysis. Relative standard deviations were found to be within ±3%. Microsoft Excel 2007 program was employed for data processing. Linear regression analysis was used to determine slopes and intercepts of the linear plots and for statistical analysis of the data.

3. Theory

3.1. Adsorption isotherm

The equilibrium sorption isotherm is fundamental in describing the interactive behavior between sorbates and sorbent and is important in the design and analysis of sorption systems. Adsorption equilibrium data are widely evaluated by different isotherm models. In the present investigation the isotherm study of CV was conducted at different temperatures by keeping the initial CV concentration fixed at 50 mg L^{-1}. The Freundlich (Chowdhury & Saha, 2010; Freundlich, 1906), Langmuir (Langmuir, 1916; Chowdhury & Saha, 2010) and Dubinin–Radushkevich (D–R) (Chowdhury and Saha, 2010; Dubinin & Radushkevich, 1947) isotherm models were used to describe the equilibrium biosorption data.

$$\text{Langmuir}: \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{3}$$

$$\text{Freundlich}: \log \quad q_e = \log \quad K_F + \left(\frac{1}{n}\right) \log \quad C_e \tag{4}$$

$$\text{Dubinin–Radushkevich (D–R)}: \ln \quad q_e = \ln \quad q_m - \beta\varepsilon^2 \tag{5}$$

3.2. Kinetic modeling

The data obtained from the contact time-dependent experiments were further used to evaluate the kinetics of the adsorption process. The pseudo-first-order (Lagergren, 1898; Saha et al., 2010) and pseudo-second-order (Ho & McKay, 1999; Saha et al., 2010) kinetic models were tested to obtain the rate constants and equilibrium adsorption capacity at different temperatures.

$$\text{Pseudo-first-order}: \quad \log(q_e - q_t) = \log \quad q_e - \frac{k_1}{2.303}t \tag{6}$$

$$\text{Pseudo-second-order}: \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{7}$$

Since the models mentioned above cannot identify a diffusion mechanism, the intraparticle diffusion model (Saha et al., 2010; Weber & Morris, 1963) was also tested to find the rate controlling step.

$$\text{Intraparticle diffusion}: \quad q_t = k_i t^{0.5} \tag{8}$$

3.3. Activation energy and thermodynamic parameters

The activation energy E_a for CV adsorption onto NMRH was calculated by the Arrhenius equation (Anirudhan & Radhakrishnan, 2008):

$$\ln \quad k = \ln \quad A - \frac{E_a}{RT} \tag{9}$$

E_a can be determined from the slope of a plot of $\ln k$ versus $1/T$.

Thermodynamic behavior of adsorption of CV on NMRH was evaluated by the thermodynamic parameters – Gibbs free energy change (ΔG°), enthalpy (ΔH°) and entropy (ΔS°). These parameters were calculated using the following equations (Anirudhan & Radhakrishnan, 2008):

$$\Delta G^\circ = -RT \ln \quad K_C \tag{10}$$

$$K_C = \frac{C_a}{C_e} \tag{11}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{12}$$

A plot of ΔG° versus temperature, T will be linear with the slope and intercept giving the values of ΔH° and ΔS°.

4. Results and discussion

4.1. Characterization of NMRH adsorbent

The pore area and average pore diameter of NMRH as calculated by BET method were found to be 116 $m^2\,g^{-1}$ and 65.1 nm, respectively. These values were significantly greater than previously reported values of pore area (17 $m^2\,g^{-1}$) and average pore diameter (51.3 nm) of rice husk (Akhtar, Bhanger, Iqbal, & Hasany, 2006). The difference may be attributed to NaOH treatment methodology, which may significantly affect the pore area, pore volume and micropore structure of rice husk.

Fig. 2(a) shows the X-ray diffraction analysis of rice husk (A) and NMRH (B). The X-ray diffractograms show an increase in the degree of crystallinity of cellulose after treatment with NaOH, as evident from the sharper diffraction peak of B compared to that of A. This is due to the fact that NaOH removes natural fats, waxes, silica, lignin and hemicelluloses from the cellulose fiber surface.

SEM examination of rice husk before and after NaOH treatment gives further insight on the rice husk morphology and its modification during the treatment. The SEM micrographs of rice husk (A) and NMRH (B) are illustrated in Fig. 2(b). As seen in Fig. 2(b), the surface of rice husk before treatment was characterized by ridges. The surface appeared highly undulated due to the presence of regularly spaced conical protrusions and bright spots which can be attributed to silica which is more highly concentrated in regions corresponding to dome-shaped protrusions and adjoining sloping areas (Ciannamea, Stefani, & Ruseckaite, 2010). The morphological characteristic of rice husk was altered by alkali treatments. Treatment with NaOH induced the cracking of the conical protrusions, and increased the surface roughness. The surface of NaOH treated rice husk showed the conical protrusions broken at the top and there was little brightness in this region which can be attributed to the loss of silica. In addition, the surface also showed higher roughness and cracks in the direction of the major axis of rice husk. This could be a consequence of the preferential elimination of the cementing materials of the interfibrillar region (mainly hemicelluloses and lignin) (Ciannamea, Stefani, & Ruseckaite, 2010).

4.2. Effect of operating parameters

4.2.1. Effect of pH

It is well established that the pH of the system exerts profound influence on the adsorptive uptake of adsorbate molecule presumably due to its influence on the surface properties of the adsorbent and ionization/dissociation of the adsorbate molecule (Saeed et al., 2010). As such, the adsorption characteristic of CV onto NMRH was studied over a pH range of 2–10. Results are shown in Fig. 3(a). The percentage removal of CV by NMRH increases with the increase in pH of the dye solution, appreciably up to pH 7.0. With further increase in pH from 7.0 to 10.0 the percentage CV removal increases but the difference in the percentage increase is not very significant. Since maximum removal is obtained at pH 8.0, all further experiments were carried out at pH 8.0. Similar trend of pH effect

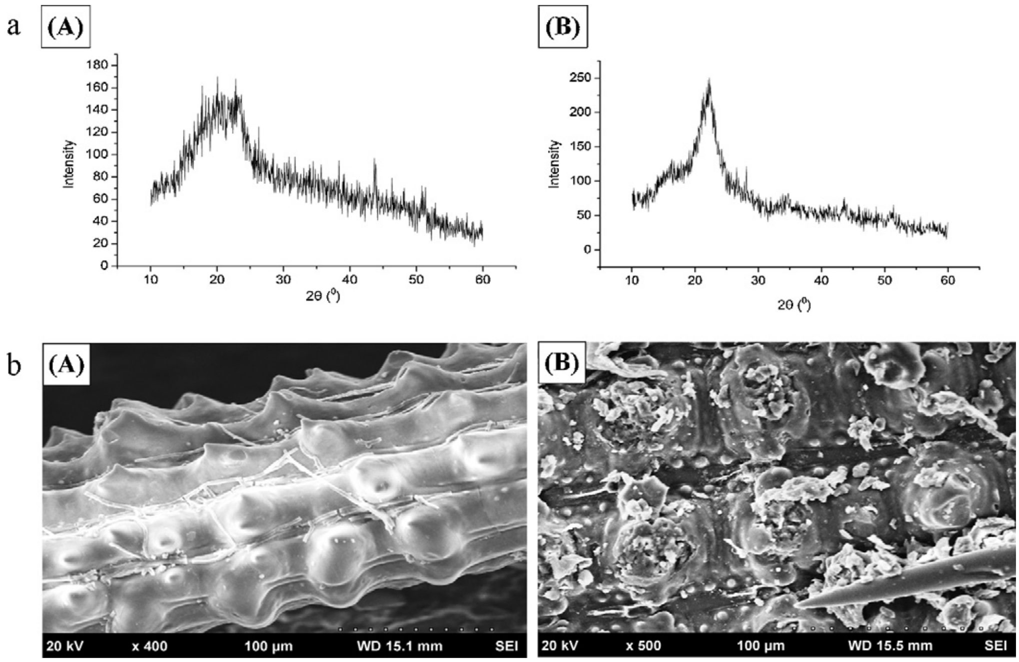

Fig. 2. (a) X-ray diffractograms: natural rice husk (A) NMRH (B) and (b) SEM micrographs: natural rice husk (A) NMRH (B).

was observed for the adsorption of CV on wood apple shell (Jain & Jayaram, 2010). Solution pH affects both aqueous chemistry and the surface binding sites of the adsorbent. At low pH values, protonation of the functional groups present on the adsorbent surface easily takes place. The surface of the adsorbent becomes positively charged, and this decreases the adsorption of the positively charged dye ions through electrostatic repulsion. As the pH of the dye solution increases, a proportional increase in adsorption takes place due to the successive deprotonation of positively charged groups on the adsorbent and electrostatic attraction between negatively charged sites on the adsorbent and dye cations.

4.2.2. Effect of adsorbent dose

Adsorbent dose is an important parameter that strongly influences the adsorption process by affecting adsorption capacity of the adsorbent. Therefore the influence of adsorbent dose on CV adsorption by NMRH was investigated in the range of 0.5–5.0 g. The adsorption efficiency increased from 96.78% to 98.17% as the adsorbent dose increased from 0.5 to 1 g. The increase in the percentage of dye removal with adsorbent dose could be attributed to an increase in the adsorbent surface area, augmenting the number of adsorption sites available for adsorption, as already reported (Ahmad, 2009; Saeed et al., 2010). Further increase in adsorbent dose reduced the maximum removal of CV. The decrease in sorption capacity with increasing dose of adsorbent at constant dye concentration and volume may be attributed to saturation of adsorption sites due to particulate interaction such as aggregation (Aksakal & Ucun, 2010). Such aggregation would lead to a decrease in total surface area of the adsorbent and increase in diffusional path length (Crini, Peindy, Gimbert, & Robert, 2007). Therefore, in the following experiments, the adsorbent dose was fixed at 1 g. These observations are in agreement with those reported previously by other researchers for the sorption of dyes by different biological materials (Aksakal & Ucun, 2010; Crini et al., 2007).

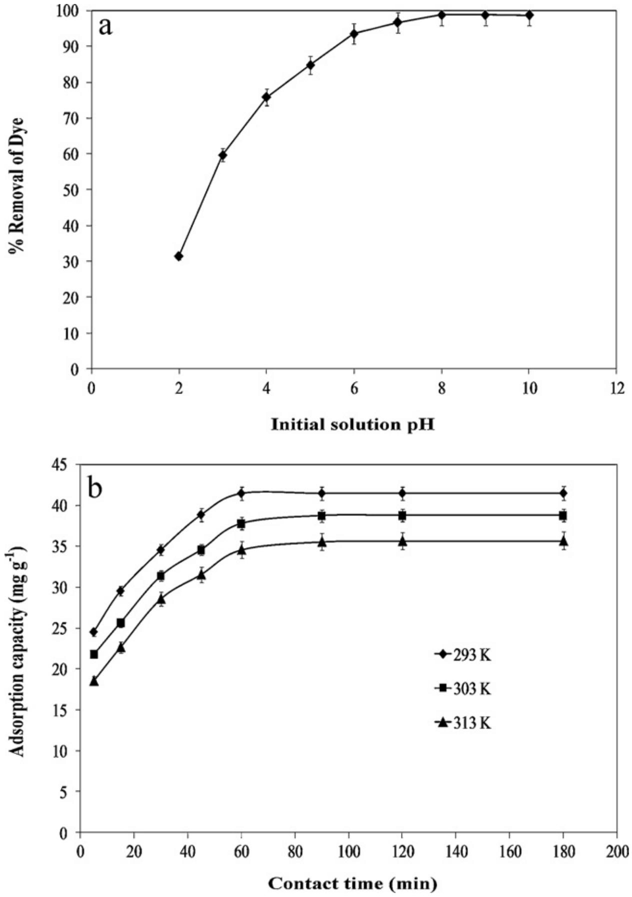

Fig. 3. (a) Effect of pH on adsorption of CV by NMRH and (b) time profiles for adsorption of CV by NMRH at different temperatures.

4.2.3. Effect of temperature and contact time

Fig. 3(b) presents the adsorption of CV at different temperatures as a function of contact time. As depicted in Fig. 3(b), the percentage removal of dye decreases with increasing temperature. This may be attributed to weakening of the bonds between the dye molecules and the binding sites of the adsorbent (Chowdhury & Saha, 2010). The observed trend in decreased dye removal capacity with increasing temperature suggests that adsorption of CV by NMRH is kinetically controlled by an exothermic process. In addition, CV shows a fast rate of adsorption during the first 60 min of the dye–sorbent contact. The fast adsorption rate is due to the large amount of surface area available for adsorption of the dye molecules. At higher contact time the rate of adsorption decreases, gradually leading to equilibrium. This decline is due to decrease in total adsorbent surface area and less available binding sites (Saha et al., 2010). The equilibrium time for maximum dye uptake is 90 min. After this equilibrium period, the amount of dye adsorbed does not show time-dependent change. Similar results have been reported in literature for adsorption of CV onto coniferous pinus bark powder (Ahmad, 2009).

4.3. Adsorption isotherms

The parameters and correlation coefficients obtained from the plots of Freundlich (log q_e versus log C_e), Langmuir (C_e/q_e versus C_e), and D–R (ln q_e versus ε^2) (figures not shown) are listed in Table 1. A typical example of adsorption isotherm data (at $T = 303$ K) fitted using the three isotherm models is shown in Fig. 4(a).

As observed from Table 1, although the equilibrium data fitted well to both the Langmuir and Freundlich adsorption isotherm models, the Freundlich model exhibited a slightly better fit to the adsorption data than the Langmuir model. The value of the Freundlich constant, K_F represents the degree of adsorption. The decrease of K_F values at higher temperatures suggests that the adsorption process was favourable at lower temperatures. The n is an empirical parameter that varies with the degree of heterogeneity and is related to the distribution of bonded ions on the sorbent surface. In general $n > 1$ illustrates that adsorbate is favourably adsorbed on an adsorbent, and the higher the n value the stronger the adsorption intensity. In particular, the value of n is significantly higher than unity at all the temperatures studied. However, n decreases with increasing temperature showing that adsorption rate decreases with the rise of temperature. In addition, the values of the Langmuir constants q_m and K_L decreases with increasing temperature. Seen overall, the information thus obtained specifies an exothermic nature of the existing process. The maximum adsorption capacity of NMRH for CV as determined from the Langmuir isotherm is 44.87 mg g^{-1} at 293 K.

The D–R isotherm model constant β gives an idea about the mean free energy of adsorption (E) and can be computed using the following relationship (Chowdhury & Saha, 2010):

$$E = \frac{1}{\sqrt{2\beta}} \tag{13}$$

The magnitude of E may characterize the type of the adsorption as chemical ion exchange ($E = 8$–16 kJ mol^{-1}), or physical sorption ($E < 8$ kJ mol^{-1}) (Chowdhury & Saha, 2010). The mean free energy of adsorption for the present study was found to be >8 kJ mol^{-1} at different temperatures (Table 1), which implies that, the adsorption of CV on NMRH may be considered as a chemical adsorption process.

4.4. Adsorption kinetics

As already mentioned, the pseudo-first-order and pseudo-second-order kinetic models were tested to obtain the rate constants and equilibrium adsorption capacity at different temperatures. The values of pseudo-first-order rate constants, k_1 and q_e were calculated from slopes and intercepts of the plots of log($q_e - q_t$) versus t (figure not shown) and are listed in Table 2. The results show that the correlation coefficients (R^2) obtained at different temperatures for the pseudo-first-order kinetic model is in the range of 0.921–0.887. In addition, the theoretical and experimental equilibrium adsorption capacities, q_e obtained from this kinetic model varied widely at all temperatures. These findings suggest that adsorption of CV on NMRH cannot be described by the pseudo-first-order kinetic model.

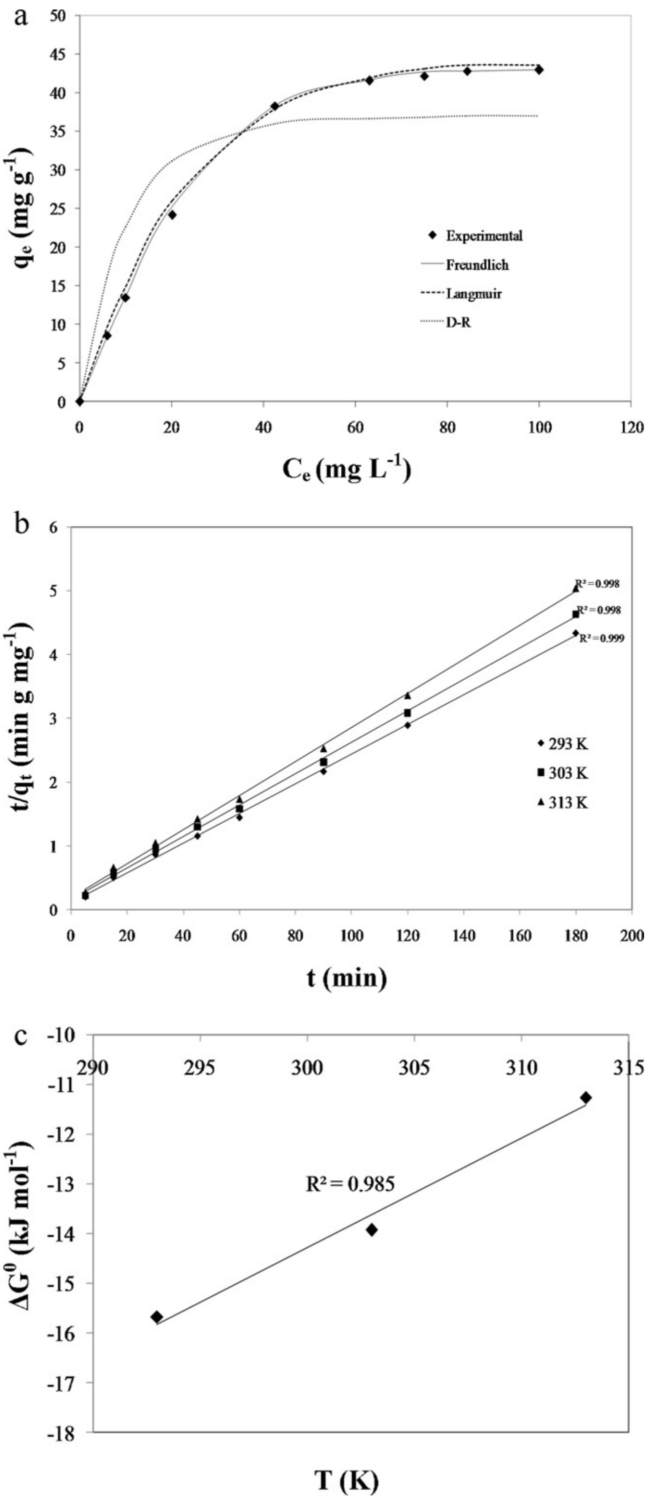

Fig. 4. (a) Comparison between the measured and modelled isotherm profiles for the adsorption of CV by NMRH at $T = 303$ K, (b) pseudo-second-order kinetic plots for adsorption of CV onto NMRH at different temperatures and (c) plot of Gibb's free energy change versus temperature for adsorption of CV onto NMRH.

Table 1
Adsorption isotherm constants for sorption of CV onto NMRH at different temperatures.

T (K)	Langmuir isotherm parameters			Freundlich isotherm parameters			D–R isotherm parameters			
	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F (mg g^{-1}) (L mg^{-1})$^{1/n}$	n	R^2	q_m (mg g^{-1})	β (mmol^2 J^{-2})	E (kJ mol^{-1})	R^2
293	44.876	5.632	0.992	24.459	6.435	1.000	37.784	2.35×10^9	14.567	0.946
303	41.035	4.174	0.989	19.225	5.266	0.999	35.856	2.57×10^9	13.925	0.944
313	39.962	3.298	0.985	15.437	4.197	1.000	33.193	2.94×10^9	13.025	0.932

Table 2
Kinetic parameters for adsorption of CV onto NMRH.

T (K)	$q_{e,\mathrm{exp}}$ (mg g^{-1})	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		$q_{e,\mathrm{cal}}$ (mg g^{-1})	k_1 (min^{-1})	R^2	$q_{e,\mathrm{cal}}$ (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2
293	41.483	27.974	0.0523	0.921	42.053	0.00234	0.998
303	38.805	23.691	0.0351	0.903	39.714	0.00135	0.998
313	35.677	19.582	0.0237	0.887	36.128	0.00062	0.999

Conversely, the kinetic data exhibited an excellent compliance with pseudo-second-order kinetic equation. The plots of t/q_t against t at different temperatures showed excellent linearity (Fig. 4b). The pseudo-second-order rate constant k_2, the calculated q_e values and the corresponding linear regression correlation coefficients values R^2 are given in Table 2. As seen in Table 2, the calculated q_e values agree with experimental q_e values well, and also, the correlation coefficients for the pseudo-second-order kinetic plots at all the studied temperatures are significantly higher ($R^2 > 0.99$). The best correlation for the system provided by the pseudo-second-order model suggests that chemical sorption involving valency forces through sharing or exchange of electrons between adsorbent and adsorbate might be significant. A similar phenomenon was also observed in the adsorption of CV on wheat straw (Gong et al., 2008).

In a well-agitated batch adsorption system, there is a possibility of intraparticle pore diffusion of adsorbate ions, which can be the rate-limiting step. Therefore, the possibility of intra-particle diffusion resistance affecting the adsorption process was explored using the intra-particle diffusion model (Eq. (8)). According to Eq. (8), a plot of q_t versus $t^{0.5}$ should be a straight line with a slope k_i and intercept I when the adsorption mechanism follows the intra-particle diffusion process. However, if the data exhibit multi-linear plots, then the process is governed by two or more steps. The plots for biosorption of CV on NMRH at different temperatures were multimodal with three distinct regions (figure not shown). The initial curved region is attributed to the external surface adsorption in which the adsorbate diffuses through the solution to the external surface of the adsorbent. The second stage relates the gradual uptake reflecting intraparticle diffusion as the rate limiting step. The final plateau region refers to the gradual adsorption stage and the final equilibrium stage, in which the intraparticle diffusion starts to slow down and level out. The present finding implies that although intraparticle diffusion is involved in the adsorption process, but it is not the sole rate-controlling step and that some other mechanisms also play an important role.

4.5. *Activation energy and thermodynamic parameters*

From the pseudo-second-order rate constant k_2 (Table 2), the activation energy E_a for adsorption of CV onto NMRH was determined using the Arrhenius equation (Eq. (9)). By plotting $\ln k_2$ versus $1/T$ (figure not shown), E_a was obtained from the slope of the linear plot and was estimated to be around 50.51 kJ mol^{-1}. The magnitude of activation energy gives an idea about the type of adsorption which is mainly physical or chemical. Low activation energies (<40 kJ mol^{-1}) are characteristics for physical adsorption, while higher activation energies (>40 kJ mol^{-1}) suggest chemical adsorption (Anirudhan & Radhakrishnan, 2008). The activation energy obtained for the adsorption of CV onto NMRH indicates that the adsorption process is chemisorption. This value is consistent with the values in the literature where the activation energy was found to be 45.82 kJ mol^{-1} for the adsorption of Malachite Green—a cationic dye on clayey soil (Saha et al., 2010).

The Gibb's free energy (ΔG°) for adsorption of CV onto NMRH at all temperatures was obtained from Eq. (10). The values of ΔH° and ΔS° were determined from the slope and intercept of the plot of ΔG° versus T (Fig. 4c). The values of ΔG° were found to be (−15.67, −13.93 and −11.26) kJ mol^{-1} at T = (293, 303 and 313 K), respectively. The negative value of ΔG° at all temperatures indicates the spontaneous nature and the feasibility of the dye adsorption process. Increase in value of ΔG° with increase in temperature suggests that lower temperature makes the adsorption easier. The negative value of ΔH° (−80.43 kJ mol^{-1}) implies that the adsorption phenomenon is exothermic. The magnitude of ΔH° may give an idea about the type of sorption. The heat evolved during physical adsorption is of the same order of magnitude as the heats of condensation, i.e., 2.1–20.9 kJ mol^{-1}, while the heats of chemisorption generally falls into a range of 80–200 kJ mol^{-1} (Liu and Liu, 2008). Therefore, CV adsorption by NMRH may be attributed to a chemical adsorption process. The negative value of ΔS° (−220.00 J mol^{-1}) suggests that the process is enthalpy driven.

4.6. *Adsorption mechanism*

The major challenge in an adsorption study is to elucidate the adsorption mechanism. However, before understanding the adsorption mechanism it is necessary to consider to two points: firstly the structure of the adsorbate; and secondly the adsorbent surface properties. In this connection, it must be pointed out that CV is a cationic dye having amine groups in its structure. In aqueous solutions, CV dissociates into CV$^+$ and Cl$^-$ ions (Kumar & Ahmad, 2011). The results of BET, XRD and SEM put forward that NaOH treatment change the rice husk morphology, eliminate hemicelluloses and lignin components, reduce silica content and probably increase the crystallinity of cellulose fraction. This possibly will favour chemical interactions between the more exposed hydroxyl groups of rice husks' and the dye ions and mechanical bonding because the dye ions could penetrate more easily into rice husk microstructure.

In this study, the removal of CV by adsorption on NMRH was found to be rapid at the initial period of contact time and then to become slow and stagnate with increase in contact time (Fig. 3b). The adsorption was strongly pH-dependent (Fig. 3a). CV was adequately adsorbed for pH between 7.0 and 10.0. It was also observed that the modelling of intraparticle diffusion showed a contribu-

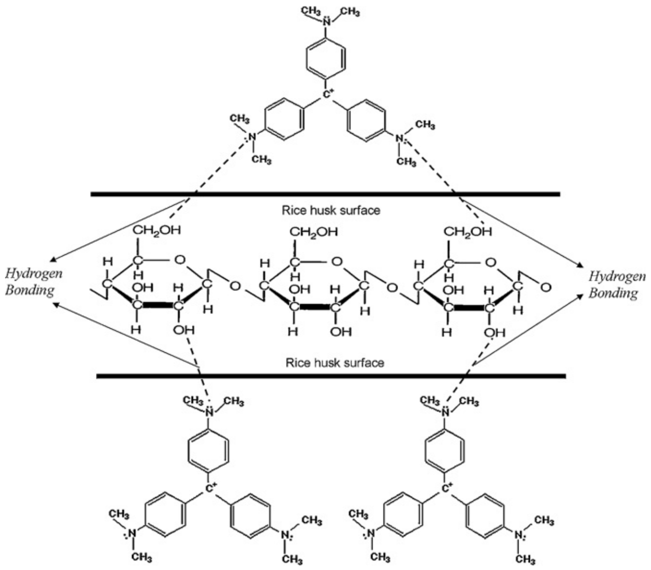

Fig. 5. Adsorption mechanism of CV onto NMRH.

tion of film diffusion on the control of sorption kinetics; however intraparticle diffusion was not the dominating mechanism.

According to the experimental findings of the present study, and based on the structure of the adsorbate and adsorbent surface properties, the adsorption mechanism of CV onto NMRH may be assumed to involve the following steps:

- Migration of dye from bulk of the solution to the surface of the adsorbent
- Diffusion of dye through the boundary layer to the surface of the adsorbent
- Adsorption of dye on the surface of NMRH, which may be due to the formation of surface hydrogen bonds between the hydroxyl groups on the rice husk surface and the nitrogen atoms of CV as suggested in Fig. 5 or through a possible mechanism of a dye–hydrogen ion exchange process as shown below:

$$\text{Ricehusk–OH} \rightleftharpoons \text{ricehusk–O}^- + \text{H}^+$$

$$\text{Ricehusk–O}^- + \text{CV}^+ \rightleftharpoons \text{ricehusk–O–CV} + \text{H}^+$$

- Intraparticle diffusion of dye into the interior pores of the adsorbent

4.7. Comparison of NMRH with other sorbents

Table 3 summarizes the comparison of the maximum CV adsorption capacities of various sorbents including NMRH. The comparison shows that NMRH has higher sorption capacity of CV than many of the other reported adsorbents. In addition, NMRH is quite a cheap material. In our previous study, the total cost for the preparation of 1 kg of NMRH was estimated at 32.19 INR (Chowdhury et al., 2011). The CV loaded NMRH can be dried and used as a fuel in boilers/incinerators, or can be used for the production of fire briquettes. The ash may be used to make fire-bricks, thus disposing of CV through chemical fixation. This approach of adsorbent disposal entails energy recovery from the adsorbent and the safe disposal of the adsorbed CV. Thus the use of NMRH as an adsorbent is a thoughtful and economic attempt for its valuable, necessitous and needy utilization for wastewater treatment processes.

Table 3
Comparison of CV sorption capacity of NMRH with other reported low-cost adsorbents.

Sorbent	q_{max} (mg g^{-1})	Reference
Coniferous pinus bark powder	32.78	Ahmad (2009)
Rice bran	42.25	Wang, Liu, Wen, Zhou, and Li (2008)
Calotropis procera leaf	4.14	Ali and Muhammad (2008)
Orange peel	14.3	Annadurai, Juang, and Lee (2004)
Sugarcane dust	3.8	Khattri and Singh (1999)
Neem sawdust	3.8	Khattri and Singh (2009)
Jute fiber carbon	27.99	Porkodi and Kumar (2007)
Skin almond waste	85.47	Atmani, Bensmaili, and Mezenner (2009)
Coir pith	2.56	Namasivayam et al. (2001a)
Treated coir pith	94.7	Namasivayam, Radhika, and Suba (2001)
Sawdust	37.83	Parab, Sudersanan, Shenoy, Pathare, and Vaze (2009)
Sugarcane fiber	10.44	Parab et al. (2009)
Jalshakti® polymer	12.9	Dhodapkar, Rao, Pande, Nandy, and Devotta (2007)
NMRH	44.87	This study

5. Conclusion

The present study shows that NMRH is an effective adsorbent for the removal of CV from aqueous solutions. The operational parameters such as pH, adsorbent dose, contact time, and temperature, were found to have an effect on the adsorption efficiency of NMRH. The adsorption was highly dependent on reaction temperature and solution pH. The dye was optimally adsorbed at pH 8. High temperature did not favour the CV adsorption process and the optimal removal was observed at 293 K. The adsorption kinetics followed pseudo-second-order model indicating chemisorption. Intraparticle diffusion was not the sole rate controlling step. CV adsorption onto NMRH followed both Freundlich and Langmuir isotherm models. The nature of CV adsorption on NMRH was chemical adsorption as inferred from the Dubinin–Radushkevich (D–R) isotherm model. The calculated thermodynamic parameters showed the exothermic and spontaneous nature of the adsorption process. The maximum CV adsorption capacity of NMRH was comparable and found to be moderately higher than that of many corresponding sorbent materials under quite similar conditions. Taking into consideration all the above obtained results, it can be concluded that NMRH should be a promising and cost-effective adsorbent for the removal of colour and dyes from water and wastewater.

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