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Removal of methylene blue using *Phoenix dactylifera*/PVA composite; an eco-friendly adsorbent

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ABSTRACT

Phoenix dactylifera leaf extract was immobilized within cross-linked polyvinyl alcohol (PVA) for the removal of methylene blue (MB) from aqueous solutions. The Ultraviolet–visible (UV–vis) and Fourier transform infrared spectroscopic techniques were utilized to shed light on the functional groups accountable for the adsorption process. The adsorption experiments were conducted as a function of different operating variables (contact time, adsorbent dosage, initial dye concentration, and pH value). The developed *P. dactylifera*/PVA matrix can be considered as a low-priced green adsorbent with high efficiency for the removal of MB from aqueous solution.

Keywords: Phoenix dactylifera; PVA; UV irradiation; Methylene blue; Adsorption

1. Introduction

Reactive dyes are widely used in agricultural research, textile industry, food technology, leather tanning, and paper production. As a result, huge amounts (more than 70,000 tons per year) of the dye residues were discharged as liquid wastes [1]. The release of such dye effluents in water streams causes considerable environmental pollution to the living organisms [2]. Some of these dyes have carcinogenic effects on the human systems, especially when they find their way into the drinking water [3]. In addition, the high dye concentration in water bodies reduces the sun penetration causing disturbance to aquatic life [4]. Hence, the removal and/or treatment of such wastes before discharging to the environment using efficient and inexpensive strategies comes on top of the priorities of the researchers' interests.

There are several techniques have been proposed for successful removal of reactive dyes such as photocatalytic degradation, flocculation, membrane separation, sonolysis, oxidative degradation, biological treatments, reverse osmosis, ion exchange, adsorption. Although these techniques demonstrate success in the treatment of dye-contaminated water, they are expensive, time- and energy-consuming and produce huge amount of chemical wastes.

On the other hand, biosorption of pollutants from water appears as a good alternative to the conventional methods. The biosorption process is a cost-effective "green" technology featured with flexible design, ease of operation, and high removal performance. In addition, the use of biosorbents minimizes the production of chemical and hazardous sludge [5]. A wide

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variety of biosorbents for the treatment of dye effluents are used such as bacteria, fungi, yeast, algae [5], and plants [6].

Different plants have been used for the removal of dye effluents such as bagasse pith [7], paddy straw [8], gulmohar leaf [9], cotton fiber [10], banana peel [11], coir pith [12], neem (*Azadirachta indica*) husk [13], and date palm (*Phoenix dactylifera*) [1,14]. Researchers have followed one of two strategies in using these plants as biosorbent. The first is transferring different parts of the plant to activated carbon via heating the plant at high temperature in inert condition. The second path is based on grinding the dried parts of plants and sieving the resulted powder to different sizes for a set of adsorption tests. Both approaches face some hardships such as complicated steps of adsorbent preparation, mass transport, and difficulties in separation.

Herein, we develop a new pathway in using plants as biosorbent thereby binding the plant extract to insoluble polymer matrix. To achieve this, polyvinyl alcohol (PVA) is cross-linked with *P. dactylifera* leaf extract with the aid of UV irradiation. This new composite collects the mechanical strength of the polymeric support and the characteristic functionalities of the plant extract. *P. dactylifera*/PVA composite was prepared via facile procedure under mild and eco-friendly conditions with the aid of elementary apparatus (see Fig. 1). *P. dactylifera*/PVA composite showed a promising performance in pollutant cleaning. In addition, the resulting composite can be easily handled and/or separated from the aqueous medium which promotes its recyclability.

2. Experimental

2.1. Preparation of P. dactylifera extract

The freshly collected leaves (20 g) of Egyptian date palm were washed carefully with tap water to get rid of dust and sliced into pieces. The sliced leaves were soaked within 100 mL of 70% methanol/water solution for one week at room temperature. The methanolic extract was filtered using Whatman filter paper No. 1. The methanolic solution was removed and the extract was concentrated with the aid of a rotary evaporator. The filtrate was collected and stored at 4˚C for further studies [15].

2.2. Preparation of P. dactylifera/PVA composite

The PVA solution was prepared by dissolving 3 g PVA powder (M. wt = 20,000, EA chemicals Inc, Egypt) in 50 ml distilled water at 85˚C for 12 h. After a clear solution is obtained, the polymeric solution was allowed to cool to ambient temperature. *P. dactylifera* extract (0.5 g) was added to the PVA solution and the stirring was conducted for 2 h to achieve a highly homogeneous mixture. The mixture was poured on Petri dish and allowed to dry to get the desired film.

2.3. UV irradiation

The *P. dactylifera*/PVA films were stripped from the petri dish and subjected to UV irradiation from Vilber Lourmat Lamp, SVL, France, at wavelength 254 nm for 4 h at 10 cm distance.

2.4. Equipment

A double beam Jasco V-630 UV–vis spectrophotometer was used for recording the absorption spectra. The dried extract and methylene blue (MB) were mixed with KBr to make pellet, and the Fourier transform infrared (FTIR) spectra were collected using Jasco FT/IR 6100 spectrometer. A Hanna pH meter was used for pH measurements.

2.5. Gel and swelling determination

The UV-irradiated *P. dactylifera*/PVA films were cut into square pieces and their weight was accurately determined (W_1). The square films were soaked in deionized water for 24 h at room temperature for sol extraction. The swollen samples were left from the water, and superficial moisture was dried using filter paper. The weight of the swollen sample was immediately determined to be (W_2). Thereafter, the swollen composites were dried in an oven at 40˚C until a constant weight was attained (W_3). The gel content % and swelling % of the composite films are calculated according to the following relation [16]:

$$\text{Gel content}\,\% = (W_3/W_1) \times 100$$

$$\text{Swelling}\,\% = (W_2/W_1) \times 100$$

2.6. Adsorption test

The adsorption experiments were performed in a set of 100 mL glass vials containing different masses of *P. dactylifera*/PVA and 50 mL of MB aqueous solutions with initial concentration (C_i). The mixture within the vial was magnetically stirred and withdrawn at predetermined time intervals for analysis with UV–vis spectrophotometer. The concentrations at

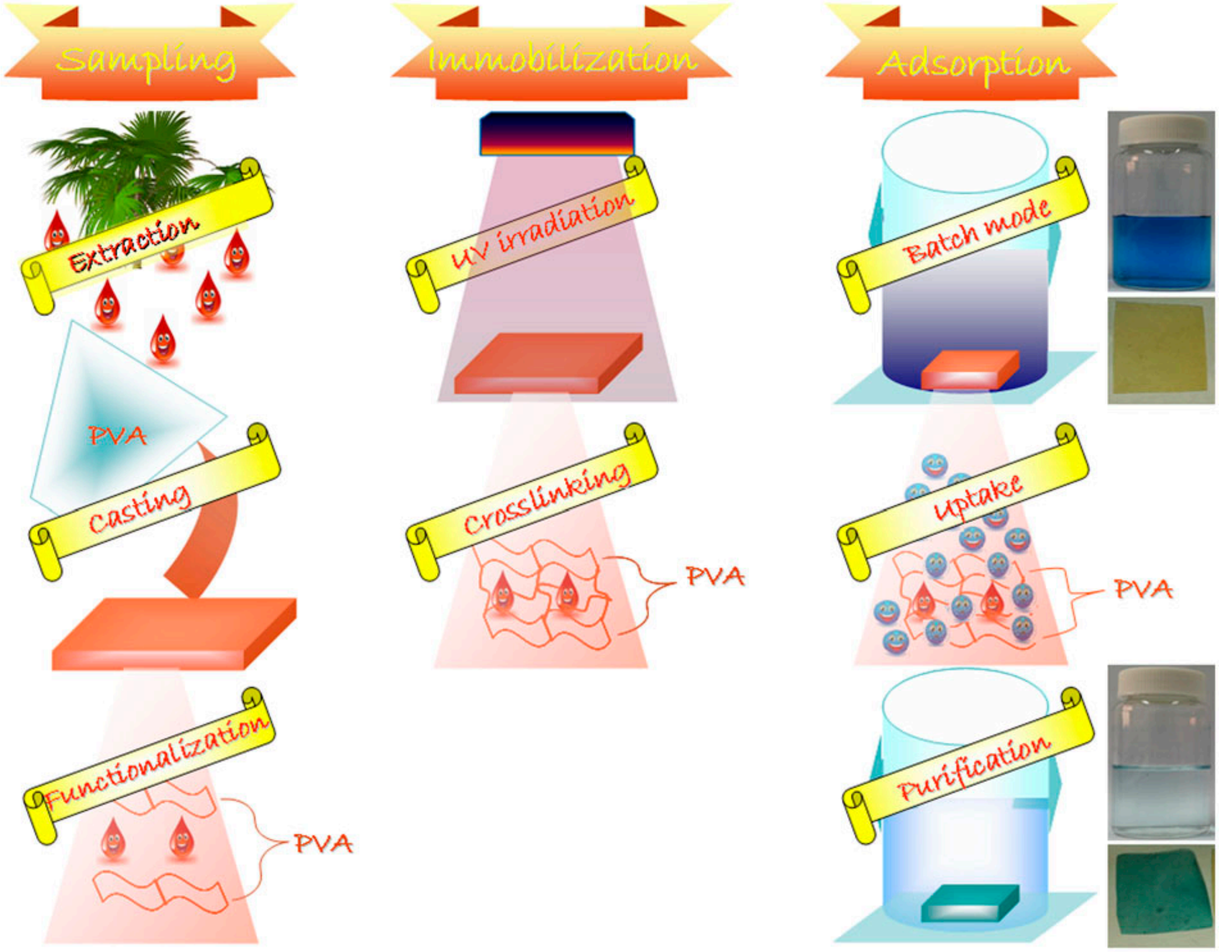

Fig. 1. The preparation and utilization of PVA/PDE composite for MB removal from water.

equilibrium (C_e) and at a given time (C_t) were calculated by recording the corresponding absorbance of the MB characteristic peak at 662 nm. The pH value was controlled using either 0.1 M HCl or 0.1 M NaOH. The removal percent of the MB ($R\%$) was calculated using the following equation [1]:

$$R\% = (C_i - C_e/C_i) \times 100$$

All tests were carried out in triplicate under the similar conditions, and the average values were recorded to minimize the experimental errors.

3. Results and discussion

3.1. Adsorption mechanism

In order to recognize the adsorption mechanism of MB removal with *P. dactylifera*/PVA composite, we resort to study the direct interaction between aqueous solutions of free *P. dactylifera* extract and MB. The visual inspection showed that upon addition of *P. dactylifera* extract, the color of MB solution changed immediately from blue to greenish blue. This observation was further proved by recording UV–vis spectra. Fig. 2 depicted the optical absorbance spectrum of MB and MB after the addition of *P. dactylifera* extract. The spectrum of the MB showed a strong absorption peak at 662 nm with absorption shoulder at 614 nm which was assigned to π–π^* electronic transitions [17]. After addition of *P. dactylifera* extract, the UV–vis spectrum of MB showed 12 nm bathochromic shift for its two absorption maxima. The spectral shift of the absorption peaks attributed to the difference in the stabilization of ground and excited states (π–π^* electronic transitions) and thus causes a change in energy gap between these electronic states. This observation led us to predict that there may be a

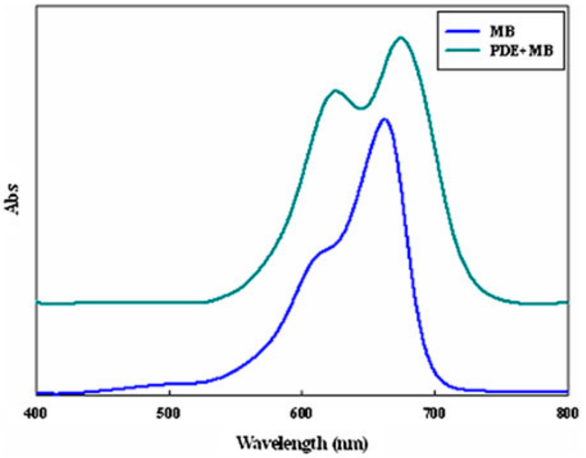

Fig. 2. The UV–vis spectra of MB before and after the addition of PDE solution.

chemical reaction between MB and *P. dactylifera* extract.

FTIR spectroscopy is an efficient tool used to identify the functional groups which are responsible for the binding between *P. dactylifera* extract and MB. *P. dactylifera* is commonly known as a rich source of different phytochemicals including flavonoids, alkaloids, carbohydrates, tannins, saponins, and steroids [18]. Fig. 3 displayed the FTIR spectra of *P. dactylifera* extract before and after interaction with MB. The vibrational bands of the extract suffered from some deformation in both shape and position upon addition of MB. The stretching vibration of –OH group is shifted markedly from 3,423 to 3,378 cm^{-1} and became to somewhat broader. The −NH band of the amide A was shifted from 3,253 to 3,240 cm^{-1}. The extract spectrum showed an intense IR peak at 1,625 cm^{-1} due to stretching vibrations of the –C=O group. The interaction between the extract and MB led to the displacement of this peak to the lower energy side (1,600 cm^{-1}). These spectral changes lead us to believe that the hydroxyl, amino, and carbonyl groups may have the key role in the adsorption of MB. Similar results were reported in the literature [1,19,20].

The next step in this study, the UV radiation, was used to induce a cross-linking reaction between the PVA segments in order to immobilize the extract macromolecules within the polymer matrix. This treatment enabled the easy separation of the adsorbent from the aqueous medium. Hence, the gel % was used to measure the cross-linking density of *P. dactylifera*/PVA composite [21]. Fig. 4 clarified that the gel % increased with an increase in radiation time. Actually, the gel content increased dramatically from 40 to 92% with irradiation interval up to 2.5 h. Thereafter, the gel % responded slowly to the UV irradiation process reaching its maximum value (97%) after 4 h.

When brought in contact with water, the cross-linked *P. dactylifera*/PVA swelled but not dissolved. The swelling % was measured at different irradiation times and the results are shown in Fig. 4. The swelling % tends to decrease with the passage of irradiation time. As a result, the cross-linked polymeric composite can adsorb and retain large quantities of water.

The penetrations of dyed water into the polymer segments give the opportunity to the adsorbing sites (hydroxyl, amino, and carbonyl groups) to pick up the MB molecules dissolved in water. Consequently, the

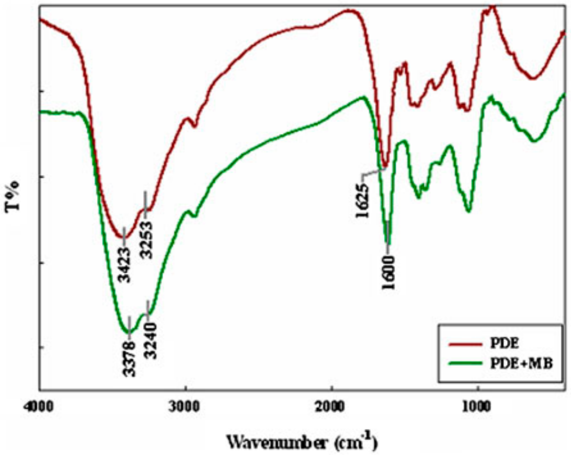

Fig. 3. FTIR spectra of PDE before and after interaction with MB.

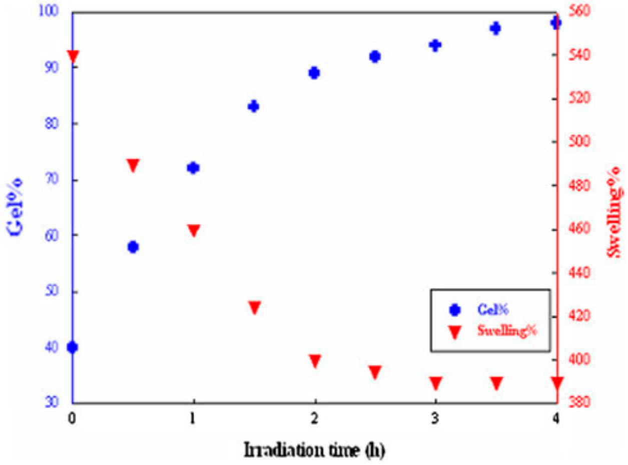

Fig. 4. Effect of irradiation time on gel % and swelling % of PVA/PDE.

water inside the polymeric matrix is diluted against the dye molecules. Under the action of osmotic driving force, the composite network will absorb additional dyed water instead of purified one. The process is continued until the dye is totally removed or the cross-linked *P. dactylifera*/PVA is saturated with MB. Hence, the *P. dactylifera*/PVA composite is suitable for use in water adsorbing applications without thawing and/or wearing out.

3.2. Effects of operating parameters on MB adsorption

3.2.1. Effect of contact time and initial MB concentration

Fig. 5 shows the impact of initial MB concentration on the removal percentage, evaluated at pH 6.5, adsorbent dosage of 1 g and contact time of 30 min. It was found that the MB removal increased with increase in contact time to an equilibrium state was attained. The *R%* of MB was sharply increased within the first 10 min, reaching to 88, 83, 76, 64, and 55% for 0.5, 3, 4, 7, and 10 mg/L, respectively. Extra contact time did not increase the *R%* significantly due to deposition of dye molecules on the available binding sites on the adsorbent.

According to Fig. 5, one finds that the *R%* of MB at equilibrium decreases with increasing the initial MB concentration. For 0.5 mg/L, the maximum *R%* is about 89%, while the minimum *R%* is about 70% for the initial concentration of 10 mg/L. This could be explained as follows: in the case of low MB concentrations, there are a large number of the binding sites of the adsorbent that are available for dye adsorption and hence higher *R%* is obtained. At higher dye concentrations, the binding sites are saturated and cannot adsorb more dye molecules so lower *R%* is obtained [22].

3.2.2. Effect of adsorbent dosage

The adsorption of MB on *P. dactylifera*/PVA composite was evaluated using different masses (0.5, 1, 1.5, and 2 g) of the adsorbent in 50 ml of solution at pH 6.5 and initial MB concentration of 10 mg/L. Fig. 6 showed that the adsorption proceeded faster as the adsorbent dose increased. The *R%* of MB at equilibrium increased from 53.6 to 91.5% as the adsorbent dose increased from 0.5 to 2 g. The incremental MB adsorption with increasing *P. dactylifera*/PVA composite dose is attributed to the availability of a large number of functional groups (adsorption sites) and/or the presence of a greater surface area responsible for the adsorption process [23].

3.2.3. Effect of initial pH value

Fig. 7 showed the role of varying the initial pH value on the *R%* of 10 mg/L of MB from solution using 1 g of *P. dactylifera*/PVA composite. It is clear that the *R%* is very sensitive to the pH value tuning, i.e., the *R%* at equilibrium enhanced dramatically from 41 to 93% as the pH value varied from 4 to 10. It is well known that MB is a cationic dye and exists in solutions as positive ions [24]. In an acidic medium (low pH values), the H^+ ions jostle the dye cations for adsorption on the active functional sites leading to a lower *R%* value. On the other hand, in basic medium, the OH^- ions increase the negativity of the adsorbent

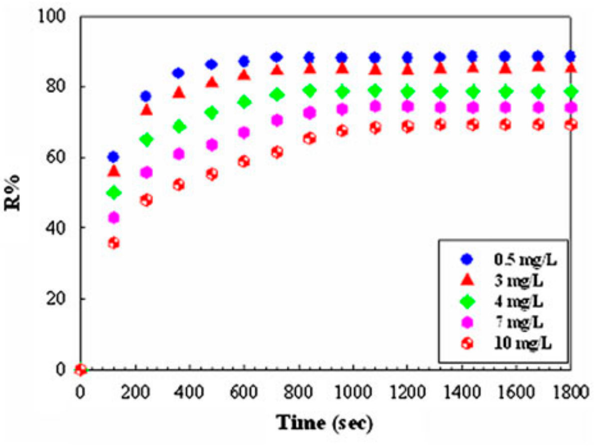

Fig. 5. Effect of contact time on *R%* of MB at different initial concentrations.

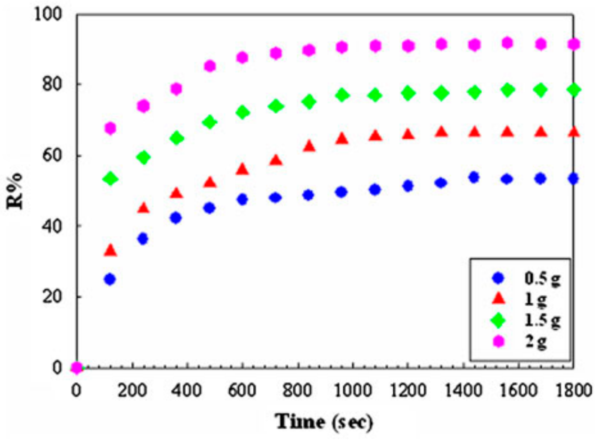

Fig. 6. The *R%* of MB vs. contact time at different adsorbent dosages.

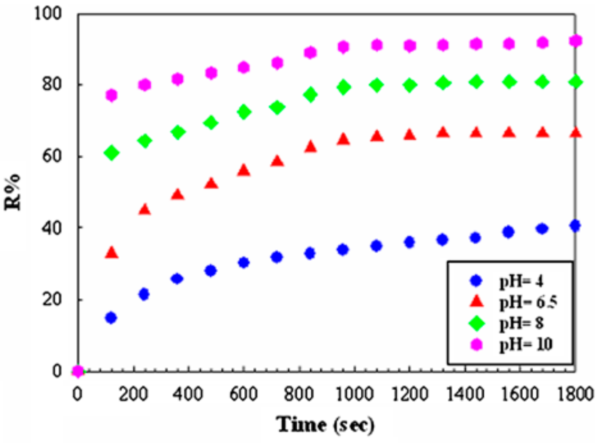

Fig. 7. The *R*% of MB vs. contact time at different pH values.

and thus the *R*% of the dye cation was enhanced through the electrostatic force of attraction.

4. Conclusion

The *P. dactylifera*/PVA composite has been proved to possess good potential to be an alternative to conventional adsorbents for the removal of MB from the aqueous solution. The spectroscopic data ascribed the reactivity of such composite to a possible chemical interaction between the plant extract and MB. The FTIR results indicated that the hydroxyl, amino, and carbonyl groups of *P. dactylifera* extract are the active sites responsible for the adsorption process. The results clarified that the MB removal was achieved within 30 min. The removal% increased with increasing the adsorbent dosage and pH while it decreased with increasing initial dye concentration.

References

[1] G. Asgari, B. Ramavandi, S. Sahebi, Removal of a cationic dye from wastewater during purification by *Phoenix dactylifera*, Desalin. Water Treat. 52 (2013) 7354–7365.

[2] W. Qasim, A.V. Mane, Characterization and treatment of selected food industrial effluents by coagulation and adsorption techniques, Water Resour. Ind. 4 (2013) 1–12.

[3] S. Srivastava, R. Sinha, D. Roy, Toxicological effects of malachite green, Aquat. Toxicol. 66 (2004) 319–329.

[4] V. Janaki, K. Vijayaraghavan, B.-T. Oh, K.-J. Lee, K. Muthuchelian, A.K. Ramasamy, S. Kamala-Kannan, Starch/polyaniline nanocomposite for enhanced removal of reactive dyes from synthetic effluent, Carbohydr. Polym. 90 (2012) 1437–1444.

[5] B. Zhang, R. Fan, Z. Bai, S. Wang, L. Wang, J. Shi, Biosorption characteristics of *Bacillus gibsonii* S-2 waste biomass for removal of lead(II) from aqueous solution, Environ. Sci. Pollut. Res. 20 (2013) 1367–1373.

[6] G. Bayramoglu, N. Adiguzel, G. Ersoy, M. Yilmaz, M. Yakup Arica, Removal of textile dyes from aqueous solution using amine-modified plant biomass of *A. caricum*: Equilibrium and kinetic studies, Water Air Soil Pollut. 224 (2013) 1–16.

[7] G. McKay, M. El Geundi, M.M. Nassar, Equilibrium studies during the removal of dyestuffs from aqueous solutions using Bagasse pith, Water Res. 21 (1987) 1513–1520.

[8] S. Chakraborty, S. Chowdhury, P. Das Saha, Adsorption of crystal violet from aqueous solution onto NaOH-modified rice husk, Carbohydr. Polym. 86 (2011) 1533–1541.

[9] V. Ponnusami, V. Gunasekar, S.N. Srivastava, Kinetics of methylene blue removal from aqueous solution using gulmohar (*Delonix regia*) plant leaf powder: Multivariate regression analysis, J. Hazard. Mater. 169 (2009) 119–127.

[10] S. Rattanaphani, M. Chairat, J.B. Bremner, V. Rattanaphani, An adsorption and thermodynamic study of lac dyeing on cotton pretreated with chitosan, Dyes Pigm. 72 (2007) 88–96.

[11] R.-L. Liu, Y. Liu, X.-Y. Zhou, Z.-Q. Zhang, J. Zhang, F.-Q. Dang, Biomass-derived highly porous functional carbon fabricated by using a free-standing template for efficient removal of methylene blue, Bioresour. Technol. 154 (2014) 138–147.

[12] C. Namasivayam, M. Dinesh Kumar, K. Selvi, R. Ashruffunissa Begum, T. Vanathi, R.T. Yamuna, ‘Waste’ coir pith—A potential biomass for the treatment of dyeing wastewaters, Biomass Bioenergy 21 (2001) 477–483.

[13] H.A. Hegazi, Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents, HBRC J. 9 (2013) 276–282.

[14] M. Gouamid, M.R. Ouahrani, M.B. Bensaci, Adsorption equilibrium, kinetics and thermodynamics of methylene blue from aqueous solutions using date palm leaves, Energy Proc. 36 (2013) 898–907.

[15] M.F. Zayed, W.H. Eisa, A.A. Shabaka, *Malva parviflora* extract assisted green synthesis of silver nanoparticles, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 98 (2012) 423–428.

[16] S. Kudo, E. Otsuka, A. Suzuki, Swelling behavior of chemically crosslinked PVA gels in mixed solvents, J. Polym. Sci., Part B: Polym. Phys. 48 (2010) 1978–1986.

[17] S. Thomas, C.H. Chan, L. Pothen, J. Joy, H. Maria, Natural Rubber Materials: Volume 2: Composites and Nanocomposites 2013, p. 749.

[18] M.F. Zayed, W.H. Eisa, *Phoenix dactylifera* L. leaf extract phytosynthesized gold nanoparticles; controlled synthesis and catalytic activity, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 121 (2014) 238–244.

[19] S. Altenor, B. Carene, E. Emmanuel, J. Lambert, J.-J. Ehrhardt, S. Gaspard, Adsorption studies of methylene blue and phenol onto vetiver roots activated carbon prepared by chemical activation, J. Hazard. Mater. 165 (2009) 1029–1039.

[20] D. Park, Y.-S. Yun, J.M. Park, Studies on hexavalent chromium biosorption by chemically-treated biomass of Ecklonia sp, Chemosphere 60 (2005) 1356–1364.
[21] R.M. Ottenbrite, K. Park, T. Okano, Biomedical Applications of Hydrogels Handbook, 2010, pp. 1–15.
[22] S. Cengiz, L. Cavas, Removal of methylene blue by invasive marine seaweed: *Caulerpa racemosa* var. cylindracea, Bioresour. Technol. 99 (2008) 2357–2363.
[23] M.A. Al-Ghouti, M.A.M. Khraisheh, M.N.M. Ahmad, S. Allen, Adsorption behaviour of methylene blue onto Jordanian diatomite: A kinetic study, J. Hazard. Mater. 165 (2009) 589–598.
[24] A. Aluigi, F. Rombaldoni, C. Tonetti, L. Jannoke, Study of methylene blue adsorption on keratin nanofibrous membranes, J. Hazard. Mater. 268 (2014) 156–165.