

Room-temperature fabrication of core-shell nano-ZnO/pollen grain biocomposite for adsorptive removal of organic dye from water

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Abstract

A new core-shell nano-ZnO/pollen grain (n-ZnO/PG) biocomposite have been successfully synthesized *via* simple and low-temperature two-step liquid precipitation method. The synthetic strategy consists of grafting the surface of pine pollen grains (PG) with Zn^{2+} -organic complexes followed by a treatment in $\text{Zn}(\text{CH}_3\text{COO})_2/\text{NaOH}$ solution, thus producing a closed n-ZnO shell around the organic core, with a thickness of ~ 450 nm. Scanning electron microscopy, X-ray diffraction, FTIR, XPS and UV-vis spectroscopy measurements along with N_2 adsorption/desorption were used to characterize the resulting n-ZnO/PG biocomposite. The as-prepared core-shell microparticles are meso-/macro-porous with BET surface area of $25 \text{ m}^2 \text{ g}^{-1}$ and total pore volume of $0.26 \text{ cm}^3 \text{ g}^{-1}$. The adsorption properties of n-ZnO/PG were evaluated through adsorption of Malachite Green (MG) from aqueous medium at room temperature (25°C). For the sake of comparison, the physico-chemical and adsorptive properties of the raw PG and pure n-ZnO were also examined. Results indicate that n-ZnO/PG is the most favorable for the adsorption of MG under the conditions used in this study. The adsorption kinetic data for PG, n-ZnO and n-ZnO/PG follow the pseudo-second order equation and the maximum adsorption capacity follows an order of $\text{n-ZnO/PG} > \text{n-ZnO} > \text{PG}$. For n-ZnO/PG an adsorption uptake up to 145.9 mg g^{-1} is observed. The as-prepared core-shell biocomposite material is a promising cost-effective and environmentally friendly adsorbent due to its textural properties, surface chemistry, adsorption capacity and recyclability.

Keywords: Zinc oxide; Pollens; Core-shell microparticles; Adsorption; Organic dyes

1. Introduction

There is a continuous concern of the increased environmental pollution of aqueous media. Among the common contaminants in the industrial wastewater are dyes, heavy metals, organic matters, pesticides and pharmaceuticals [1]. Dye-containing effluent is a significant source of water pollution. Dyes are used in textile, paper, printing, carpet, leather, tanning, rubber, plastics, food and cosmetic industries. Synthetic dyes are a serious health hazard since they easily give rise to the carcinogenicity, teratogenicity, and even mutagenicity due to the high toxicity [2,3]. Various physico-chemical methods like solvent extraction, coagulation, photocatalytic degradation and biodegradation are used for their removal [4]. Among these, adsorption is conventional but efficient technique for dye removal [5]. Adsorption is a very attractive technology because of its high efficiency, low process cost, simplicity of design and ease of operation. Activated carbon is the most widely used adsorbent but alternative cost-effective and non-conventional adsorbents including natural materials, nanoporous silica, porous metal oxides and hydroxides, as well as waste materials from industry and agriculture have also been proposed [4-11].

Nanostructured metal oxides are increasingly finding applications as adsorbents for the removal of dyes from solution [12]. The advantages of using nanomaterials are mainly associated with their large specific surface area, high surface-to-volume ratio and high reactivity. Inorganic oxide materials with porous architecture are especially attractive as adsorbents because these structures are beneficial to transfer reactants to the active sites. A variety of efficient, cost-effective and environmentally friendly oxide-based nano-adsorbents, such as Fe_3O_4 [13], MgO [14], SnO_2 [15], CuO [16], TiO_2 [17], ZnO [15,18,19] and their composites have been developed. Among oxide nanoparticles, ZnO is one of the most intensively studied material due to its unique

properties, such as high chemical, thermal and mechanical stability, low toxicity, biocompatibility, biodegradability and wide variety of particle morphologies [20]. As reported recently, ZnO demonstrates suitable sorption properties toward heavy metal ions in wastewater [21] and, furthermore, exhibits efficient adsorption performance for the removal of dyes, such as Malachite Green Oxalate [15], Remazol Brilliant Blue R [19], C.I. basic blue 41 [22] and Congo red [23].

Herein, we present a facile method for the fabrication of ZnO-coated scots pine (*Pinus sylvestris* L.) pollens at room temperature. The advantages of applying pollens as substrates are that they are inexpensive, environmentally benign and renewable biomaterials with chemically resistant outer surface and uniformity in particle size. The outer pollen wall, known as the exine, consists primarily of sporopollenin, a solvent-resistant polymer composed of long-chain fatty acids and oxygenated aromatic and phenylpropanoid residues [24]. This stability suggests that pollen grain could be used as a core biomaterial to produce differently coated microparticles for technological applications, promoting their durability and functionality.

The main goal of the present work is to develop a new type of nano-ZnO core-shell adsorbent for dye removal by using low-cost pine pollen grains as templates. The nano-ZnO/pine pollen grain (n-ZnO/PG) biocomposite microparticles were prepared *via* simple and low temperature two-step liquid precipitation method. We first immersed the pollen grains (PG) in zinc acetate ($\text{Zn}(\text{OAc})_2$) water solution to tune the grains' surface. The as-obtained Zn^{2+} -organic complexes are essential for the subsequent growth of nanostructured ZnO coatings in the solution of NaOH as a precipitating agent, and $\text{Zn}(\text{OAc})_2$, as a source of zinc. The first part of the paper presents comparative results on the microstructure, chemical, optical and textural properties of the newly synthesized n-ZnO/PG, PG and pure nano-ZnO (n-ZnO). After that, the possible formation mechanism of the organic/inorganic core-shell architecture of the biocomposite microparticles was

discussed. The adsorption properties of the n-ZnO/PG were evaluated in the third part of the paper through adsorption of Malachite Green (MG), a cationic triphenylmethane dye, from aqueous solution at room temperature (25 °C). For the sake of comparison, the adsorptive properties of the raw PG and n-ZnO were also examined. The results of this work highlight the feasibility of utilizing pollen as a bio-organic template and the potential for designing pollen-derived microparticles as functional composite materials.

2. Experimental

All the reagents involved in the experiments were of analytical grade and were used without any further purification. Pine pollen grains were thoroughly rinsed in ethanol and bi-distilled water and then dried at room temperature for 24 h. The growth of nano-ZnO coatings on the surface of PGs was accomplished *via* simple two-step process. At first step, 0.15 g pollen grains were rinsed in 100 ml 0.2 M Zn(OAc)₂ water solution (4.4 g dissolved Zn(OAc)₂·2H₂O) for 2 h under magnetic stirring. After that, 0.5 M NaOH aqueous solution was gradually added until a pH value of 12 was reached and the as-obtained solution was continuously stirred for 1 h at room temperature. The final product was filtered through 0.22 μm Millipore membrane filter in order to separate the biocomposite microparticles from the attendant pure n-ZnO. Finally, n-ZnO/PG was washed with bi-distilled water and ethanol and dried in air at room temperature for 24 h. Pure n-ZnO was synthesized *via* precipitation from Zn(OAc)₂/NaOH solution following the second step of the above mentioned procedure.

The morphology and microstructure of the samples were examined by scanning electron microscopy (SEM, JEOL 5510) applying gold coating before the observations. Powder X-ray diffraction (XRD) patterns were recorded at room temperature on the Bruker D8 Advance

diffractometer using CuK α radiation. The Fourier transform infrared (FTIR) spectra (KBr pellets) of the studied samples were recorded between 4000 and 400 cm⁻¹ by using Nicolet 6790 FT-IR (Thermo Scientific) spectrometer. The XPS studies were carried out on an ESCALAB MK II (VG Scientific) system with base pressure of 1.10⁻⁸ mbar. The XPS spectra were taken using an unmonochromatized Mg K α source (h ν =1256.6 eV) with the sample surface positioned normal to the detector. The photoemission spectra have been fitted into spectral components using Lorentzian line shapes convoluted with a major Gaussian contribution as model functions. The UV-Vis spectra were recorded using Evolution 300 Thermo Scientific spectrophotometer.

The texture characteristics were determined by low-temperature (77.4 K) nitrogen adsorption in a Quantachrome Instruments NOVA 1200e (USA) apparatus. The nitrogen adsorption-desorption isotherms were analyzed to evaluate the following parameters: the specific surface areas (S_{BET}) were determined on the basis of the BET equation, the total pore volume (V_t) was estimated in accordance with the Gurvich rule at a relative pressure close to 0.99. Pore distributions were made by the desorption branches of the isotherms using Barrett-Joyner-Halenda (BJH) method. All samples were outgassed for 16 h in vacuum before the measurements.

Malachite green (MG) was chosen as a study model in the adsorption experiments. The adsorptive performance of PG, n-ZnO and n-ZnO/PG samples were evaluated by measuring the adsorption of MG from aqueous solution in the dark at room temperature (25 °C). The experiments were carried out in a set of 250 mL Erlenmeyer flasks containing 0.05 g of the sample and 150 mL MG solution (50 mg L⁻¹). The flasks were capped and agitated at 120 rpm. MG concentrations in the supernatant solutions were measured spectrophotometrically. The adsorption capacity was calculated using the following equation:

$$q_t = (C_0 - C_t)V/m \quad (1)$$

where C_0 and C_t (mg L^{-1}) are the concentrations of MG dye at initial and any time t , respectively. V (L) is the solution volume and m (g) represents the mass of adsorbent. The removal efficiency was calculated as follows:

$$\text{removal (\%)} = (C_0 - C_t)100/C_t \quad (2)$$

3. Results and discussion

3. 1. Microstructure and physico-chemical characterization

The insert of Fig. 1a depicts SEM panoramic view of the raw pollen grains and in Fig. 1a a high magnified image of a single PG (equatorial profile view) is displayed. As shown, the grains exhibit a typical ellipsoidal morphology with mean average size of 40 μm , which consists of a body (labeled 1 in the figure) with two laterally-placed bladders (labeled 2). The SEM close-up views of the body and bladders, shown in Fig. 1b and c, reveal the very rough sculpture of the body and the reticulate pattern of the bladders. In contrast, the SEM image of a n-ZnO/PG biocomposite microparticle shows none of these features (Fig. 1d). It could be seen that after coating procedure, the surface features of the PG disappeared and the irregular and shaggy morphology of n-ZnO/PG is obvious. This remarkable difference in morphology suggests nearly complete wrapping of the PG with ZnO. Furthermore, a color change of the pristine PG from yellow to light grey can be clearly observed as a result of our synthesis procedure. The high magnification SEM images of n-ZnO/PG (see Fig. 1e and f) show that the pollen matrix is coated with continuous porous film constructed of many irregularly shaped and randomly arranged platelets with a wide size distribution from 50 nm to 400 nm. Furthermore, large aggregates attached to the primary ZnO

shell are also observed. SEM image of the cross section of a bladder from ZnO-covered PG is shown in Fig. 1g. Along with the internal honeycomb-like structure, the peripheral ZnO cover is also visible in the micrograph. The close-up view of the ZnO coating (Fig. 1h) reveals that the ZnO nanoparticles are firmly anchored to the PG exine, forming a closed shell around the organic core with a thickness of ~450 nm. The SEM image of pure n-ZnO prepared following the same procedure but without addition of PG is shown in Fig. 1i. As one can see, the n-ZnO differ considerably in shape and size from the platelets observed in the SEM images of n-ZnO/PG. The as-synthesized ZnO nanoparticles are spherical with a mean diameter of 55.6 nm (standard deviation 13 nm).

The X-ray diffraction results confirm the formation of n-ZnO shell around the PG. XRD pattern of n-ZnO/PG is displayed in Fig. 2a and shows that the nanoparticles in the biocomposite coatings are of ZnO wurtzite type hexagonal structure and all the diffraction peaks agreed with the reported data (JCPDS no. 36-1451) and no characteristic peaks were observed other than ZnO. The average crystallite size, calculated by Sherrer equation from the most intensive peak located at $2\theta = 36.33^\circ$ is found to be 63 nm. The XRD pattern of the pure n-ZnO is also shown in Fig. 3a and the XRD-derived average crystallite size equals to 46 nm.

Formation of ZnO on the surface of the PG was also verified by Zn2p XPS scans. The Zn2p core-level spectra of n-ZnO/PG and n-ZnO are compared in Fig. 2b and, as shown, they are essentially identical. Zn2p_{3/2} and Zn2p_{1/2} peaks of the Zn2p doublet located at 1018.4 eV and 1041.4 eV are detected for each sample. In both cases, the spin orbit splitting of 23 eV for Zn2p_{3/2} and Zn2p_{1/2} is observed, which is in accordance with the literature value for ZnO [25,26]. The O1s XPS spectra of n-ZnO/PG and n-ZnO are shown in Fig. 2c. For n-ZnO/PG, the deconvolution procedure shows the presence of several chemistries of oxygen. The component O_I

at ~530 eV is typical for O^{2-} ions in fully oxidized, stoichiometric environment of ZnO [27,28]. The one at ~531.1 eV (O_{II}) is associated with O^{x-} ions ($x < 2$) in the oxygen-deficient regions within the ZnO matrix and is related to oxygen vacancies [28]. As shown, the O1s spectrum of n-ZnO/PG contains a large component at ~532.2 eV (O_{III}), which is typically attributed to chemisorbed oxygen, dissociated oxygen, or OH^- groups on the surface [28]. These three spectral components are also present in the fitted O1s spectrum of n-ZnO (Fig. 2c). Finally, the spectrum of n-ZnO/PG shows an additional component at ~533.3 eV (O_{IV}) ascribed to oxygen-containing species from the surface of PG (see below). Remarkably, the intensities of the first three peaks observed in the O1s photoemission spectra of n-ZnO/PG and n-ZnO shown in Fig. 3c differ significantly. The area ratio of $O_I/(O_I + O_{II} + O_{III})$ related to the Zn-O bond in ZnO is 22.4 for the n-ZnO/PG, and 50.9 for the n-ZnO. The higher concentration of oxygen vacancies and chemisorbed species in n-ZnO/PG could be attributed to the differences in the initial nucleation and growth processes of ZnO onto PG surface compared to n-ZnO.

Fig. 2d illustrates the FTIR spectrum of n-ZnO/PG along with the spectrum of the pure n-ZnO. FTIR spectra of the samples show similar bands with some intensity variations. The broad bands observed at ~3425 cm^{-1} indicate the existence of free and intermolecular bonded hydroxyl groups. The spectra show an increase in the intensity of the band at 3425 cm^{-1} for n-ZnO/PG, thus implying a higher concentration of hydroxyl group in the core-shell biocomposite. The band at 2924 cm^{-1} and its shoulder at 2853 cm^{-1} are attributed to the C-H stretching and bending vibrations, respectively. The bending at ~2370 cm^{-1} is because of absorption of CO_2 molecules present in air [29]. In the lower frequency range (600-1800 cm^{-1}) the peaks can be attributed to the different residual groups and reaction byproducts. The peaks at 1632 cm^{-1} and at 1385 cm^{-1} represent the asymmetric and symmetric stretching of acetate species [30,31], whereas peak at 1525 cm^{-1}

represents C=O stretching mode [32]. The band around 1050 cm^{-1} is attributed to the stretching mode of C–O bond [33] and the peak observed at 900 cm^{-1} can be attributed to the C–H out of plane bending [32]. Finally, the peak located at $\sim 440 \text{ cm}^{-1}$ is assigned to the characteristic stretching mode of Zn–O bond [34].

Fig. 2e presents UV-Vis absorption spectra of n-ZnO/PG and n-ZnO. As shown, the optical absorption region due to ZnO nanoparticles appears in the range 300-360 nm. This region is broader for n-ZnO/PG (see the insert of Fig. 2e), thus indicating the broader size distribution of oxide nanoparticles in the biocomposite shell. The absorption at visible wavelengths increases for n-ZnO/PG, consistent with the light grey biocomposite powder color. In addition, the larger absorption in the visible-NIR absorption ($\lambda \geq 400 \text{ nm}$) of n-ZnO/PG can be associated with the larger number of oxygen vacancies in the n-ZnO shells [33], as revealed by O1s XPS spectra. The corresponding band gaps (E_g) of the samples were calculated using Tauc plots, i.e. an extrapolation of $(\alpha E_{\text{photon}})^2$ vs. E_{photon} , where α is the absorption coefficient and E_{photon} is the photon energy (see Fig. 2f). The E_g values of n-ZnO/PG and n-ZnO are found to be 3.27 eV and 3.31 eV, respectively. The observed red shifts in the band gaps of our samples from the bulk band gap energy of ZnO (3.37 eV) [33] is attributed to the size confinement effect. The variation between the band gap values of n-ZnO/PG and n-ZnO may also be caused by the differences in grain boundary, defects and impurities in the samples.

Fig. 3 compares the N_2 adsorption-desorption isotherms and the BJH pore size distributions (PSDs) of PG, n-ZnO and n-ZnO/PG. The related textural parameters modelled from the adsorption data are summarized in Table 1. As shown, the raw pollen grains are poorly porous, bearing a small S_{BET} value of 3 $\text{m}^2 \text{ g}^{-1}$ and low total pore volume (0.01 $\text{cm}^3 \text{ g}^{-1}$). The PSD curve of the sample is multimodal and shows the presence of narrow pore size distributions at $\sim 3.6 \text{ nm}$,

~4.5 nm and ~6.2 nm (see the insert of Fig. 3b). n-ZnO/PG and n-ZnO materials show type IV isotherms according to the classification of IUPAC, whose characteristic features are type H3 hysteresis loops in the higher partial pressure range ($P/P_0=0.44-0.99$), deriving from nanoparticle aggregates with slit-shaped pores. Furthermore, the adsorption branches of the isotherms show type II due to the presence of macropores. A closer inspection of the N_2 adsorption-desorption isotherms (insert of Fig. 3a) reveals differences in the porous structure of n-ZnO/PG and n-ZnO. Namely, n-ZnO/PG exhibits an additional small hysteresis loop at $P/P_0=0.11-0.35$. This capillary condensation loop represents the mesoporosity confined in the framework of the material. As shown in Table 1, the S_{BET} of n-ZnO ($40 \text{ m}^2 \text{ g}^{-1}$) is higher than the measured value of n-ZnO/PG ($25 \text{ m}^2 \text{ g}^{-1}$) and this could be explained by the smaller size of n-ZnO particles. On the other hand, the highest values of V_t and D_p are demonstrated for n-ZnO/PG ($0.26 \text{ cm}^3 \text{ g}^{-1}$ and 41 nm, respectively). As can be seen from Fig. 3c and d, the PSD curves of n-ZnO/PG and n-ZnO exhibit a multimodal porosity with a narrow pore size around 3.8 nm and also larger distributions centered towards higher pore sizes (~18 nm and ~50 nm for n-ZnO, and ~14 nm and ~25 nm for n-ZnO/PG). Such well-developed surfaces appear very efficient as sorption systems due to the high contact surface area and high speed transport channels (large mesopores and macropores).

3. 2. *Formation mechanism*

As established earlier, when NaOH reacts with zinc salt precursors in aqueous solution, the product $Zn(OH)_2$ is dissolved in superfluous OH^- and $Zn(OH)_4^{2-}$ is formed [35,36]. The as-prepared $Zn(OH)_4^{2-}$ is then converted to ZnO nanoparticles at pH values between 8.5 and 12.5 [36]. The size and shape of the as-obtained nanoparticles depend on the zinc salt, pH, temperature and reaction time [37,38]. Obviously, our synthesis procedure enables the nucleation of the oxide nanoparticles on the surface of $Zn(OAc)_2$ -pretreated PGs, where they grow in size during the

stirring and finally form a closed ZnO film. If the $\text{Zn}(\text{OAc})_2$ rinsing step is omitted, the surface morphology of PG is very similar to that of the starting PG and only several nanoparticles are detected, as shown in Fig. 4a and b. The latter nanoparticles are analogous to the nanoparticles of pure n-ZnO (see Fig. 1i). This observation strongly implies that the immersion of the starting grains in the $\text{Zn}(\text{OAc})_2$ solution is essential for the growth of n-ZnO shell on the surface of PGs.

FTIR measurements have been performed in order to elucidate the chemical changes of PG during $\text{Zn}(\text{OAc})_2$ rinsing step. Fig. 5a shows the FTIR spectra of the intact PG and $\text{Zn}(\text{OAc})_2$ -pretreated PG. The spectrum of PG is very similar to the FTIR spectra of pollen grains reported recently [39,40]. The main signals from lipids, proteins and sporopollenin present on the PG surface are observed at 3400 cm^{-1} (hydroxyl groups), 1745 cm^{-1} (C=O stretch from carboxylic acids and esters), 1650 cm^{-1} (C=O stretch from amides), 1436 cm^{-1} (CH_2 deformation) and 1060 cm^{-1} (C–O stretch from carboxylic acids, alcohols and esters). In addition, the sporopollenin bands at 1515 cm^{-1} and 1172 cm^{-1} (marked with asterisks) can be associated with the vibrations of aromatic rings [40]. FTIR spectrum of Zn^{2+} -grafted PG (Fig. 5a) is similar to the spectrum of initial PG, but characterized by changes in intensity and shift in position of the peaks due to metal sorption. The first change is the attenuation of the intensity and shift of the peak at 3430 cm^{-1} , indicating a decrease of the free hydroxyl group on the grains. The minor shift of the peaks at 1745 , 1650 and 1060 cm^{-1} to lower wavenumbers suggests the involvement of the C–O group in metal binding as well. These changes can be explained by the formation of Zn^{2+} -organic complexes with carboxyl and hydroxyl groups present on the surface of PG.

The surface chemistry of the raw PG and of $\text{Zn}(\text{OAc})_2$ -pretreated PG is also monitored by Zn2p and O1s XPS, as shown in Fig. 5b and c. As can be seen, the Zn2p_{3/2} spectrum of $\text{Zn}(\text{OAc})_2$ -pretreated PG contains a signal centered at $\sim 1021.6\text{ eV}$. Since the binding energy of Zn^{2+} in zinc

acetate dihydrate is much higher, i.e., 1026.3 eV [41], we attribute this peak to the Zn^{2+} complexation in a coordination type of compound on the surface of PG. A similar $\text{Zn}2p_{3/2}$ peak with a binding energy of about 3.3 eV higher than that of pure ZnO was previously observed by Bazant et al. [42] after stirring α -cellulose in $\text{Zn}(\text{OAc})_2$ solution. They assigned this photoemission signal to the binding of Zn^{2+} to various carboxyl, carbonyl, aldehyde, acetal and alcohol groups on the α -cellulose surface. The O1s spectrum of PG (Fig. 5c) is essentially composed by a broad peak centered at 532.7 eV, which contains photoemission signals from oxygen in the C–OH, C–O, and O–C–O species, present on the PG surface [43]. This peak is also present in the spectrum of $\text{Zn}(\text{OAc})_2$ -pretreated PG, as revealed by the deconvolution procedure. The latter spectrum also contains two Gaussian components at 534.6 eV and 533.6 eV. The first one is associated with adsorbed H_2O from the environment, while the low energy peak can be ascribed to the Zn-coordinated oxygen atoms. This result is analogous to the high-energy shift of the O1s signal observed for the terephthalic acid coordination bonding with Cu surface [44] and demonstrates that the metal-organic coordination interactions lead to the formation of Zn^{2+} -organic complexes on the PG surface.

On the basis of our microscopy and spectroscopy results, one can conclude that during the $\text{Zn}(\text{OAc})_2$ rinsing step the adsorption of Zn^{2+} onto the PG *via* complexation with carboxyl and hydroxyl functional groups occurs. In the $\text{Zn}(\text{OAc})_2/\text{NaOH}$ solution, the as-formed PG– Zn^{2+} complexes serve as a seed layer for the formation of surface-stabilized $\text{Zn}(\text{OH})_2$. According to Xu and Wang [45] at higher OH^- concentration $\text{Zn}(\text{OH})_2$ converts to intermediate $\text{Zn}(\text{OH})_4^{2-}$ agglomerates. Due to dehydration of the complex in the alkaline medium (pH=12), wurtzite type (tetrahedral coordination) ZnO domains are then nucleated in the central region of the aggregates. It has been proposed that once the growth of ZnO is initiated, the remaining parent $\text{Zn}(\text{OH})_2$ serves

as a template holding the ZnO microcrystals until its complete dissolution [46]. As the reactions continue, more ZnO clusters appear and when the solution becomes supersaturated, particles grow in size and finally combine to produce closed shells around the PG. These reactions can be expressed as follows:



The formation mechanism of PG-nZnO is shown schematically in Fig. 6. Two aspects are worth pointing out: first, our results clearly show that the Zn^{2+} -functionalized surface of PG directly determines the structural characteristics of n-ZnO layers and thereby the textural properties of the entire biocomposite; second, the room-temperature synthetic strategy keeps the construction of PG intact in the final organic-core/inorganic-shell configuration of the biocomposite microparticles.

3. 3. MG adsorption

Although several countries have banned using MG due to carcinogenic, genotoxic, mutagenic, and teratogenic properties [47], it is still being used in fish farming industry and for dyeing silk, wool, jute, leather and cotton because of its low price and availability [47]. Thus, there is a constant need of developing novel cost-effective adsorbents for MG removal. PG, n-ZnO and n-ZnO/PG powders were tested in the liquid phase adsorption of MG at room temperature (25 °C) and pH of 6.6. Fig 7 displays UV-Vis spectra of MG at different time intervals and, as can be seen, the absorbance intensity at the maximum wavelength (617 nm) decreases with increasing agitation

time for all three samples. The dye removal efficiencies by PG, n-ZnO and n-ZnO/PG as a function of time are presented in Fig. 7d. Apparently, n-ZnO/PG demonstrates highest removal efficiency of 97.3%. The removal efficiency of n-ZnO for MG from aqueous solution reaches 91.9%, while for PG sample it reaches only 36.8%. Furthermore, the time profile of MG adsorption on PG differs significantly from the profiles of n-ZnO and n-ZnO/PG. The adsorption rates of the n-ZnO and n-ZnO/PG are extremely fast during the first 2 min, due to the adsorption of the MG molecules on the external surface of the particles. After that, there is a slight increase in adsorption with increase in time and, as shown in Fig 7d, equilibrium is reached after 180 min of contact time for both samples. The slow adsorption stage can be associated with the low diffusion of dye molecules into the porous structure of the adsorbents because most of the surface area of the particles is covered by the MG molecules and no more external sites are available for the adsorption. In contrast, PG demonstrates slower adsorption rate with maximum uptake reached after 60 min. These results imply that the core-shell n-ZnO/PG biocomposite is the most favorable material for the adsorption of MG under the conditions used in this study. The latter can be attributed to the textural characteristics of the material, i.e., the largest average pore width and the largest pore volume.

The adsorption capacities at equilibrium are compared in Fig. 8a. The adsorption uptake of MG on PG, n-ZnO and n-ZnO/PG are 55.4, 137.9 and 145.9 mg g⁻¹, respectively. The adsorption capacity of the biocomposite for MG removal is higher than the previously reported values of ZnO nanorod-loaded activated carbons (20 and 59.17 mg g⁻¹) [48,49] and mechanochemically obtained ZnO hexagonal disks (75.18 mg g⁻¹) [50]. Furthermore, the result obtained for n-ZnO/PG is comparable with the adsorption capacity of ZnO nanoparticles (147.0 mg g⁻¹) [15], but it is lower than the adsorption capacity of ZnO: Cr nanoparticles loaded activated carbon (214.0 mg g⁻¹) [51] and ZnO-loaded activated carbon (322.58 mg g⁻¹) prepared *via* sol-gel method [52]. Nevertheless,

the newly prepared n-ZnO/PG biocomposite appears to be very attractive for MG removal from water due to its simple, eco-friendly and cost-effective fabrication process. Fig. 7b shows the adsorption capacity normalized by the S_{BET} of the samples and the MG uptake is in order of PG > n-ZnO/PG > n-ZnO. This result indicates that the pore volume/width and/or particle surface area are important, but not the only factors to determine the adsorption capacity of the samples. Based on our FTIR and XPS observations (see above), it can be assumed that the highest concentration of hydroxyl and carboxyl functional groups on the raw PG in comparison to the other samples leads to the significant electrostatic interactions between the biomass surface and the cationic dye (MG). Gong and co-authors [53] reported that surface carboxyl group is the major functional group in the adsorption of cationic dyes. The hydroxyl group is also important functional group in the adsorption of cationic and anionic dyes [53]. Thus, the surface functionality of the grains is beneficial for the adsorption performance of PG and can be considered as the reason for its highest normalized adsorption capacity. This interpretation is also applicable to the n-ZnO/PG adsorption behavior. Specifically, the biocomposite surface is more favorable for MG adsorption than that of n-ZnO because of the larger amount of hydroxyl and carboxyl functional groups, as revealed by FTIR and O1s XPS measurements (see Fig. 2).

The pseudo-first order and pseudo-second order adsorption kinetic models were applied to examine the rate of the adsorption processes and to investigate the possible adsorption mechanisms of MG removal by PG, n-ZnO and n-ZnO/PG. The pseudo-first order and pseudo-second order equations are expressed as follows:

Pseudo-first order model:

$$\lg (q_e - q_t) = \lg q_e - k_1 t \quad (7)$$

Pseudo-second order model:

$$t/q_t = t/k_2 q_e^2 + t/q_e \quad (8)$$

where q_e and q_t are the amounts of dye adsorbed (mg g^{-1}) at equilibrium and at any time t (min), k_1 and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the pseudo-first order and pseudo-second order rate constants.

Linear plots of $\lg (q_e - q_t)$ vs. t and t/q_t vs. t are shown in Fig. 9a and Fig 9b, respectively. The relevant constants calculated from the slopes and intercepts of the plots are summarized in Table 2. As shown, the experimental data of MG adsorbed by the three adsorbents fitted very well with the pseudo-second order kinetic model with the higher correlation coefficients ($R^2 > 0.999$) compared to the pseudo-first order model. Furthermore, according to the data presented in Table 2, the values of q_{model} from pseudo-second order model are closer to the values of experimentally determined adsorption capacities at equilibrium. Thus, it appears that the adsorption processes of MG on PG, n-ZnO and n-ZnO/PG obey the pseudo-second order kinetic model. This suggests that the adsorption depends on the adsorbate as well as the adsorbent and involves chemisorption [54].

Intra-particle diffusion (Weber and Morris' equation) and Bangham's model (pore diffusion) were also used to analyze the kinetic data in order to gain insight into the rate controlling steps in the adsorption systems. The linearized forms of these two models are given by the following equations:

Intra-particle diffusion model:

$$q_t = k_{\text{id}} t^{0.5} + C \quad (9)$$

Bangham model:

$$\ln q_t = \ln k_B + (1/m) \ln t \quad (10)$$

where k_{id} is the intra-particle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{0.5}$), m and k_b are the related constants of the Bangham's model. The respective graphs for the models are shown in Fig. 9 and the calculated kinetic parameters are listed in Table 2. In general, if the regression of q_t versus $t^{0.5}$ is linear and passes through the origin, the adsorption process is only controlled by the intra-particle diffusion. As observed in Fig. 9c, the straight lines obtained when fitting experimental data for PG, n-ZnO and n-ZnO/PG do not pass through the origin, indicating that in the adsorption process intra-particle diffusion is not the only rate-controlling step. Moreover, the intra-particle diffusion plot for PG demonstrates two linear portions: the first part (k_{id1}), which is a fast one, represents the early adsorption of MG, while the second part (k_{id2}) is attributed to the final equilibrium stage. The sorption data were also characterized by Bangham's equation in order to confirm that the pore diffusion as one of the rate-controlling steps. Fig. 9d and Table 2 depict the fittings of the experimental data to the Bangham's model. As shown, the obtained graphs for all three adsorbents are linear with good correlation coefficients ($R^2 > 0.944$). This result demonstrates that the contribution of pore diffusion to the mechanism of MG adsorption on PG, n-ZnO and n-ZnO/PG could not be ignored and may take part in controlling the rate of adsorption.

The recyclability of adsorbent is one of the crucial factors for its actual applications. The regeneration and reuse of n-ZnO and n-ZnO/PG were investigated using ethanol as eluent. The used adsorbents were washed for many times with pure ethanol until no green color was detected in the ethanol solution. Finally, the regenerated n-ZnO and n-ZnO/PG samples were dried at room temperature overnight. Fig. 10 shows the adsorption amount of MG over five successive adsorption-desorption cycles. It can be seen that the adsorption capacity of n-ZnO and n-ZnO/PG are 122.1 mg g^{-1} (88.5% of the removal amount in first cycle) and 133.0 mg g^{-1} (91.2% of the removal amount in first cycle) up to five cycle, respectively. This outcome indicates that n-ZnO

and n-ZnO/PG could be regenerated effectively by ethanol solution and reused for MG removal from water over multiple cycles. Besides, n-ZnO/PG biocomposite demonstrates better recyclability compared to n-ZnO which implies that the core-shell structure is sufficiently stable under the adsorption conditions used in the present study.

4. Conclusions

In the absence of any heat treatment, a novel core-shell nano-ZnO/pollen grain (n-ZnO/PG) biocomposite was successfully obtained by a facile chemical precipitation method, and confirmed by SEM, XRD, FTIR, XPS and UV-vis measurements. The meso-/macro-pore shells consist of irregularly shaped and randomly arranged platelets with sizes between 50 nm and 400 nm. A reasonable growth mechanism was proposed to elucidate their formation. The properties of the as-prepared biocomposite, the raw pollen grains and the pure nano-ZnO related to their adsorption performance for removal of cationic dye (Malachite Green, MG) from water were comparatively tested. It was found that n-ZnO/PG has a maximum adsorption capacity (145.9 mg g^{-1}) among all samples due to its suitable textural properties (BET surface area of $25 \text{ m}^2 \text{ g}^{-1}$ and total pore volume of $0.26 \text{ cm}^3 \text{ g}^{-1}$) and surface chemistry. The adsorption of MG onto the samples followed the pseudo-second-order model and the diffusion into the pores of the adsorbents was not the only rate-determining process. Overall, the combination of low-cost raw materials, facile preparation method and satisfying dye adsorption performance, makes the n-ZnO/PG biocomposite a promising material for addressing the environmental pollution caused by organic dyes.

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Figure captions

Fig. 1. SEM images of (a-c) raw PG, (d-h) n-ZnO/PG and (i) pure n-ZnO. The insert of (a) shows a panoramic view of the starting PG. (b) and (c) show higher magnification images of 2 and 1 in (a), respectively. (e) and (f) show higher magnification images of (d). (g) and (h) show SEM cross-sectional views of a bladder from a n-ZnO/PG microparticle.

Fig. 2. (a) XRD patterns, (b) Zn2p XPS spectra, (c) O1s XPS spectra, (d) FTIR spectra, (e) UV-Vis absorption spectra and (f) the band gap spectra of n-ZnO and n-ZnO/PG.

Fig. 3. (a) Nitrogen adsorption-desorption isotherms of PG, n-ZnO and n-ZnO/PG. The insert shows enlarged view of the lower partial pressure range. Pore size distributions obtained by using Barrett-Joyner-Halenda (BJH) method of (a) PG, (b) n-ZnO and (c) n-ZnO/PG.

Fig. 4. SEM images of a PG, treated in $\text{Zn}(\text{OAc})_2/\text{NaOH}$ solution without a preliminary $\text{Zn}(\text{OAc})_2$ rinsing step.

Fig. 5. (a) FTIR and (b) O1s XPS spectra of the starting and $\text{Zn}(\text{OAc})_2$ -pretreated PG.

Fig. 6. Schematic illustration of two-step synthetic strategy for the preparation of n-ZnO/PG biocomposite microparticles.

Fig. 7. Changes in the UV-Vis absorbance spectra of MG dye after different time intervals at room temperature in the presence of (a) PG, (b) n-ZnO and (c) n-ZnO/PG. Percentage removal for MG by PG, n-ZnO and n-ZnO/PG.

Fig. 8. (a) Adsorption capacities and (b) surface area normalized adsorption capacities of MG at equilibrium (25 °C).

Fig. 9. (a) Pseudo-first order, (b) pseudo-second order, (c) intra-particle diffusion and (d) Bangham's model for the adsorption of MG onto PG, n-ZnO and n-ZnO/PG.

Fig. 10. Reusability of n-ZnO and n-ZnO/PG for adsorption/desorption of MG during five cycles.