Enhanced Malachite Green uptake using chemically-modified reed-based powder: equilibrium, kinetics, mechanism, and reusability

Rim Ben Arfi, Sarra Karoui, Karine Mougir, Cyril Vaulot, Ludovic Josien, Gautier Schrodi, Laure Michelini and Achraf Ghorbal

ABSTRACT

Novel bio-adsorbents based on abundant and invasive plants such as reeds represent an original and ecological route for the development of innovative biomaterials. Sustainable, eco-efficient, and facile processes have been suggested to improve the adsorptive performances and physicochemical properties of reed particles. The morphological, textural, and physicochemical characteristics of the prepared reed-based adsorbents, namely untreated reed particles (RP), NaOH-treated RP (NaOH-RP), and sodium dodecyl sulphate impregnated RP (SDS-RP) were assessed by SEM, FTIR, XRD, BET, and TGA/DTG. The adsorptive performances of RP, NaOH-RP, and SDS-RP were evaluated for a triphenylmethane dye (Malachite Green, MG) elimination from water. The experimental results and kinetic models proved the improvement of MG uptake by modified reed-based adsorbents. The maximum MG uptake capacity of NaOH-RP and SDS-RP materials reached 82.64 and 102.88 mg g⁻¹, respectively, but it only attained a value of 75.93 mg g⁻¹ for RP at the same conditions. The used reed-based adsorbents can regenerate four times with an MG removal capacity permanently superior to 80%. Besides, their experimental data obeyed the Freundlich equation and the pseudo second-order kinetic model, indicating the heterogeneous multilayer adsorption of MG onto reed-based materials. The adsorption/desorption, kinetic, isotherm, and thermodynamic studies, and physicochemical characterisations revealed that electrostatic interactions might be the governing mechanism of MG dye adsorption onto RP, NaOH-RP, and SDS-RP. Nonetheless, interactions such as H-bonding interactions, π-π stacking interactions, and hydrophobic interactions would also exist.

1. Introduction

Dyes are commonly used in the textile, leather, and plastic industries. Effluents of these industrial activities contain significant amounts of dye residues, which reduces the...
concentration of dissolved oxygen and hinders photosynthesis by blocking light penetration in the aquatic systems [1]. Besides, the new generation of dyes resists degradation, sunlight exposure, detergents, and oxidising agents, making them hard to remove when discharged into water. Among all the existing and possibly used dye pollutants, malachite green (MG) – a triphenylmethane dye-represents a ‘good’ candidate as it is one of the most extensively used cationic dyes. Indeed, malachite green is widely used as an antifungal and antibacterial material, a textile and leather dye, a histological stain, a wound antiseptic, and an intestinal antihelminthic [2]. However, MG is a harsh water-soluble chemical with carcinogenic and mutagenic potentialable to cause respiratory toxicity, chromosomal fractures, and teratogenicity [3]. Hence, the elimination of such a pollutant from water is of extreme importance.

When aquatic systems are contaminated, human health is directly and indirectly affected. Various water treatment methods such as nanofiltration, coagulation, flocculation, photocatalysis, oxidation, ozonation, precipitation, ionexchange, Fenton technique, and adsorption [4] were thus developed for toxic dyes removal. Numerous methods have many disadvantages, such as prohibitive process cost and secondary pollutant generation. Among the previously mentioned methods, the adsorption technique is generally known as one of the most feasible processes because it is simple, energy-saving, cost-effective, and efficient in toxic pollutant elimination [5]. Recently, bioadsorbents – including agricultural by-products and invasive plants such as almond shells [6,7], olive stones [8], cinnamon bark [9], and reeds [10,11] – have been proven to be interesting for pollutants uptake, but low sorption efficiencies have limited their large-scale use. On the other hand, various techniques, including chemical grafting [12], impregnation [13], and acid or alkali treatments [14], have been proposed to modify lignocellulosic materials surface and bulk properties. Indeed, it has already been observed that raw biomaterials modification using these techniques enhances the pollutants’ adsorption efficiency.

Reeds have been used for years for heavy metal ions and metalloids sorption from aquatic systems [11,15–17]. However, the studies focusing on the uptake of dye ions by raw and modified reeds are fairly limited [10,18]. Hence, the present investigation purports to attempt to develop new green sorbents derived from invasive reeds from Tunisian wetlands. In this study, the influence of the NaOH-treated reed particles (RP) and their surface modification using sodium dodecyl sulphate (SDS) on the toxic triphenylmethane dye removal from the water was reported. To the best of our knowledge, NaOH-treated RP (NaOH-RP) and SDS modified-RP (SDS-RP) have not been explored towards cationic dyes uptake yet. The impact of parameters such as solution’s pH, initial dyeconcentration, adsorbent concentration, contact time, and temperature on MG dye uptake by RP, NaOH-RP, and SDS-RP was assessed in a batch mode process.

To further understand the MG adsorption progress and mechanisms onto RP, NaOH-RP, and SDS-RP, kinetic data by chemical reaction-based kinetic models (Lagergren pseudo 1st order, pseudo 2nd order, and Elovich), diffusion-based kinetic models (Weber–Morris intraparticle diffusion and Boyd), and isotherm data by Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich models were investigated. The thermodynamic parameters (∆G°, ∆H°, and ∆S°) were also calculated, and the recycling of MG from RP, NaOH-RP, and SDS-RP was studied. The adsorption mechanisms of RP, NaOH-RP, and SDS-RP were determined, and their differences were revealed.
2. Materials and methods

2.1. Adsorbate and chemicals

The malachite green dye (MG, Table S1) was purchased from Loba Chemie (India) and used without further purification. Methanol, acetic acid, sodium hydroxide pellets, hydrochloric acid (37%), and sodium dodecyl sulphate (SDS, Table S1) were obtained from Merck (Germany). The working solutions were freshly prepared by diluting a stock solution (1 g L⁻¹) with freshly prepared double-distilled water. The solution’s initial pH was adjusted with 0.1 N HCl and/or 0.1 N NaOH to the desired values.

2.2. Adsorbent preparation

Reed stems were collected from Oued Gabes wetland in Gabes governorate (Tunisia). Before the impregnation process, stems had been extensively washed in running tap water, followed by rinsing with distilled water several times and then crushed into small pieces. These pieces were air-dried at room temperature for one day, followed by an oven drying at 70°C overnight. The air-dried materials were subsequently milled in a Retsch SM100 mill (Retsch GmbH, Germany) and sieved using a (106 μm)-sieve. The obtained powder was dried in the oven at 70°C until constant weight and then placed in a desiccator for characterisation, adsorption experiments, and further modification. This powder was referred to as (RP).

In this study, the SDS was used to modify the RP surface. The surfactant solution’s concentration was calculated based on three times the SDS critical micelle concentration (~8.2 mmol L⁻¹). 20 g of RP was immersed in the SDS solution and stirred for one day. The mixture was then filtered and repeatedly washed with double-distilled water using vacuum filtration to remove surfactant excess until the eluent pH reached neutral. The SDS-modified RP was dried at 70°C until constant weight.

RP mercerisation was conducted onto reed stems powder. A specified amount of RP powder was immersed into 30% (wt.) NaOH solution. The mixture was stirred for one hour at 30°C. The reacted RP powder was then filtered and repeatedly washed by double-distilled water using vacuum filtration until neutral pH. The NaOH-treated RP was dried at 70°C until constant weight. The SDS-modified RP and NaOH-treated RP were denoted as SDS-RP and NaOH-RP, respectively.

2.3. Materials characterisation

The surface morphology of the prepared adsorbents was characterised by a scanning electron microscopy (SEM) technique employing an XL30 apparatus (Philips Co., Netherlands) and operated at an accelerating potential of 15 kV. The Brunauer, Emmett, and Teller (BET) surface area of the sorbents were determined by the N₂ gas adsorption-desorption method using the ASAP 2420 (Micrometrics Instrument Corp., USA) BET analyser. The X-ray powder diffraction (XRD) measurement was taken using an X’Pert Pro X-ray diffractometer (PANalytical, Netherlands) connected to monochromated CuKα radiation (λ = 1.5406 Å, 45 kV, 40 mA) at a 2° min⁻¹ scanning rate and a 0.02° step size in the 10–60° 2θ range. The adsorbents surface functional groups were determined using a
Spectrum Two (PerkinElmer, USA) Fourier transform infrared spectrometer equipped with an attenuated total reflection (ATR) attachment with a diamond crystal. Materials spectra were recorded in the 450 cm\(^{-1}\)-4000 cm\(^{-1}\) wavelength range with a 2 cm\(^{-1}\) resolution and 32 scans per sample. The MG concentrations were determined using a T80 UV-V is spectrophotometer (PG instruments LTD, United Kingdom) based on a linear calibration curve obtained by plotting absorbance towards the MG dye concentration over the desired concentration range. The thermogravimetric analysis (TGA) and the first derivative thermogravimetric (DTG) curves of RP, NaOH-RP, and SDS-RP were obtained using a thermogravimetric analyser (TGA/DSC3+, Mettler Toledo, USA). The experiments were done under an N\(_2\) atmosphere, at a flow rate of 100 mL min\(^{-1}\), and a heating rate of 10°C min\(^{-1}\) in the 30–900°C range. The solutions’ pHs were controlled by an Orion Star A211 pH metre (Thermo Fisher Scientific, USA). And, the adsorbents point of zero charge (PZC) was determined according to the method reported by Rejeb et al [19] in a previous paper.

2.4. Batch adsorption efficiency measurement

The MG uptake study was carried out by RP, NaOH-RP, and SDS-RP, using 0.1 g of the sorbent in 50 mL of the MG dye solution (100 ppm, pH 6.0). The mixture was shaken at a speed of 350 rpm at a temperature of 22°C. After specific time intervals in the 2–300 min range, solution aliquots were withdrawn, and the remaining dye concentrations were determined to evaluate the RP, NaOH-RP, and SDS-RP dye uptake capacity and equilibrium sorption time for further experiments. The impact of RP, NaOH-RP, and SDS-RP dosage, ranging from 0.2 to 12 g L\(^{-1}\) of 100 ppm MG solution, was studied. The effect of the temperature (22, 30, 40°C), the pH (4.0–10.0), and the initial MG dye concentration (25, 50, 75, 100, 200 ppm) on the sorption capacity was studied at the optimised time. All experiments were performed in duplicate, and average values were reported.

The uptake amount of MG dye per unit dry mass of RP, NaOH-RP, and SDS-RP at time t (q\(_t\)) and equilibrium (q\(_e\)) was calculated using the following expression:

\[ q_t = V \times \frac{(C_0 - C_t)}{m} \]  \hspace{1cm} (1)

where C\(_0\) and C\(_t\) (ppm) are the initial and final MG dye concentrations, respectively, V (L) is the solution’s volume, and m (g) is the (RP, NaOH-RP, or SDS-RP) mass.

The q\(_e\) can be calculated using the same equation as given above when t is equal to the equilibrium time (C\(_t\) = C\(_e\), and q\(_t\) = q\(_e\)).

The removal percentage of the MG dye (\(\eta\)) was calculated using the following expression:

\[ \eta = 100 \times \frac{(C_0 - C_e)}{C_0} \]  \hspace{1cm} (2)

2.5. Desorption study

At first, reed-based adsorbents were loaded with the MG dye at their optimised sorption conditions. The MG-loaded adsorbents were then filtered and dried before being used for desorption study. Four successive adsorption-desorption cycles were performed to
determine the repeated use of RP, NaOH-RP, or SDS-RP. The MG desorption percentage was determined using the following equation:

\[
\text{Desorption percentage} (\%) = 100 \times \frac{\text{Desorbed MG concentration} (\text{mg/L})}{\text{Adsorbed MG concentration} (\text{mg/L})}
\]  

(3)

2.6. Statistical analysis

The validity of the kinetic and isotherm models was analysed based on the computation of the linear coefficient of determination \((R^2)\), the Pearson’s chi-squared test analysis \((\chi^2)\), as well as the normalised standard deviation, \(\Delta q(\%)\)

\[
\chi^2 = \frac{(q_{e,\text{exp}} - q_{e,\text{cal}})^2}{q_{e,\text{cal}}}
\]  

(4)

\[
\Delta q(\%) = 100 \sqrt{\frac{\sum (q_{e,\text{exp}} - q_{e,\text{cal}})^2}{n_m}}
\]  

(5)

where \(q_{e,\text{exp}}\) is the experimental value of the adsorption capacity (mg g\(^{-1}\)), \(q_{e,\text{cal}}\) is the calculated adsorption capacity (mg g\(^{-1}\)), and \(n_m\) is the number of measurements. The most appropriate model can be determined when the \(R^2\) value is equal to or near one, whereas \(\chi^2\) and \(\Delta q(\%)\) are as small as possible.

3. Results and discussion

3.1. RP, NaOH-RP, and SDS-RP characterisation

3.1.1. FTIR-ATR

FTIR–ATR analysis was performed to get a better understanding of the physicochemical-surface properties of the RP, NaOH-RP, and SDS-RP pre- and post-MGuptake. The MG-free RP and SDS-RP have similar characteristic peaks corresponding to functional groups typical of lignocellulosic materials, as shown in Figure 1. The RP and SDS-RP spectra showed peaks at 3337 cm\(^{-1}\) (O-H) and 1604 cm\(^{-1}\) (asymmetric COO\(^{-}\)) \([10,20]\). These functional groups offer the possibility of interactions between the adsorbents and the

![Figure 1. FTIR spectra of RP, NaOH-RP, and SDS-RP biosorbents (a) before and (b) after MG adsorption.](image_url)
MG dye. The *SDS-RP* spectrum displays an intensification of peaks in the range of 2850–2925 cm\(^{-1}\), which can be assigned to the alkyl C-H stretching vibrations of the surfactant. This result confirms that SDS molecules are bound to the *RP* surface.

FTIR–ATR analysis allows highlighting several changes that occurred after treating *RP* with NaOH. While comparing the *NaOH-RP* spectrum with the *RP* spectrum, confirmation of the lignin dissociation from polysaccharides (i.e., the disruption of the linkages between lignin and cellulose) was provided. Indeed, the drastic attenuation of lignin and polyose characteristic bands at 1731 cm\(^{-1}\) (ketone carbonyl stretching characteristic of the p-hydroxyphenyl unit), 1604 cm\(^{-1}\) (aromatic skeletal vibrations), 1513 cm\(^{-1}\) (aromatic ring vibrations), 1371 cm\(^{-1}\) (aromatic ring and C = O stretching characteristic of the guaiacyl unit), and 1241 cm\(^{-1}\) (C – O–C stretching) allows validating the partial elimination of lignin by the mercerisation process [21]. Moreover, the *RP* spectrum showed significant peaks at 3337 cm\(^{-1}\) and 3280 cm\(^{-1}\) attributable to the intra-(3-OH…O-5) and inter-(6-OH…O-3′) molecular hydrogen bonds in the native cellulose I [22]. When treated with NaOH, the maximum absorbance of hydrogen-bonded O–H stretching is shifted to higher wave numbers (3337 cm\(^{-1}\) → 3442 cm\(^{-1}\)), proving the rearrangement of polysaccharide chains from native cellulose I to cellulose II *Figure 1a*.

Besides, the spectra of MG-loaded *RP*, MG-loaded *NaOH-RP*, and MG-loaded *SDS-RP* reflected that no significant changes took place in the sorbents surfaces after the MG uptake, which implies there is no evidence regarding the formation of any chemical bonding between MG molecules and the adsorbents *Figure 1b*.

### 3.1.2. XRD

*Figure 2(a)* displays the XRD patterns of *NaOH-RP* and *SDS-RP* powders. In total agreement with a previous Ben Arfi et al.’s XRD characterisation of *RP* [10], the *SDS-RP* material shows typical lignocellulosic materials XRD patterns, exhibiting (101), (002), and (040) cellulose I (ICDD no. 00–056-1718) crystallographic plane reflections located at 2\(\theta\) = 16°, 22°, and 34.5°, respectively.

These patterns indicate that the *RP* lignocellulosic structure was well preserved during the SDS functionalization process. One can thus say that the SDS molecules were fixed only on their surfaces [10,23]. However, the *NaOH-RP* diffractogram peaks located at 2\(\theta\) = 12° (101), 20° (10\(\bar{1}\)), 21.6° (002), and 34.5° (040) are typical of cellulose II (ICDD no.

![Figure 2](image-url). XRD patterns of (a) *NaOH-RP* and *SDS-RP* powders before dye adsorption, (b) XRD patterns of *RP*, *NaOH-RP*, and *SDS-RP* powders after MG sorption.
00–056-1717) polymorph, proving the polymorphic transformation of cellulose I to cellulose II. The XRD analyses are in good agreement with FTIR-ATR observations. Besides, the MG-loaded RP, MG-loaded NaOH-RP, and MG-loaded SDS-RP XRD patterns show that there is no substantial change observed after the MG uptake. This finding provides evidence that the MG molecules were adsorbed onto the RP, NaOH-RP, and SDS-RP particle’s surface [10].

3.1.3. SEM
We used the scanning electron microscopy (SEM) images to examine the morphology of the MG-free and MG-loaded RP, the NaOH-RP, and the SDS-RP powders. As seen in Figure 3(a), the raw RP particles have relatively smooth surface traces of impurities on the particles’ surface. Figure 3(b) shows that the SDS impregnation has considerably changed the surface morphology. Indeed, the SDS-RP surface is smoother and more regular compared with the RP surface morphology, indicating the presence of SDS molecules onto the RP surface. Besides, Figure 3(b) exhibits small cavities on the SDS-RP surface, attributable to a potential co-existence of SDS monolayer and multilayer arrangement onto the RP surface. Figure 3(c), on the other hand, reveals that after NaOH treatment, the RP surface becomes rougher and cleaner. Indeed, it is given that the raw lignocellulosic materials’ surface is composed mainly of wax, pectin, ash, lignin, and hemicelluloses enclosing the cellulose fibres, the morphological structure variation of the NaOH-RP particles may indicate a partial removal of the non-cellulosic protective layer surrounding the cellulose fibres. Furthermore, Figures 3(d-f) show that the RP, NaOH-RP, and SDS-RP surface morphologies have gained a smoother state after the MG adsorption. SEM images, for instance, demonstrate the MG molecules cover the adsorbents’ surfaces.

3.1.4. BET and BJH
The RP, NaOH-RP, and SDS-RP N₂ adsorption-desorption isotherms illustrated in Figure 4(a) clearly correspond to type II (IUPAC classification) with type H3 hysteresis loop, suggesting

![Figure 3](image-url) SEM images of the surfaces of (a) raw RP particles, (b) SDS-RP particles, (c) NaOH-RP particles, (d) raw RP particles after MG adsorption, (e) NaOH-RP after MG adsorption, and (f) SDS-RP after MG adsorption (at optimal conditions).
the presence of meso- (<2–50 nm) and macro- (<50 nm) pores [24]. In line with a previous Ben Arfi et al.'s BET characterisation of RP [10], these inverse-S shaped isotherms are very common in cellulose and lignocellulosic materials [25]. After NaOH and SDS treatment, the BJH adsorption average pore diameter of RP decreased from ~49 nm to ~38 nm and ~24 nm, respectively. This pore size reduction is probably related to the polymorphic transformation of cellulose I to cellulose II coupled with the lignin dissociation from RP polysaccharides during NaOH-RP preparation. Furthermore, these structural modifications are accompanied by an increase in the numbers of hydrogen bonds between the adjacent cellulose molecules, leading to an increase in crystallinity [26], and therefore, to a possible reduction in interfacial spaces. However, the smaller pore size of SDS-RP is ascribable to the adsorption of SDS molecules inside the RPs and macro-pores, which is expected given the SDS molecules dimensions estimated using Chem3D software (Fig. S1).

The dV/dD pore volume vs. pore diameter curves Figure 4b and Table S2 also indicate that the meso-pores made a substantial contribution to the RP, NaOH-RP, and SDS-RP total pore volume. The pore volume (cm³/g-nm) versus pore diameter (nm) curve Figure 4b illustrates apores’ maximum concentration of RP, NaOH-RP, and SDS-RP, and displays a BJH adsorption average pore diameter of ~49 nm, ~38 nm, and ~24 nm, respectively.

Besides, Table S2 indicates that the BET surface area and the BJH cumulative desorption volume of pores of RP, NaOH-RP, and SDS-RP are inferior to 1.4 m² g⁻¹ and 0.008 cm³ g⁻¹, respectively. The adsorbents’ poor porosity suggests that the contribution of pore filling in the MG dye adsorption mechanism would remain negligible. Thus, the dye ions uptake will be more efficient through interactions with specific functional groups on prepared sorbents’ surfaces than through steric hindrance [27].

3.1.5. Thermal stability and degradation
The NaOH-RP, and SDS-RP TGA and DTG curves are shown in Fig. S2. The SDS-RP thermograph could be divided into three major weight loss regions. This result is in total agreement with a previous Ben Arfi et al.'s TGA/DTG RP characterisation [10] where the first small weight loss (30–110°C) and the second weight loss (200–295°C) of RP are attributable to the evaporation of water from the material, and hemicelluloses and a part of lignin.
degradation, respectively. However, the third weight loss (295–360°C) of RPs traceable to cellulose decomposition. Despite the striking similarity between the RP and SDS-RP thermographs, the thermal stability of the SDS-RP is higher than that of RP because the onset of its thermal degradation is about 215°C. This SDS-RP thermal behaviour improvement is attributable to SDS molecules adsorption on the RP grains. The NaOH-RP thermograph shows only two weight loss regions. The sample started to decompose at 260°C. Such an increase in the decomposition temperature, compared with RP and SDS-RP, is assignable to the removal of lignin and hemicellulose after the alkaline treatment [28]. The RP, NaOH-RP, and SDS-RP thermal stabilities were also verified and compared based on 5% and 10% weight loss temperatures (T_5% and T_10% respectively), and Broido’s method. Broido’s model is a mathematical model used for the determination of activation energies (E_a) – at a constant heating rate – of materials thermal degradation processes.

The activation energies with respect to each decomposition stage are given by [29]

\[
\ln \ln \left( \frac{1}{y} \right) = \left( \frac{-E_a}{R} \right) \frac{1}{T} + C
\]

(6)

\[
y = \frac{W_f - W_\infty}{W_i - W_\infty}
\]

(7)

where R is the ideal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), W_f is the weight at temperature T, W_i is the initial weight, W_\infty is the weight at the end of pyrolysis, and C is the constant of the linear plot. The activation energy of the pyrolytic reaction is obtained from the slope (-E_a/R) of the plot between [ln ln (1/y)] versus (1/T).

For characterising the prepared materials flammability degree, the limiting oxygen index (LOI) was calculated based on the Van Krevelen equation [30] with LOI = 17.5 + 0.4×(Char Yield in wt% at 850°C).

The adsorbents 5% and 10% weight loss temperatures, activation energy, and limiting oxygen index were calculated and gathered in Table 1.

The T_5% and T_10% weight loss temperatures and activation energies confirm that the thermal stability was more significant in the order of RP < SDS-RP < NaOH-RP. Nonetheless, the LOI values indicate that the SDS-RP possesses the best flame retardance. This result can be explained by the increase in char formation, which limits the production of combustible carbon and reduces the material’s surface thermal conductivity. Considering the LOI values, RP and SDS-RP can be considered as ‘self-extinguishing’ materials (LOI ≥26) [31], and they are therefore safer compared with NaOH-RP and other various synthetic materials used to remove pollutants from aqueous solutions [32].

3.2. Determination of RP, NaOH-RP, and SDS-RP dosage effect

Fig. S3 exhibits the effect of RP, NaOH-RP, and SDS-RP dosage (from 0.2–4 g L\(^{-1}\)) on Malachite Green removal. The MG dye uptake soared from 59.65% to 92.80%, 66.10% to 95.80%, and 79.44% to 99.88%, with increasing the RP, NaOH-RP, and SDS-RP concentration from 0.2 to 2 g L\(^{-1}\), respectively. This result is ascribable to the availability of a larger surface area and more active binding sites for the MG dye uptake. A downward trend in the removed MG amount per adsorbent unit weight was observed with increasing adsorbent concentrations. This result is attributable to the sorbent particles
aggregation that has led to an exposed surface area decrease and a diffusional path length increase. Hence, the minimum RP, NaOH-RP, and SDS-RP dosage corresponding to the maximum MG removal is determined to be the optimum dosage, which is 2 g L\(^{-1}\).

### 3.3. pH Effect

It is well known that the initial pH value greatly affects the aqueous chemistry and the active sites on the adsorbent’s surface [33]. The pH effect on the MG uptake by RP, NaOH-RP, and SDS-RP was studied at the 3.0–10.0 pH range. The experimental results depicted in Figure 5(a) show that the MG uptake by RP, NaOH-RP, and SDS-RP went up considerably with the pH increase from 3.0 to 7.0. Above the optimum pH (pH = 7.0), the dye removal capacity remained stable for all MG adsorbents. This result is assignable to the electrostatic attraction between the cationic dye and the negatively-charged active sites on the adsorbent surfaces above the pH (7.0). These findings are in good agreement with the determined values of adsorbents point of zero charge (pHpzc). The RP, NaOH-RP, and SDS-RP pHpzc values are equal to 6.12, 6.44, and 6.86, respectively Figure 5b. This indicates that RP, NaOH-RP, and SDS-RP surfaces acquire positive charge by protonation at pH <pHpzc (resulting in the electrostatic repulsion of pollutant cations) and negative charge by deprotonation at pH >pHpzc (resulting in the electrostatic attraction of pollutant cations) [34]. For this reason, pH 7.0 was selected for all further adsorption experiments.

### 3.4. Time effect and adsorption kinetics

To determine the sorption process kinetics and know the MG maximum removal equilibration time, the dye uptake by RP, NaOH-RP, and SDS-RP was assessed as a function of the contact time for MG solutions having concentrations varying from 25 to 200 ppm. Fig. S4 demonstrates that for all the adsorbents, the MG uptake reaction was swift at the initial 5 mins, probably owing to the external surface diffusion. However, after these 5 mins, the dye sorption process slows down considerably due to the progressive decrease in the available active sites, to finally become stable after 20 min due to active site saturation [35]. Besides, these studies revealed that an increase in the initial dye concentration does not have any significant effect on the time of reaching equilibrium.

To better understand the MG uptake by RP, NaOH-RP, and SDS-RP, chemical reaction-based kinetic models (Lagergren pseudo 1\(^{\text{st}}\)order, pseudo 2\(^{\text{nd}}\) order, and Elovich models) and diffusion-based kinetic models (Weber–Morris and Boyd models) were applied to analyse adsorption data. The chemical reaction-based and diffusion-based kinetic model equations are displayed in Table S3. The kinetic model parameters gathered in Table S4 were determined from the equations tabulated in Table S3. Based on the highest R\(-2\) squared values (close to unity) and the lowest Δq (%) and χ\(^2\) values, the best linear plot
was obtained from the pseudo 2nd order model at all the initial concentrations for all the adsorbents. Moreover, the \((q_{e,\text{cal}})\) values determined from the pseudo 2nd order kinetic model were closer to the experimental values \((q_{e,\text{exp}})\). This better fit to the pseudo 2nd order kinetic model may suggest that the rate of adsorption is more dependent on the adsorption site availability rather than the MG dye concentration in the bulk solution [36,37].

Because the overall dye removal rate is controlled by the slowest diffusion mechanism, the main mechanisms involved in the ionic pollutant adsorption process are external (molecular) diffusion, intraparticle (internal) diffusion, and adsorption. The speedy last step is often considered negligible. Thus, the dye adsorption-controlling step may be the film diffusion or intraparticle diffusion.

The data of the contact time effect were used to postulate the MG uptake mechanisms by \(RP\), \(NaOH-RP\), and \(SDS-RP\). The experimental data were fitted to the intraparticle diffusion equation and analysis results were gathered in Table S5.

Table S5 clearly illustrates that none of the adsorbents has C (intercept in the plot of \(q_{e}\) vs.\(t^{0.5}\)) values equal to zero, indicating that at all the initial concentrations for all the adsorbents, the intraparticle diffusion is not the solute-limiting step. The larger the C value, the greater the boundary layer effect. As shown in Table S5, the C values were more significant in the order of \(RP < NaOH-RP < SDS-RP\), indicating that the NaOH treatment and the SDS impregnation promote the boundary layer effect. Therefore, the Boyd model (Table S5) was used to identify the diffusional mechanism that governs the overall adsorption rate. If the \((B_{e}\) vs.\(t)\) plot is linear and passes through the origin, then the particle diffusion is the rate-limiting step. Otherwise, the adsorption process is governed by film diffusion. The table also shows that the intercept values in the plot of \((B_{e}\) vs.\(t)\) are superior to zero for \(RP\), \(NaOH-RP\), and \(SDS-RP\) at all the MG initial concentrations, suggesting that the MG dye cation transport occurred at the external surface and the film diffusion mechanism could be considered as the rate-limiting step.

### Table 3. Thermodynamic parameters for MG sorption onto \(RP\), \(NaOH-RP\), and \(SDS-RP\).

| Adsorbents | \(T \ (\degree C)\) | \(K_d\) | \(\Delta G^\circ\) (kJ mol\(^{-1}\)) | \(\Delta H^\circ\) (kJ mol\(^{-1}\)) | \(\Delta S^\circ\) (kJ mol\(^{-1}\) K\(^{-1}\)) | \(R^2\) |
|------------|----------------------|---------|----------------------------------|----------------------------------|---------------------------------|-------|
| \(RP\)    | 22                   | 7.362   | −4.899                           | −37.433                          | −0.110                           | 0.98217 |
|            | 30                   | 4.571   | −3.830                           |                                   |                                 |       |
|            | 40                   | 3.051   | −2.904                           |                                   |                                 |       |
| \(NaOH-RP\)| 22                   | 25.010  | −7.900                           | −81.666                          | −0.251                           | 0.96123 |
|            | 30                   | 8.180   | −5.297                           |                                   |                                 |       |
|            | 40                   | 3.646   | −3.368                           |                                   |                                 |       |
| \(SDS-RP\) | 22                   | 56.318  | −9.89162                         | −107.459                         | −0.332                           | 0.95847 |
|            | 30                   | 12.798  | −6.42517                         |                                   |                                 |       |
|            | 40                   | 4.466   | −3.8963                          |                                   |                                 |       |
3.5. Dye concentration effect and adsorption isotherm modelling

As shown in Fig.S4, the MG dye uptake by RP, NaOH-RP, and SDS-RP as a function of contact time for five different concentrations (25, 50, 75, 100, and 200 ppm) indicated that the number of pollutant cations adsorbed per gram of adsorbent went up with the initial concentration rise. This behaviour is ascribable to the augmentation of the driving force that overcomes the mass transfer resistance at the adsorbent-aqueous solution interface [35]. The equilibrium data for the MG uptake by RP, NaOH-RP, and SDS-RP were fitted to the linearised form of the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherm modelequations. The fitted model data are gathered in Table S6. For all the adsorbents, comparatively higher regression coefficient ($R^2$) values, and lower normalised standard deviation [$\Delta q(\%)$] and Pearson’s chi-square test ($\chi^2$) values were obtained for the Freundlich model than for the Langmuir, Temkin, and Dubinin–Radushkevich models.

As it is evident from $R^2$, $\Delta q(\%)$ and $\chi^2$ values shown in Table S6, neither the Langmuir model, assuming a dye monolayer coverage over a homogenous adsorbent surface, nor the Temkin model, assuming that the heat of adsorption declines linearly with surface coverage if extreme concentrations are neglected [38], nor the Dubinin-Radushkevich model that determines if the pollutant uptake mechanism is physical or chemical in nature suitably described the MG adsorption onto RP, NaOH-RP, and SDS-RP.

These results thus suggest that the MG uptake by RP, NaOH-RP, and SDS-RP might involve multi-layer adsorption with interactions between the cationic dye molecules, and a non-uniform distribution of sorption heat and affinities over the heterogeneous surfaces [39].

Nonetheless, the Langmuir model provides the maximum monolayer sorption capacity value, which was detected to grow from 75.93 to 82.64 mg g$^{-1}$ and from 75.93 to 102.88 mg g$^{-1}$ as the RP was NaOH-treated or SDS-modified, respectively. Besides, Table S6 shows that the Freundlich affinity coefficient ($k_F$) and Freundlich linearity index ($n_F$) are more significant in the order of RP ($k_F = 6.42; n_F = 1.18$) < NaOH-RP($k_F = 10.63; n_F = 1.24$) < SDS-RP ($k_F = 63.89; n_F = 3.41$). The Freundlich ($k_F$) coefficient reveals the affinity of dye ions to adsorbents, and thus a higher MG coefficient value indicates a better affinity.
to the modified materials. The index ($n_p$) value ranging between 1 and 10 confirmed the propitious MG cations uptake by all adsorbents.

Herein, one question can be posed, i.e., why modified reed-based sorbents show better adsorptive performance? Indeed, it is well known that materials adsorptive capacity is directly dependent on the existence of active adsorption sites [10]. Thus, the chemical treatment might have promoted the powder’s adsorption capacity as a result of either the increase in the number of active sites (e.g., hydroxyl and carboxyl groups for NaOH-RP) or the creation of new active functional groups (e.g., sulphonate anions for SDS-RP).

The $R^2$ values indicate that experimental data did not fit the Temkin and Dubinin–Radushkevich models. Indeed, for both models, the $R^2$ values remained less than 0.90. The apparent sorption energy ($E$) was determined to be equal to 0.552, 0.816, and 7.542 kJ mol$^{-1}$ for RP, NaOH-RP, and SDS-RP, respectively. The adsorption is considered chemical in nature when $E$ is in the 8–16 kJ mol$^{-1}$ range. However, lower values ($E < 8$ kJ mol$^{-1}$) indicate a physisorption process. One can therefore say that the MG uptake by RP, NaOH-RP, and SDS-RP was physical in nature.

### 3.6. Adsorptive capacity comparative study

A comparative study was conducted to determine the applicability of reed-based sorbents for MG uptake compared to other materials. The theoretical maximum monolayer adsorption capacity predicted by the Langmuir model ($q_{ml}$) and contact time are gathered in Table 2. These results unveil that the MG uptake by RP, NaOH-RP, and mainly SDS-RP requires a shorter time to attain superior sorption capacities with a smaller amount of material compared with many of previously used adsorbents.

### 3.7. Thermodynamics

The thermodynamic data for the MG uptake by RP, NaOH-RP, and SDS-RP are gathered in Table 3. The changes in Gibbs free energy ($\Delta G^0$), enthalpy ($\Delta H^0$), and entropy ($\Delta S^0$) at (295.15, 303.15, and 313.15 °K) were calculated from the $\ln K$ vs. $1/T$ plots; where $K$ is equal to $q_e/C_e$. The $\Delta G$ values calculated using ($\Delta G^0 = -RT \ln K$) had negative values, which indicates that the MG sorption on all the studied adsorbents is spontaneous and thermodynamically possible. The enthalpy change was determined to be $-37.433$, $-81.666$, and-
Figure 7. Speculated mechanisms of MG sorption on (a) RP or NaOH-RP, (b) SDS-RP, and (c) RP, NaOH-RP, or SDS-RP after a first sorbed MG layer.
107.459 kJ mol\(^{-1}\) for \(\text{RP, NaOH-RP, and SDS-RP}\), respectively, which suggests the exothermic nature of the MG uptake by all the studied adsorbents. The negative \(\Delta S^0\) values reveal a decreased randomness at the adsorbent-solution interface during the MG adsorption onto \(\text{RP, NaOH-RP, and SDS-RP}\).

### 3.8. Reusability of adsorbents

For economical and practical considerations in pollutant removal from water, an adsorbent should have good desorption and reuse properties. The studied adsorbents (\(\text{RP, NaOH-RP, and SDS-RP}\)) were subjected to consecutive cycles of adsorption (under optimal conditions) and desorption. The desorption of MG dye was performed in an eluent composed of 95% (v/v) methanol and 5% (v/v) acetic acid [40]. Figure 6 shows that the adsorption efficiency of \(\text{RP, NaOH-RP, and SDS-RP}\) after four cycles decreased by 8%, 7%, and 12%, respectively. This finding confirms previous findings by Zbair et al. [41]. These scholars rightly explained this decrease in adsorption efficiency by the structure filling mechanism. It is clearly observed that \(\text{RP, NaOH-RP, and SDS-RP}\) sorbents still possessed more than 80% MG removal capacities even after four reuse cycles. This finding would present the three adsorbents as promising materials for MG removal. Indeed, the reed-based materials can be considered economical due not only to the high abundance and low price of their precursor, but also to their good reusability. Moreover, Figure 6 shows that \(\text{RP}\) exhibited the lowest adsorption capacity and the highest desorption capacity. Conversely, the \(\text{SDS-RP}\) sorbent showed the highest adsorption capacity and the lowest desorption capacity. Hence, these findings corroborated very well with the Freundlich and Dubinin–Radushkevich isotherm results, indicating a better affinity of MG to the \(\text{SDS-RP}\) adsorbent.

### 3.9. Adsorption mechanism

The reed-based adsorbents are lignocellulosic materials composed of cellulose, hemicellulose, and lignin. These materials have similar polar functional groups such as carbonylic, carboxylic, hydroxyl, and phenolic groups, which would provide abounding active sites for cationic dyes adsorption. Furthermore, the SDS-coated reed particles were well-covered by dodecyl sulphonate anions (\(\text{C}_{12}\text{H}_{25}\text{SO}_{3}^-\)), which would confirm that sulphonate anions are one of the interaction sites.

Overall, the data obtained from the FTIR, SEM, adsorption-desorption, kinetic, isotherm, and thermodynamic studies along with the pH\(_{\text{pzc}}\) results confirm that at a pH higher than 7.0, the oppositely charged functional groups of the MG dye and the three studied adsorbents indicate that electrostatic interactions might be the underlying mechanism of the MG dye adsorption onto \(\text{RP, NaOH-RP, and SDS-RP}\). Nonetheless, interactions such as H-bonding interactions, π-π stacking interactions, and hydrophobic interactions would also exist. Adsorption experiments, for instance, revealed that when the prepared reed-based adsorbents and the MG ions have the same charge, the dye uptake is satisfied [42].

The mechanism of the MG uptake by \(\text{RP}\) and \(\text{NaOH-RP}\) shown in Figure 7(a) would be the result of: first, an electrostatic attraction between the ionised form of MG ([\text{dye}]^+-(\text{CH}_3)_2\text{N}^+) and the cellulose and hemicellulose deprotonated hydroxyl ([\text{cellulose/hemicellulose}]-\text{O}^-) and carboxyl ([\text{cellulose/hemicellulose}]-\text{COO}^-) groups; second, a stacking interaction.
between the lignin aromatic compounds (e.g., p-coumaryl, coniferyl, and sinapyl alcohols) and MG aromatic rings; third, a hydrogen bonding between the dye nitrogen atom and adsorbents hydroxylic groups; and fourth a polar-π interaction between MG benzene rings and hydroxylic groups. Bearing in mind that FTIR-ATR results confirmed the partial elimination of lignin by the mercerisation process, the electrostatic interactions, H-bonding interactions, and polar-π interactions for the MG dye sorption onto NaOH-RP would be the predominant adsorptive mechanisms. Similarly, the mechanism of the MGuptake by SDS-RP exhibited in Figure 7(b) is attributable to various interactions. Firstly, there would be electrostatic attractions between the ionised dye ([dye]−(CH₃)₂N⁺) and dodecyl sulphonate anions (C₁₂H₂₅SO₃⁻). Secondly, there could be hydrophobic interactions between the SDS tail (hydrophobic end) and the MG hydrophobic functional groups (-CH₃).

Besides, the first layer of the adsorbed MG molecules onto the studied adsorbents surfaces could act as new hydrophobic binding sites for the incoming MG ions and form hydrophobic interactions (between methyl groups of different MG molecules) or stacking interactions between the MG aromatic rings. The same phenomenon can be observed between the second layer and a hypothetical third adsorbed layer of MG molecules. This postulation can be used to describe the prediction of a multi-layer MG adsorption onto RP, NaOH-RP, and SDS-RP made using the Freundlich isotherm model Figure 7c.

4. Conclusion

Renewable resources from urban or rural wastes and agricultural residues have enormous potential for the development of high added-value sustainable bio-based materials. Among the candidates, invasive reed plants were converted into high performing and regenerative bio-sorbents. A facile, inexpensive, and ecological modification process has been proposed. In this study, NaOH treated reed particles (NaOH-RP) and Sodium Dodecyl Sulphate modified reed particles (SDS-RP) were successfully prepared and then compared with untreated reed particle (RP) performances for removing the Malachite Green (MG) dye from aqueous media. According to morphochemical characterisations assessed by SEM, FTIR, XRD, BET, and TGA/DTG, these modifications did change the bulk and surface properties of the reed-based materials, thus improving the adsorption capacity of NaOH-RP (82.64 mg g⁻¹) and SDS-RP (102.88 mg g⁻¹) compared with the RP (75.93 mg g⁻¹). The experimental data revealed that RP, NaOH-RP, and SDS-RP sorption profiles followed the Freundlich equation and pseudo 2nd order kinetic model, indicating the heterogeneous multilayer adsorption of MG onto the different studied materials. The MG removal process would be underlain by the film diffusion mechanism as confirmed by the diffusion-based kinetic models. Besides, the adsorption/desorption studies revealed that RP, NaOH-RP, and SDS-RP could be efficiently reused for MG elimination at least four times with a final sorption capacity permanently superior to 80%. The adsorption/desorption, kinetic, isotherm, and thermodynamic studies and physicochemical characterisations showed that the mechanism of the MG dye adsorption onto RP, NaOH-RP, and SDS-RP is governed mainly by electrostatic interactions. Meanwhile, other interactions would also co-exist (e.g., H-bonding interactions, π-π stacking interactions, polar-π interactions, and hydrophobic interactions). Due to these specific physicochemical surface properties, reed-based adsorbents appear to be a worthwhile biodegradable and recyclable material adept of contributing to ridding the environment of the highly contaminating dyes released in
aqueous media, which valorises the invasive reeds occupying Tunisian, European, and elsewherewetlands, and provides a new profuse, inexpensive and easy-to-design product to the water decontamination industry.

**Acknowledgments**

The author (R.B.A.) would like to express her gratitude for the funding support from the Ministry of Higher Education and Scientific Research of Tunisia through the research program (Programme d’encouragement des jeunes chercheurs – 1ère edition - 2017) - (Grant number: 18 PEJC 12-02). The author (A.G.) acknowledges the innovative work of all the scholars who have developed green materials, processes, and tools for aqueous media decontamination. Authors are also grateful to Prof. Rim Najjar for her assistance in proofreading this work.

**Disclosure statement**

On behalf of all authors, the corresponding author states that there is no conflict of interest.

**Funding**

This work was supported by the Ministère de l’enseignement Supérieur et de la recherche Scientifique Tunisien [18 PEJC 12-02].

**ORCID**

Rim Ben Arfi [http://orcid.org/0000-0002-0614-0640](http://orcid.org/0000-0002-0614-0640)

Sarra Karoui [http://orcid.org/0000-0001-8254-2417](http://orcid.org/0000-0001-8254-2417)

Karine Mougin [http://orcid.org/0000-0002-0481-1594](http://orcid.org/0000-0002-0481-1594)

Achraf Ghorbal [http://orcid.org/0000-0001-7340-3095](http://orcid.org/0000-0001-7340-3095)

**References**

[1] J.Y.C. Lim, S.S. Goh, S.S. Liow, K. Xue and X.J. Loh, J. Mater. Chem. A. 7, 18759 (2019).

[2] A.M. Aldawsari, I.H. Alsohaimi, A.A. Al-Kahtani, A.A. Alqadami, Z.E. Ali Abdalla and E.A.M. Saleh, Sep. Sci. Technol. 1 (2020). doi:10.1080/01496395.2020.1737121

[3] R. Ben Arfi, S. Karoui, K. Mougin and A. Ghorbal, Euro-Mediterranean J. Environ. Integr. 2, 20 (2017). doi:10.1007/s41207-017-0032-y.

[4] S. Karoui, R. Ben Arfi, K. Mougin, A. Ghorbal, A.A. Assadi and A. Amrane, J. Hazard. Mater. 387, 121675 (2020). doi:10.1016/j.jhazmat.2019.121675.

[5] M. Ebrahimipour, S.K. Hassaninejad-Darzi and H. Zavvar Mousavi, Int. J. Environ. Anal. Chem. 2020, 1 doi:10.1080/03067319.2020.1757085

[6] N. Maaloul, P. Oulego, M. Rendueles, A. Ghorbal and M. Diaz, J. Environ. Chem. Eng. 5, 2944 (2017). doi:10.1016/j.jece.2017.05.037.

[7] N. Maaloul, P. Oulego, M. Rendueles, A. Ghorbal and M. Diaz, Environ. Sci. Pollut. Res. (2020). doi:10.1007/s11356-020-10158-8

[8] T. Bohli, A. Ouederni and I. Villaescusa, Euro-Mediterranean J. Environ. Integr 2, 1 (2017). doi:10.1007/s41207-017-0030-0.

[9] M. Güler, S. Çetintaş and D. Bingöl, Int. J. Environ. Anal. Chem. 1, (2019). doi:10.1080/03067319.2019.1670171

[10] R. Ben Arfi, S. Karoui, K. Mougin and A. Ghorbal, Polym. Bull. 76, 5077 (2019). doi:10.1007/s00289-018-2648-8.
[11] S. Karoui, R. Ben Arfi, M.J. Fernández-Sanjurjo, A. Nuñez-Delgado, A. Ghorbal and E. Álvarez-Rodríguez, Environ. Sci. Pollut. Res. (2020). doi:10.1007/s11356-020-09493-7.
[12] S.-H. Park, S.S. Shin, C.H. Park, S. Jeon, J. Gwon, S.-Y. Lee, S.-J. Kim, H.-J. Kim and J.-H. Lee, J. Hazard. Mater. 394, 122512 (2020). doi:10.1016/j.jhazmat.2020.122512.
[13] U. Pathak, A. Jhunjhunwala, A. Roy, P. Das, T. Kumar and T. Mandal, Environ. Sci. Pollut. Res. 27, 20629 (2020). doi:10.1007/s11356-019-06014-z.
[14] N. Maaloul, P. Oulego, M. Rendueles, A. Ghorbal and M. Díaz, Environ. Sci. Pollut. Res. 27, 23447 (2020). doi:10.1007/s11356-018-3812-2.
[15] G. Bonanno and R. Lo Giudice, Ecol. Indic. 10, 639 (2010). doi:10.1016/j.ecolind.2009.11.002.
[16] M. Kumari and B.D. Tripathi, Ecotoxicol. Environ. Saf. 112, 80 (2015). doi:10.1016/j.ecoenv.2014.10.034.
[17] Z. Ren, X. Xu, S. Qi, Y. Li, B. Gao, W. Song, P. Jiang and J. Taiwan Inst, Chem. Eng. 72, 85 (2017).
[18] G.B. Kankılıç, A.Ü. Metin and İ. Tüzün, Ecol. Eng. 86, 85 (2016). doi:10.1016/j.ecoleng.2015.10.024.
[19] R. Rejeb, G. Antonissen, M. De Boeuvre, C.C. Detavernier, M. Van de Velde, S. De Saeger, R. Ducatelle, M. Hadj Ayed and A. Ghorbal, Toxins (Basel). 11, 602 (2019). doi:10.3390/toxins11100602.
[20] M. Lahouioui, R. Ben Arfi, M. Fois, L. Ibos and A. Ghorbal, Waste Biomass Valorization. 11, 4441 (2020). doi:10.1007/s12649-019-00745-3.
[21] C.E. Maepa, J. Jayaramudu, J.O. Okonkwo, S.S. Ray, E.R. Sadiku and J. Ramontja, Int. J. Polym. Anal. Charact. 20, 99 (2015). doi:10.1080/1023666X.2014.961118.
[22] A. El Oudiani, Y. Chaabouni, S. Msahli and F. Sakli, Carbohydr. Polym. 86, 1221 (2011). doi:10.1016/j.carbpol.2011.06.037.
[23] U.A. Guler, M. Ersan, E. Tuncel and F. Düğenci, Process Saf. Environ. Prot. 99, 194 (2016). doi:10.1016/j.psep.2015.11.006.
[24] R. Mohammed, H.H. El-Maghrabi, A.A. Younes, A.B. Farag, S. Mikhail and M. Riad, J. Mol. Liq. 231, 499 (2017). doi:10.1016/j.molliq.2017.02.041.
[25] J. Li, Y. Lu, D. Yang, Q. Sun, Y. Liu and H. Zhao, Biomacromolecules 12, 1860 (2011). doi:10.1021/bm200205z.
[26] N. Johar, I. Ahmad and A. Dufresne, Ind. Crops Prod. 37, 93 (2012). doi:10.1016/j.indcrop.2011.12.016.
[27] G. Xiao, R. Wen, D. Wei and D. Wu, J. Hazard. Mater. 280, 97 (2014). doi:10.1016/j.jhazmat.2014.07.057.
[28] N. Phinchika and S. Kaenthong, J. Mater. Res. Technol. 7, 55 (2018). doi:10.1016/j.jmrt.2017.04.003.
[29] A. Srima and G. Swaminathan, Bioreourc. Technol. 265, 236 (2018). doi:10.1016/j.biortech.2018.05.043.
[30] D. van Krevelen, Polymer (Guildf). 16, 615 (1975). doi:10.1016/0032-8885(75)90157-3.
[31] V.S. Srinivasan, S. Rajendra Boopathy, D. Sangeetha and B. Vijaya Ramnath, Mater. Des. 60, 620 (2014). doi:10.1016/j.matdes.2014.03.014.
[32] S. Mallakpour and V. Behranvand, Colloid Polym. Sci. 295, 453 (2017). doi:10.1007/s00396-017-4022-z.
[33] S.L. Chan, Y.P. Tan, A.H. Abdullah and S.T. Ong, J. Taiwan Inst. Chem. Eng 61, 306 (2016). doi:10.1016/j.jtice.2016.01.010.
[34] H. Kais, N. Yeddou Mezzenner and M. Trari, Sep. Sci. Technol. 55, 1984 (2020). doi:10.1080/01496395.2019.1623255.
[35] M. Yusuf, M.A. Khan, M. Otero, E.C. Abdullah, M. Hosomi, A. Terada and S. Riya, J. Colloid Interface Sci 493, 51 (2017). doi:10.1016/j.jcis.2017.01.015.
[36] M.A. Islam, A. Benhouria, M. Asif and B.H. Hameed, J. Taiwan Inst. Chem. Eng. 52, 57 (2015). doi:10.1016/j.jtice.2015.02.010.
[37] Y. Liu, Colloids Surfaces A Physicochem. Eng. Asp. 320, 275 (2008). doi:10.1016/j.colsurfa.2008.01.032.
[38] M. Saad, H. Tahir and D. Ali, Ultrason. Sonochem. 38, 197 (2017). doi:10.1016/j.ultsonch.2017.03.022.
[39] S. Motahari, B.S. Heidari and G.H. Motlagh, J. Appl. Polym. Sci. 132, n/a (2015). doi:10.1002/app.42543.
[40] S. Banerjee, G.C. Sharma, R.K. Gautam, M.C. Chattopadhyaya, S.N. Upadhyay and Y.C. Sharma, J. Mol. Liq. 213, 162 (2016). doi:10.1016/j.molliq.2015.11.011.
[41] M. Zbair, H. Ait Ahsaine and Z. Anfar, J. Clean. Prod. 202, 571 (2018). doi:10.1016/j.jclepro.2018.08.155.
[42] H. Liu, L. Chen and J. Ding, RSC Adv. 6, 48884 (2016). doi:10.1039/C6RA07567C.
[43] M.K. Dahri, M.R.R. Koooh and L.B.L. Lim, J. Environ. Chem. Eng. 2, 1434 (2014). doi:10.1016/j.jece.2014.07.008.
[44] B.H. Hameed and M.I. El-Khaiary, J. Hazard. Mater. 159, 574 (2008). doi:10.1016/j.jhazmat.2008.02.054.
[45] H. Zhang, F. Zhang and Q. Huang, RSC Adv. 7, 5790 (2017). doi:10.1039/C6RA27782A.
[46] A.S. Sartape, A.M. Mandhare, V.V. Jadhav, P.D. Raut, M.A. Anuse and S.S. Kolekar, Arab. J. Chem. 10, S3229 (2017). doi:10.1016/j.arabjc.2013.12.019.
[47] H. Zheng, J. Qi, R. Jiang, Y. Gao and X. Li, J. Environ. Manage. 162, 232 (2015). doi:10.1016/j.jenvman.2015.07.057.