

# Interpretations about methylene blue adsorption by surface modified chitin using the statistical physics treatment

D. S. P. Franco<sup>1</sup> · J. S. Piccin<sup>2</sup> · E. C. Lima<sup>3</sup> · G. L. Dotto<sup>1</sup>

Received: 18 August 2015 / Revised: 11 September 2015 / Accepted: 22 September 2015 / Published online: 26 September 2015  
© Springer Science+Business Media New York 2015

**Abstract** In this work, the adsorption of methylene blue (MB) on surface modified chitin (SMC) was studied at molecular level using the statistical physics theory. SMC adsorbent was prepared, characterized and applied for MB adsorption. Equilibrium curves were obtained at different temperatures (298, 308, 318 and 328 K) and interpreted by the statistical physics formulism. The parameters, such as, ' $n$ ' (number of adsorbed molecule(s) per site), ' $N_m$ ' (receptor site density) and ' $c_{1/2}$ ' (concentration at half saturation) were estimated and interpreted in detail. At finally, an interaction mechanism was proposed. The results revealed that the MB adsorption on SMC can be successfully represented by the statistical physics theory. The statistical physics parameters showed that the physicochemical interactions between MB and SMC are dependent of the temperature. At 298 K, the MB molecules were anchored by one or two receptor sites, in parallel to the SMC surface (probably hydroxyl and *N*-acetyl groups on the SMC surface). Otherwise, at 308, 318 and 328 K, the ' $n$ ' values higher than 1, indicated a perpendicular anchorage.

**Keywords** Adsorption · Chitin · Methylene blue · Statistical physics theory

## List of symbols

|            |   |
|------------|---|
| <i>ARE</i> | Average relative error (%)                  |
| BET        | Brunauer, Emmett and Teller method          |
| BJH        | Barrett, Joyner and Halenda method          |
| $C_0$      | Initial dye concentration (mg/L)            |
| $c$        | Equilibrium dye concentration (mg/L)        |
| $c_{1/2}$  | Concentration at half saturation (mg/L)     |
| FT-IR      | Fourier transform infrared spectroscopy     |
| $k_B$      | Boltzmann constant (J/K)                    |
| MB         | Methylene blue                              |
| $M_a$      | Adsorbed quantity (mg/g)                    |
| $M_M$      | $nN_m$ (mg/g)                               |
| $m$        | $M_a/N_a$                                   |
| $N_a$      | Number of adsorbed molecules                |
| $N_i$      | Receptor site occupation state              |
| $N_m$      | Receptor site density (mg/g)                |
| $n$        | Number of adsorbed molecules per site       |
| $n'$       | Anchorage number                            |
| $R^2$      | Coefficient of determination, dimensionless |
| SEM        | Scanning electron microscopy                |
| SMC        | Surface modified chitin                     |
| $T$        | Temperature (K)                             |
| UA         | Ultrasound-assisted                         |
| $V$        | Volume of solution (L)                      |
| $X$        | Adsorbent amount (g)                        |
| XRD        | X-ray diffraction                           |
| $Z_{gc}$   | Grand canonical partition function          |

## Greek symbols

|                  |  |
|------------------|--|
| $\beta$          | $1/k_B T$                                |
| $\varepsilon$    | Receptor site adsorption energy (kJ/mol) |
| $\mu$            | Chemical potential (kJ/mol)              |
| $\lambda_{\max}$ | Maximum wavelength of MB                 |

✉ G. L. Dotto  
guilherme\_dotto@yahoo.com.br

<sup>1</sup> Environmental Processes Laboratory (LAPAM), Chemical Engineering Department, Federal University of Santa Maria, UFSM, 1000 Roraima Avenue, Santa Maria, RS 97105-900, Brazil

<sup>2</sup> Food Engineering Department, Passo Fundo University, Br 285, km 171, Passo Fundo 99052-900, Brazil

<sup>3</sup> Institute of Chemistry, Federal University of Rio Grande do Sul, UFRGS, Porto Alegre, RS, Brazil

## 1 Introduction

Synthetic dyes, such as, methylene blue (MB) are one of the major water pollutants (Tan et al. 2015). The incorrect discharge of dye containing effluents can affect the environment from different ways, for example, decreasing the photosynthetic activity in the receptor water bodies (Yagub et al. 2014). Dyes are also carcinogenic, mutagenic, or teratogenic in various microbiological and fish species. Additionally, it can also cause severe damage to human beings, such as, dysfunction of the kidney, reproductive system, liver, brain and central nervous system (Yagub et al. 2014). Taking into account this kind of problem caused by the dyes, the scientific community has performed efforts to find efficient methods to treat colored effluents. Among all these methods (coagulation, chemical oxidation, enzymatic treatment, adsorption, photocatalysis and others), adsorption is one of the most appropriate, due to the simple operation, low energy requirements and high efficiency (González et al. 2015).

The downside of adsorption is the high cost of the activated carbon. This type of problem creates the demand for the development of new low cost adsorbents (Isah et al. 2015). In this way, different low cost adsorbents have been investigated, including, peach shells (Marković et al. 2015), processed grapes (Saygılı et al. 2015), chitin (Dotto et al. 2015a), chitosan films (Dotto et al. 2015b), *Spirulina platensis* (Dotto and Pinto 2012), montmorillonitic clay (Günay et al. 2013) and others (Salleh et al. 2011). Chitin has been reported as a great potential low cost adsorbent, being a biodegradable and renewable biopolymer (Tang et al. 2012). The chitin structure contains hydroxyl and N-acetyl groups, which allows the dyes adsorption (Vakili et al. 2014). Despite of this, chitin presents low porosity, low surface area and high crystallinity. To improve the chitin characteristics, our recent works proposed its modification by ultrasound-assisted (UA) technology. The results demonstrated that the UA treatment provided chitin with higher porosity, higher surface area and lower crystallinity, improving its adsorption characteristics (Dotto et al. 2015a, c).

Aiming to describe the adsorption of a dye on surface modified chitin (SMC), it is required the knowledge of the equilibrium behavior. This study is commonly evaluated by Langmuir, Freundlich, Redlich-Peterson, Sips, Temkin and Dubinin-Radushkevich models (Crini and Badot 2008). All these models are used to predict information about the maximum adsorption capacity, affinity and spontaneity of the adsorption process (Seallaoui et al. 2015). However, these models are not able to predict physicochemical and energetic interpretations about the adsorption phenomena. With the purpose to describe the adsorption phenomena at

molecular level, the use of physics statistic is a viable alternative (Seallaoui et al. 2015). The statistical physics is the field that relates the proprieties of microscopic elements (atoms, molecules) with the proprieties of the macroscopic material (Nakhli et al. 2014). It should be pointed that there are no studies regarding dyes adsorption on chitin using the statistical physics treatment.

The main objective of this work was to study the adsorption of MB on SMC at molecular level using the statistical physics theory. For this purpose adsorption isotherm curves were obtained at different temperatures and, a suitable model, based on statistical physics theory was used to predict the parameters ' $n$ ' (number of adsorbed molecule(s) per site), ' $N_m$ ' (receptor site density) and ' $c_{1/2}$ ' (concentration at half saturation) as a function of temperature. An interaction mechanism was also proposed.

## 2 Experimental and modeling

### 2.1 MB dye

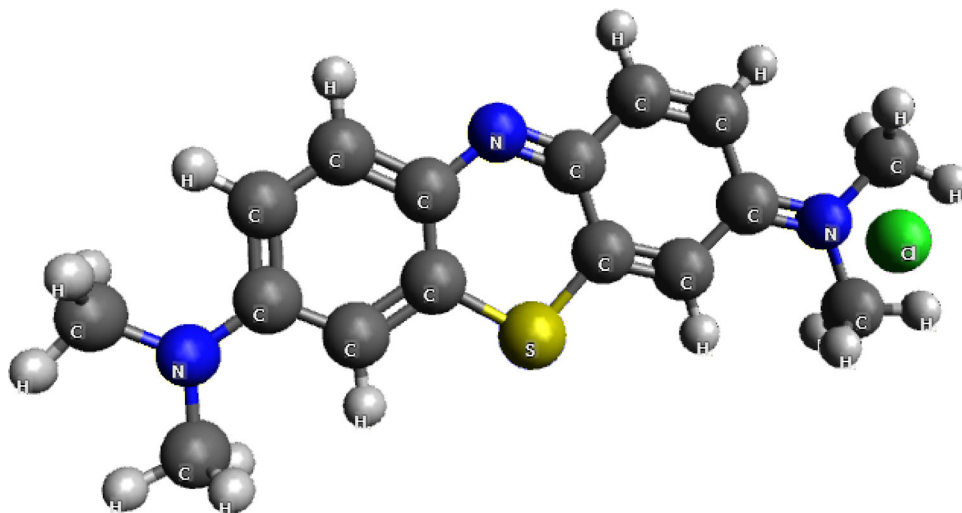
The synthetic cationic dye MB was used in this work. MB (color index 52015, molar weight of 319.8 g/mol,  $\lambda_{\max} = 664$  nm) was purchased from Sigma Aldrich with purity of 99 %. Figure 1 shows the 3D structural model of MB dye (Avogadro: an open-source molecular builder and visualization tool version 1.1.1 <http://avogadro.openmolecules.net/>). All experiments were performed with deionized water and all reagents were of analytical grade.

### 2.2 Obtention and characterization of surface modified chitin

Chitin was obtained from shrimp wastes (*Penaeus brasiliensis*), which were obtained from a seafood industry in Brazil southern (Rio Grande-RS-Brazil). To obtain the chitin biopolymer, shrimp wastes were submitted to sequential steps of demineralization, deproteinization, deodorization and drying (Dotto et al. 2011; Moura et al. 2011). After, chitin was ground until particle size ranging from 105 to 125  $\mu\text{m}$  (Wiley Mill Standard, model 03, USA). The chitin deacetylation degree was  $45 \pm 1$  %.

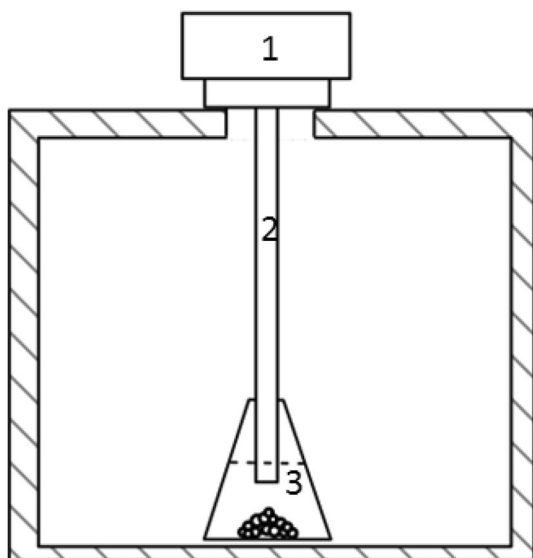
For the surface modification, 5.00 g of raw chitin were mixed with 300 mL of deionized water, being the mixture placed in an ultrasonic processor (UP400S, Hielscher, Germany) of 400 W, equipped with a titanium sonotrode. The sonication was performed at 24 kHz, cycle of 1.00, amplitude of 60 % during 1 h. These conditions were selected on the basis in previous works. At finally, chitin slurry was separated by filtration, dried (40 °C, 24 h) and stored for further characterization and use. Figure 2 shows

**Fig. 1** 3D molecular structure of methylene blue



the scheme of ultrasonic processor used for the sonication experiments.

The SMC and raw chitin were characterized by  $N_2$  adsorption isotherms using BET and BJH methods (Quantachrome Instruments, New Win 2, USA) (Brunauer et al. 1938; Barrett et al. 1951), Fourier transform infrared spectroscopy (FT-IR) (Shimadzu, Prestige 21210045, Japan) (Silverstein et al. 2007), X-ray diffraction (XRD) (Rigaku, Miniflex 300, Japan) (Waseda et al. 2011) and scanning electron microscopy (SEM) (Jeol, JSM-6610LV, Japan) (Goldstein et al. 2003). The particle diameters of SMC and raw chitin were determined using SEM images by the Image J software (NIH Image, USA) (analyze particle method) (Dotto et al. 2012).



**Fig. 2** Experimental scheme used for the ultrasonic modification: ultrasonic processor (1), sonotrode (2) and chitin/water mixture (3)

### 2.3 Batch adsorption experiments

The adsorption experiments were carried out using solutions prepared from stock solutions of MB dye. The pH was adjusted to 10.0 with 0.1 mol/L NaOH solution (Dotto et al. 2015a). The equilibrium assays were carried out in a thermostated shaker (Innova 44, New Brunswick Scientific, USA). 5.00 g/L of SMC chitin were added in Erlenmeyer flasks containing different initial MB concentrations (from 0 to 400 mg/L). The flasks were stirred at 150 rpm until the equilibrium. The experiments were performed at 298, 308, 318 and 328 K. The equilibrium MB concentration was determined by spectrophotometry (Quimis, Q108 DRM, Brazil) at 664 nm. All experiments were carried out in triplicate ( $n = 3$ ) and blanks were performed. The MB adsorbed quantity ( $M_a$ , mg/g) was calculated as:

$$M_a = \frac{C_0 - c}{X} V \quad (1)$$

where,  $C_0$  (mg/L) is the initial dye concentration,  $c$  (mg/L) is the equilibrium dye concentration,  $X$  is the adsorbent amount (g) and  $V$  is the volume of solution (L).

### 2.4 Statistical physics theory

With the purpose of apply the statistical physics treatment in the adsorption of MB on SMC, it was considered that during the phenomena, a variable number of molecules,  $c$  per unit of volume was adsorbed onto  $N_m$  receptor sites located on a unit mass of the SMC. This definition was based on Khalfaoui et al. (2003). The grand canonical partition function (Eq. 2) is a mathematical equation with describes the microscopic states of a system following the physical situation in which this system is placed (Diu et al. 1989):

$$Z_{gc} = \sum_{N_i=0}^{\infty} e^{-\beta(\varepsilon-\mu)N_i} \quad (2)$$

where,  $\varepsilon$  (kJ/mol) is the receptor site adsorption energy,  $\mu$  (kJ/mol) is the chemical potential,  $N_i$  is the receptor site occupation state and  $\beta$  is defined as  $1/k_B T$ , being  $k_B$  the Boltzmann constant ( $1.3806488 \times 10^{-23}$  J/K) and  $T$  the room temperature.

Taking into account that the adsorption of MB onto SMC is described as a type I isotherm (Dotto et al. 2015a), it was assumed that any given receptor site can be empty or occupied by one part molecule in accordance with the monolayer model (Khalfaoui et al. 2003) (Eq. 3):

$$Z_{gc} = \sum_{N_i=0}^1 e^{-\beta(\varepsilon-\mu)N_i} = 1 + e^{-\beta(\varepsilon-\mu)N_i} \quad (3)$$

Applying the definition of the adsorbed quantity expressions against the concentration of the adsorbed molecules (see elsewhere Khalfaoui et al. (2003)), the Hill model can be obtained (Eq. 4):

$$M_a = \frac{nM_M}{1 + \left(\frac{c_{1/2}}{c}\right)^n} = mN_a = \frac{nmN_m}{1 + \left(\frac{c_{1/2}}{c}\right)^n} = N_a = \frac{nN_m}{1 + \left(\frac{c_{1/2}}{c}\right)^n} \quad (4)$$

where,  $M_a$  (mg/g) is the adsorbed mass ( $M_a = mN_a$ ),  $m$  is the adsorbed molecule mass,  $N_a$  is the number of adsorbed molecules,  $n$  is the number of adsorbed molecules per site,  $M_M$  (mg/g) ( $M_M = nN_m$ ),  $N_m$  is the receptor site density and  $c_{1/2}$  (mg/L) is the concentration at half saturation.

The  $n$  parameter can be related with the anchorage number ( $n'$ ) (which represents the number of sites occupied by one molecule) by the following equation (Khalfaoui et al. 2003) (Eq. 5):

$$n' = \frac{1}{n} \quad (5)$$

For  $n < 1$  the adsorbed molecules adopt a position parallel to adsorbent surface and, for  $n > 1$ , a perpendicular anchorage occurs.

## 2.5 Parameters estimation

In this work, the statistical physics parameters, such as,  $n$ ,  $n'$ ,  $mN_m$  and  $c_{1/2}$  were determined by the fit of the model with the experimental data through nonlinear regression. The Simplex/Quasi-Newton estimation method was used and the calculations were performed through the Statistic software (Statistic 9.1, Statsoft, USA). The fit quality was measured by the coefficient of determination ( $R^2$ ) and average relative error (ARE).

## 3 Results and discussion

### 3.1 SMC characteristics

The main characteristics of SMC and raw chitin are presented in Table 1. It can be noticed in Table 1 that the values of  $S$ ,  $\varepsilon$ ,  $V_P$  and  $P_R$  were higher for the SMC than from raw chitin. The particle diameter was decreased when the ultrasound treatment was applied. This occurred because during the ultrasound treatment, cavities are formed on the liquid, and the implosion of these cavities releases liquid jets at high velocities (Price 1996), fragmenting the chitin particles.

Figure 3 shows the  $N_2$  adsorption/desorption isotherms for SMC. The  $N_2$  adsorption/desorption isotherms (Fig. 3) were similar to the type IV isotherm, according to the IUPAC classification. This shows that the SMC obtained in this work is predominantly a mesoporous material.

The FT-IR vibrational spectra of SMC and raw chitin were similar (Fig. not show), showing that the main functional groups were maintained after the ultrasound treatment. The O–H and N–H stretchings were verified at  $3300 \text{ cm}^{-1}$ .  $\text{CH}_2$  ( $3000 \text{ cm}^{-1}$ ) and  $\text{CH}_3$  ( $2800 \text{ cm}^{-1}$ ) stretchings were also observed. In the region of  $1650 \text{ cm}^{-1}$  the stretch of C=O secondary amide can be observed. The band at  $1550 \text{ cm}^{-1}$  is related to the N–H bend and C–N stretch of amide II. The right side bands ( $1020$  and  $820 \text{ cm}^{-1}$ ) are the C–O ring stretch and C–O link respectively. The NH-out-of plane was verified at  $750 \text{ cm}^{-1}$ .

In the XRD patterns (Fig. not show) diffraction planes at (020) ( $2\theta \approx 9.5^\circ$ ) and (110) ( $2\theta \approx 20^\circ$ ) of the orthorhombic crystal structure were detected for the raw chitin. For SMC, the diffraction planes were less intense, resulting in a decrease of the crystallinity, from 85 % (raw chitin) to 65 % (SMC).

Figure 4 shows the SEM images of raw chitin (a) and SMC (b). It was observed that raw chitin presented a rigid structure without pores, cavities or protuberances. Otherwise, SMC presented a surface with several cavities, protuberances and some visible pores.

As published elsewhere (Dotto et al. 2015a), these results indicated that the ultrasound treatment was appropriated to improve the chitin characteristics regarding adsorption purposes.

### 3.2 Experimental curves and model validation

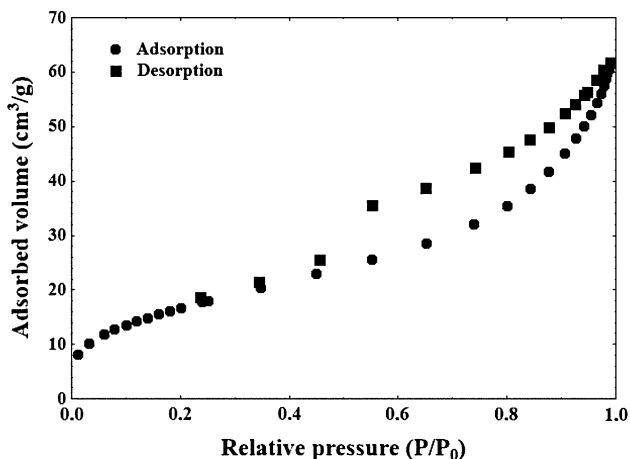
The isotherms equilibrium curves of MB adsorption onto SMC are represented in Fig. 5. It can be seen that the isotherm curves presented an initial inclined portion followed by a plateau. The initial inclined portion indicates a great number of available sites and a great affinity between



**Table 1** Characteristics of raw chitin and SMC

| Characteristic  | Raw chitin <sup>a</sup>                   | SMC <sup>a</sup>                          |
|---|---|---|
| Particle diameter ( <i>D</i> ) (μm)                       | 115 ± 10                                  | 72 ± 3                                    |
| Surface area ( <i>S</i> ) (m <sup>2</sup> /g)             | 2.3 ± 0.3                                 | 60.7 ± 2.5                                |
| Porosity ( <i>ε</i> ) (%)                                 | 0.5 ± 0.1                                 | 13.0 ± 0.2                                |
| Pore volume ( <i>V<sub>p</sub></i> ) (m <sup>3</sup> /kg) | 4.0 × 10 <sup>-6</sup> ± 10 <sup>-7</sup> | 9.0 × 10 <sup>-6</sup> ± 10 <sup>-7</sup> |
| Average pore radius ( <i>P<sub>R</sub></i> ) (Å)          | 14.7 ± 0.4                                | 38.6 ± 0.3                                |

<sup>a</sup> Mean ± standard error for n = 3

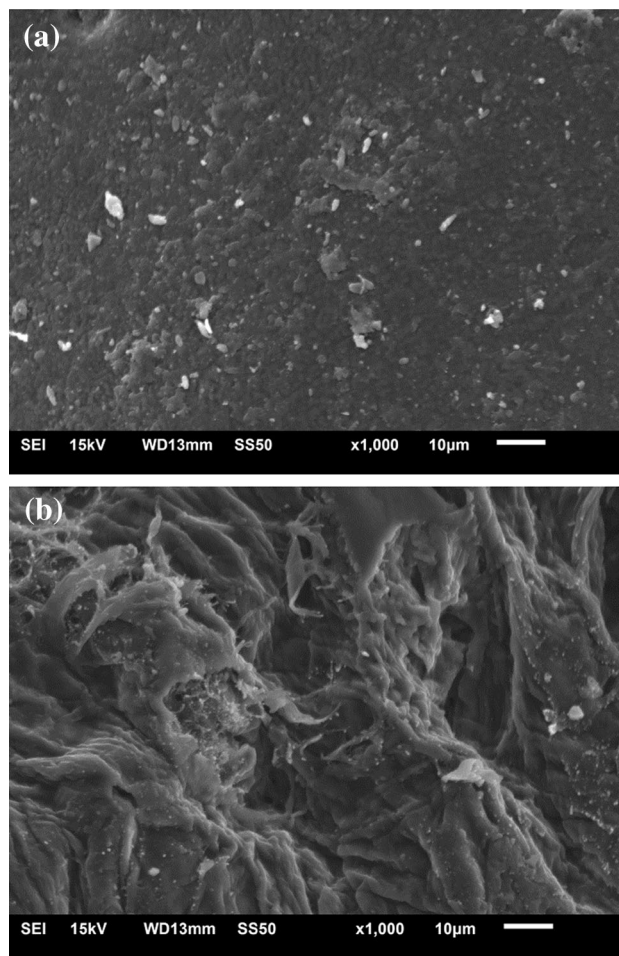


**Fig. 3** N<sub>2</sub> adsorption/desorption isotherms for SMC

MB and SMC. The plateau is relative to the maximum adsorption capacity. According to Khalfaoui et al. (2003), curves with this behavior can be classified as Type I. Based on the statistical physics treatment, the Hill model (Eq. 4) is the more adequate to represent this type of isotherm. In this way, the experimental data in Fig. 5 were fitted with the Eq. 4. The coefficients of determination (*R*<sup>2</sup>) and average relative errors (*ARE*) ranged from 0.9888 to 0.9995 and from 0.5 to 3.0, respectively. These high values for *R*<sup>2</sup> and low values for *ARE* show that the MB adsorption on SMC can be described by the statistical physics treatment. The model parameters (*n*, *mN<sub>M</sub>* and *c<sub>1/2</sub>*) were also evaluated according its significance and consistency. It was found that these parameters were significant (*p* < 0.00001) and consistent. Based on these findings, the parameters *n*, *mN<sub>M</sub>* and *c<sub>1/2</sub>* can be consistently estimated and the interpretations about the physicochemical interactions SMC–MB are possible and consistent at a molecular level.

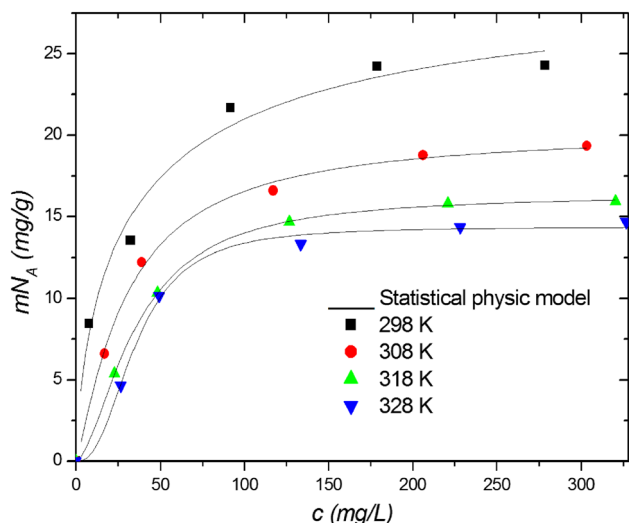
**3.3 Interpretation of the statistical physics parameters**

Figure 6 shows the dependence of *n* with the temperature. It can be verified that the number of adsorbed MB molecules per site (*n*) increased with the temperature. This can be attributed to the thermal collision (Khalfaoui et al.

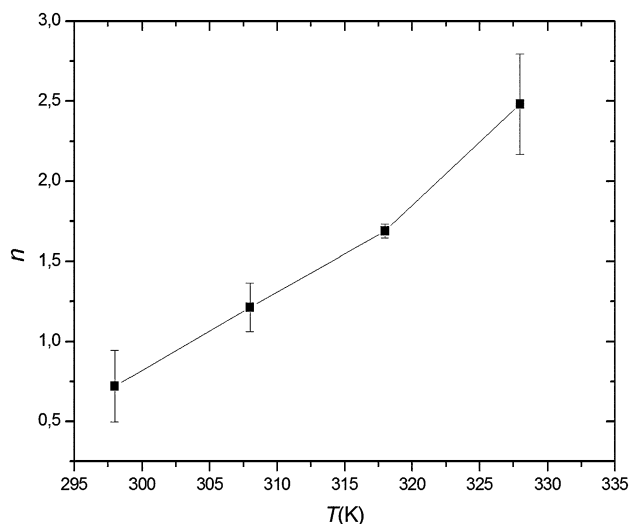


**Fig. 4** SEM images of (a) raw chitin and (b) SMC

2006). At 298 K, the *n* value was lower than 1, and consequently, the anchorage number (*n'*) was 1.38. So, it can be inferred that the MB molecules were anchored by one or two receptor sites, in parallel to the SMC surface. From the steric viewpoint, the most probable groups involved in the interactions were hydroxyl and *N*-acetyl groups on the SMC surface (Gomes et al. 2014). Otherwise, at the temperatures of 308, 318 and 328, the *n* values were higher than 1, indicating that MB was adsorbed in a perpendicular position on the SMC surface.



**Fig. 5** Equilibrium curves for the adsorption of MB on SMC at different temperatures (black square 298 K, black circle 308 K, black up-pointing triangle 318 K, black down-pointing triangle 328 K) (pH 10.0, adsorbent dosage of 5.00 g/L)

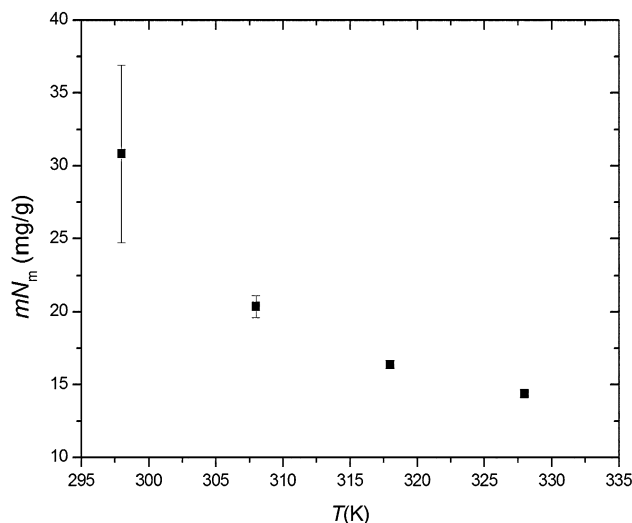


**Fig. 6** Parameter  $n$  as a function of temperature

For parallel anchorage ( $n < 1$ ), it is possible to obtain the percentage of dye molecules which are anchored by one or two receptor sites by the following relation (Knani et al. 2014):

$$n = x + (1 - x) 0.5 \tag{6}$$

being,  $x$  the percentage of molecules with a single anchorage and  $1 - x$  the percentage of molecules having two anchorages. Based on the above relation, it was found that at 298 K, 44 % of the MB molecules were anchored by one receptor site and 56 % of the MB molecules were anchored by two receptor sites.



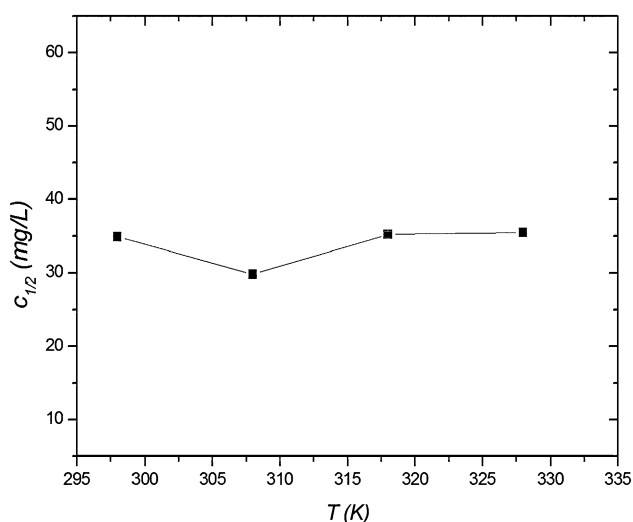
**Fig. 7** Parameter  $mN_M$  as a function of temperature

Figure 7 shows the evolution of the effectively occupied receptor sites ( $N_m$ ) as a function of the temperature. It was found that the effectively occupied receptor sites decreased with the temperature. This fact can be explained on the basis in the MB solubility. The temperature increase causes an increase in the MB solubility, so, the interaction forces between MB and the water become stronger than those between MB and SMC (Dotto et al. 2015b). These results indicated that the temperature play an important role in the occupation of the SMC receptor sites.

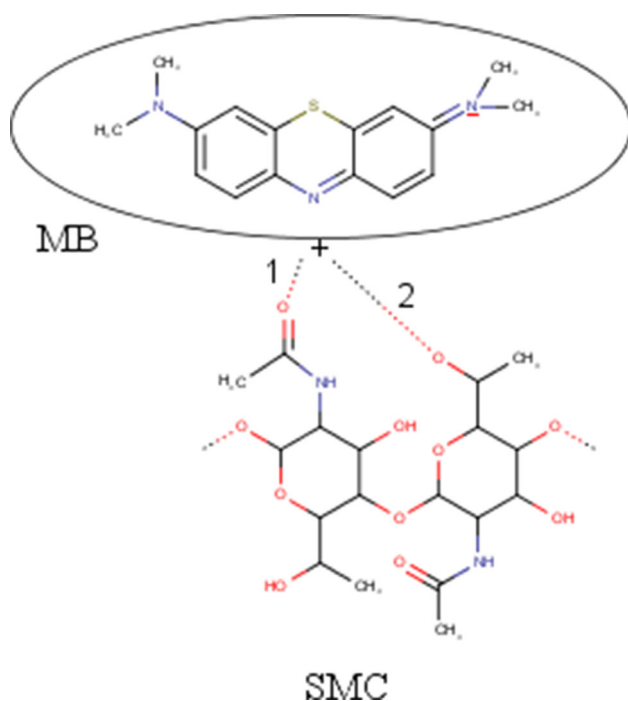
Figure 8 shows that the parameter  $c_{1/2}$  remained practically constant, indicating that, in this temperature range, MB concentration at half saturation was little influenced. Similar trends about the aforementioned parameters were found by others (Khalfaoui et al. 2006; Knani et al. 2014; Dotto et al. 2015b). In general lines, this work demonstrated three aspects: (1) the ultrasonic treatment is adequate to improve the chitin adsorption characteristics; (2) the MB adsorption on SMC can be successfully represented by the statistical physics theory; (3) the statistical physics parameters showed that the physicochemical interactions between MB and SMC are dependent of the temperature.

### 3.4 Probable interaction mechanism

Based on the statistical physics theory, FT-IR and also in the literature (Bhattacharyya and Sharma 2005; Dolphen and Thiravetyan 2011; Gomes et al. 2014; Dhananasekaran et al. 2015; Dotto et al. 2015a), it was proposed a probable mechanism for the interactions between MB and SMC at pH 10.0 and 298 K. The most probable interaction mechanism is illustrated in Fig. 9. At 298 K, 44 % of the positively charged MB molecules (the positive charge is



**Fig. 8** Parameter  $c_{1/2}$  as a function of temperature



**Fig. 9** Probable interaction mechanism between SMC and MB

located on the N or S hetero-atoms of the MB molecule) were anchored by one receptor site and 56 % were anchored by two receptor sites in parallel to the SMC surface. Coupled to this, the most probable groups of SMC involved in the interactions were hydroxyl and *N*-acetyl groups (FT-IR spectra before and after the MB adsorption presented modifications in these groups). However, at pH 10, SMC is not dissociated in anionic form and, direct electrostatic interactions are not possible. Thus the most probable interactions were: (a) weak electrostatic

interactions between the cationic dye MB and electron-rich sites of the SMC surface or; (b) weak interactions between the cationic dye MB and negative dipole induced sites of the SMC surface. For single anchorage, the MB molecules can be linked with SMC in the forms 1 or 2 (Fig. 9). For double anchorage, the MB molecules can be linked with SMC in the forms 1 and 2 (Fig. 9).

## 4 Conclusion

In this research, interpretations at molecular level about the MB adsorption on SMC were performed on the basis in statistical physics formulism. The results revealed that the statistical physics theory can be successfully applied for the adsorption system MB/SMC. The physicochemical parameters and consequently the interaction mechanism were dependent of the temperature. At 298 K, the MB molecules were anchored in parallel to the SMC surface, while, for the other temperatures, a perpendicular anchorage occurred. The hydroxyl and *N*-acetyl groups of SMC were the main responsible for the adsorption. Probably, weak electrostatic interactions between the cationic dye MB and electron-rich sites of the SMC surface occurred.

**Acknowledgments** The authors would like to thank CAPES (Coordination for the Improvement of Higher Education Personnel) and CNPq (National Council for Scientific and Technological Development) for the financial support. Furthermore, the authors would like to thank CEME-SUL/FURG (Electron Microscopy Center of South/Federal University of Rio Grande/RS/Brazil) due to the scanning electron microscopy images.

## References

- Bhattacharyya, K.G., Sharma, A.: Kinetics and thermodynamics of Methylene Blue adsorption on Neem (*Azadirachta indica*) leaf powder. *Dyes Pigm.* **65**, 51–59 (2005)
- Barrett, E.P., Joyner, L.G., Halenda, P.P.: The determination of pore volume and area distribution in porous substance I. Computations from nitrogen isotherms. *J. Am. Chem. Soc.* **73**, 373–380 (1951)
- Brunauer, S., Emmett, P.H., Teller, E.: Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **60**, 309–319 (1938)
- Crini, G., Badot, P.M.: Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: a review of recent literature. *Prog. Polym. Sci.* **33**, 399–447 (2008)
- Dhananasekaran, S., Palanivel, R., Pappu, S.: Adsorption of Methylene Blue, Bromophenol Blue and Coomassie Brilliant Blue by  $\alpha$ -chitin nanoparticles. *J. Adv. Res.* (2015). doi:10.1016/j.jare.2015.03.003
- Diu, B., Guthmann, C., Lederer, D., Roulet, B.: *Physique Statistique*. Hermann, Paris (1989)
- Dolphen, R., Thiravetyan, P.: Adsorption of melanoidins by chitin nanofibers. *Chem. Eng. J.* **166**, 890–895 (2011)
- Dotto, G.L., Cadaval, T.R.S., Pinto, L.A.A.: Use of *Spirulina platensis* micro and nanoparticles for the removal synthetic dyes

- from aqueous solutions by biosorption. *Proc. Biochem.* **47**, 1335–1343 (2012)
- Dotto, G.L., Pinto, L.A.A., Hachicha, M.A., Knani, S.: New physicochemical interpretations for the adsorption of food dyes on chitosan films using statistical physics treatment. *Food Chem.* **171**, 1–7 (2015a)
- Dotto, G.L., Pinto, L.A.A.: Analysis of mass transfer kinetics in the biosorption of synthetic dyes onto *Spirulina platensis* nanoparticles. *Biochem. Eng. J.* **68**, 85–90 (2012)
- Dotto, G.L., Santos, J.M.N., Rodrigues, I.L., Rosa, R., Pavan, F.A., Lima, E.C.: Adsorption of Methylene Blue by ultrasonic surface modified chitin. *J. Colloid Interface Sci.* **446**, 133–140 (2015b)
- Dotto, G.L., Santos, J.M.N., Rosa, R., Pinto, L.A.A., Pavan, F.A., Lima, E.C.: Fixed bed adsorption of Methylene Blue by ultrasonic surface modified chitin supported on sand. *Chem. Eng. Res. Des.* **100**, 302–310 (2015c)
- Dotto, G.L., Souza, V.C., Moura, J.M., Moura, C.M., Pinto, L.A.A.: Influence of drying techniques on the characteristics of chitosan and the quality of biopolymer films. *Drying Technol.* **29**, 1784–1791 (2011)
- Goldstein, J.I., Newbury, D.E., Echil, P., Joy, D.C., Romig Jr, A.D., Lyman, C.E., Fiori, C., Lifshin, E.: *Scanning Electron Microscopy and X-ray Microanalysis*. Springer, New York (2003)
- Gomes, J.R.B., Jorge, M., Gomes, P.: Interaction of chitosan and chitin with Ni, Cu and Zn ions: a computational study. *J. Chem. Therm.* **73**, 121–129 (2014)
- González, J.A., Villanueva, M.E., Piehl, L.L., Copello, G.J.: Development of a chitin/graphene oxide hybrid composite for the removal of pollutant dyes: adsorption and desorption study. *Chem. Eng. J.* **280**, 41–48 (2015)
- Günay, A., Ersoy, B., Dikmen, S., Evcin, A.: Investigation of equilibrium, kinetic, thermodynamic and mechanism of Basic Blue 16 adsorption by montmorillonitic clay. *Adsorption* **19**, 757–768 (2013)
- Isah, U.A., Abdulraheem, G., Bala, S., Muhammad, S., Abdullahi, M.: Kinetics, equilibrium and thermodynamics studies of C.I. Reactive Blue 19 dye adsorption on coconut shell based activated carbon. *Int. Biodet. Biodegrad.* **102**, 265–273 (2015)
- Khalifaoui, M., Baouab, M.H.V., Gauthier, R., Ben Lamine, A.: Acid dye adsorption onto cationized polyamide fibres: modeling and consequent interpretations of model parameter behaviors. *J. Colloid Interface Sci.* **296**, 419–427 (2006)
- Khalifaoui, M., Knani, S., Hachicha, M.A., Ben Lamine, A.: New theoretical expressions for the five adsorption type isotherms classified by BET based on statistical physics treatment. *J. Colloid Interface Sci.* **263**, 350–356 (2003)
- Knani, S., Aouaini, F., Bahloul, N., Khalifaoui, M., Hachicha, M.A., Ben Lamine, A.: Modeling of adsorption isotherms of water vapor on Tunisian olive leaves using statistical mechanical formulation. *Phys. A* **400**, 57–70 (2014)
- Marković, S., Stanković, A., Lopičić, Z., Stojanović, M., Uskoković, D.: Application of raw peach shell particles for removal of methylene blue. *J. Environ. Chem. Eng.* **3**, 716–724 (2015)
- Moura, C.M., Moura, J.M., Soares, N.M., Pinto, L.A.A.: Evaluation of molar weight and deacetylation degree of chitosan during chitin deacetylation reaction: used to produce biofilm. *Chem. Eng. Process.* **50**, 351–355 (2011)
- Nakhli, A., Bergaoui, M., Khalfou, M., Möllmer, J., Möller, A., Ben Lamine, A.: Modeling of high pressure adsorption isotherm using statistical physics approach: lateral interaction of gases adsorption onto metal–organic framework HKUST-1. *Adsorption* **20**, 987–997 (2014)
- Price, G.J.: Ultrasonically enhanced polymer synthesis. *Ultrason. Sonochem.* **3**, 229–238 (1996)
- Salleh, M.A.M., Mahmoud, D.K., Karim, W.A.W.A., Idris, A.: Cationic and anionic dye adsorption by agricultural solid wastes: a comprehensive review. *Desalination* **280**, 1–13 (2011)
- Saygılı, H., Güzel, F., Önal, Y.: Conversion of grape industrial processing waste to activated carbon sorbent and its performance in cationic and anionic dyes adsorption. *J. Clean. Product.* **93**, 84–93 (2015)
- Seallaoui, L., Guedidi, H., Knani, S., Reinert, L., Duclaux, L., Ben Lamine, A.: Application of statistical physics formalism to the modeling of adsorption isotherms of ibuprofen on activated carbon. *Fluid Phase Equilib.* **387**, 103–110 (2015)
- Silverstein, R.M., Webster, F.X., Kiemle, D.J.: *Spectrometric Identification of Organic Compounds*. Wiley, New York (2007)
- Tan, K.B., Vakili, M., Horri, B.A., Poh, P.E., Salamatinia, B.: Adsorption of dyes by nanomaterials: recent developments and adsorption mechanisms. *Sep. Purif. Technol.* **150**, 229–242 (2015)
- Tang, H., Zhou, W., Zhang, L.: Adsorption isotherms and kinetics studies of malachite green on chitin hydrogels. *J. Hazard. Mater.* **209–210**, 218–225 (2012)
- Vakili, M., Rafatullah, M., Salamatinia, B., Abdullah, A.Z., Ibrahim, M.H., Tan, K.B., Gholami, Z., Amouzgar, P.: Application of chitosan and its derivatives as adsorbents for dye removal from water and wastewater: a review. *Carbohydr. Polym.* **113**, 115–130 (2014)
- Waseda, Y., Matsubara, E., Shinoda, K.: *X-Ray Diffraction Crystallography*. Springer, Berlin (2011)
- Yagub, M.T., Sen, T.K., Afroz, S., Ang, H.M.: Dye and its removal from aqueous solution by adsorption: a review. *Adv. Colloid Interface Sci.* **209**, 172–184 (2014)