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Thermodynamics of adsorption of malachite green hydrochloride on treated and untreated corncob charcoal

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Abstract: The need to explore an environmentally friendly and cheaper adsorbent for removal of dye from polluted water has imposed a requirement for thorough thermodynamic studies of dye removal from synthetically polluted water. The sorption capacities of untreated corncob charcoal (UCC), treated corncob charcoal (TCC) and commercially available activated carbon (ACC) for malachite green (MG) were determined at pH 3.10 and 5.10, in the temperature range 5–30 °C using the batch adsorption method. The adsorption capacity of each adsorbent for MG decreased with the increasing temperature in a manner suggestive of exothermic process. The equilibrium adsorption data were well fitted with Freundlich isotherm. The enthalpy of adsorption is higher at pH 5.10 for any particular adsorbent type compared to data collected at pH 3.10. The adsorption of MG is greatest in activated charcoal at pH 5.10. At pH 3.10 the adsorption process results in reduction in entropy changes in each adsorbent such that $\Delta S^{\circ}_{TCC} > \Delta S^{\circ}_{UCC} > \Delta S^{\circ}_{ACC}$ following the same trend as the change in enthalpy. At pH 5.10, however, $\Delta S^{\circ}_{TCC} > \Delta S^{\circ}_{ACC} > \Delta S^{\circ}_{UCC}$ and the change of enthalpy of adsorption of MG to the adsorbent follows the same order, $\Delta H^{\circ}_{TCC} > \Delta H^{\circ}_{ACC} > \Delta H^{\circ}_{UCC}$. The values of the enthalpy changes suggest essentially physisorption in all cases.

Keywords: equilibrium; enthalpy; entropy; freundlich; isotherm; exothermic.

INTRODUCTION

Dyes have found many industrial uses in textile, paper, leather, wood, plastics, cement, glass, paints, cosmetics and food industries among others. With their use also comes their release into the environment; especially, into streams and rivers, which are located near such industries. Apart from the unwholesome colour imparted by dyes into water bodies, dyes disrupt sunlight from reaching aquatic life, thus they affect the ecological balance of such water bodies. Bioaccumulation of dye in aquatic creatures such as fishes and crustaceans can cause mild to serious danger to the aquatic animals. It can also harm humans who

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drink such water or use such water for domestic purposes. Consumption of living organisms from rivers and stream contaminated by dyes can also have fatal consequences. The danger posed by dyes range from cancer, contrast induced nephropathy (CIN), nephrogenic systemic fibrosis (NSF) in kidney, dermatitis, ulceration, nausea and skin irritation.¹ Aerobic degradation of some inherently non-toxic azo dyes results in production of potentially carcinogenic amines.² It is estimated that about 0.7 million tons of synthetic dye are produced annually worldwide.³ About 2–20 % of these dyes are discharged into the environment, mainly as textile wastewater.⁴ These problems have necessitated the exploration of cheap and effective means of dye removal from industrial effluent and dye contaminated waters.

Among the physical methods used for dye removal, adsorption appears to be most promising, and have gained significant attention in the last few decades. Understanding the thermodynamics of the efficient dye adsorption on various adsorbent is therefore central in the determination of cheap and efficient dye removal method. A number of researchers have explored the use of various adsorbent from agricultural wastes for the removal of dye from dye-impacted wastewater. Some of the previously studied adsorbent from agricultural waste sources are: carbonaceous sugarcane dust,⁵ pine sawdust,⁶ bitter orange and banana pills⁷ and groundnut shell waste,⁸ among others. These materials have been used by different groups of researchers to remove heavy metals and hydrophobic compounds such as dyes from contaminated water.

Corn production in many countries of the world has risen steadily over the years hitting 11 million metric tons in 2017. The corncob (about 30 % of the corn by weight), which constitute a huge solid waste and whose disposal in many cases, have become a problem, could be explored for their adsorptive properties in dye adsorption. However, little detailed study of the thermodynamics of adsorption of dye on carbonaceous organic waste materials have been carried out. It is with the aim to understand the effect of modification of corn carbonaceous sorbent and operating conditions on the adsorption efficiency and the thermodynamic properties that we embark on this project.

Adsorption of two carbonaceous forms of corncobs; acid treated and untreated, were compared with that of commercially available activated carbon at two pH values (3.10 and 5.10). The enthalpy and entropy changes of the adsorption were estimated from Freundlich adsorption constant, K_F , at the two pH values, to determine their effect on the ease and efficiency of adsorption.

MATERIALS AND METHODS

UV-1800 spectrophotometer was manufactured by Shimadzu Europa GmbH. Gallenkamp oven model Ov-160 was made in England. Grant thermostated water bath with CC-60 Cryocool immersion cooler were product of Thermoscientific Neslab, HI 2209 pH meter is a product of Hanna Instruments, malachite green carbinol hydrochloride ($MW = 382.93$ g/mol)

is a product of Sigma Aldrich, Saint Louis, MO, USA. The activated carbon from animal source, 300×10^{-6} m mesh size, was purchased from Qualikems, India. All chemicals were used as purchased without further purification.

Corncoobs from yellow maize grown in Obafemi Awolowo University were obtained and sun dried to remove the moisture content. The dried corncoobs were then broken into bits and then carbonized by packing them into an earthenware pot, covered and heated at high temperature. The pot content was stirred occasionally to obtain a uniform combustion product. The covering was necessary to reduce the amount of air contact such that complete combustion of the corncoobs was prevented and well-formed charcoal was ensured. When the smoke from the pot has stopped, the charcoal formed was allowed to cool. Pulverization of the untreated charcoal was done by grinding the charcoal in a ceramic mortar with a pestle. The pulverized charcoal was fractionated with a 250×10^{-6} m pore size sieve. A portion of the charcoal was activated by soaking in 1.0 M sulphuric acid for 24 h. The acid treated charcoal was then filtered and rinsed thoroughly by passing distilled water slowly through it in a column until it is free of acid. Neutrality of the effluent was confirmed with litmus paper and the absence of visible reaction with BaCl_2 . The acid treated corncob was then dried for 5 h in an oven at 150°C . The activated corncob charcoal was also pulverized and sieved in a 250×10^{-6} m pore size sieve prior to storage in an airtight plastic container in a desiccator.

The stock solution of MG (340×10^{-6} mol dm^{-3}) was prepared in separate solutions of potassium phthalate/HCl buffer pH 3.10 and potassium phthalate/NaOH buffer, pH 5.10. MG fades at higher pH therefore the upper limit of the experimental pH was limited to 5.10. Solution of 13.6×10^{-6} mol dm^{-3} MG solution, pH 3.10 and 5.10, were prepared from their respective buffer solutions. 0.01–0.07 g of pulverized corncob charcoal (diameter $\leq 250 \times 10^{-6}$ m) was weighed into 25 cm^3 of 13.6×10^{-6} mol dm^{-3} MG at the specified pH of the experiment. The mixtures were shaken then left to equilibrate for about 6 h in a water bath, maintained at constant temperature between $5\text{--}30^\circ\text{C}$. The absorbance of the equilibrium solutions was then determined at 617 nm, the wavelength of maximum absorption of MG. At this wavelength, the molar extinction coefficient value of 5.8155×10^4 $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$ determined for MG was used to determine the concentration.

Many different models have previously been used to analyse adsorption of fluid on solid.^{6,9-15} Such models include those proposed by Langmuir, Brunauer–Emmett–Teller (BET) theory and Tempkin theory. The only model, which fits the experimental data obtained in this work most satisfactorily, is the Freundlich isotherm model. We therefore discussed only the Freundlich adsorption isotherm.

The Freundlich adsorption isotherm is an empirical relationship. At sufficiently low concentration of a solute, it relates the concentration of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact. It assumes that there is an exponential variation in the adsorbent sites energies. It has been used to describe many adsorption processes qualitatively.¹⁶

The Freundlich adsorption isotherm is mathematically expressed as:

$$X/M = K_F c_{\text{eq}}^{1/n} \quad (1)$$

where X/M = amount of solute adsorbed per unit weight of adsorbent, mg/g; c_{eq} = concentration of solute remaining in solution at equilibrium, mg dm^{-3} , K_F and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively, at a given temperature.

Freundlich equilibrium constant, K_F , which is dependent on temperature can therefore be obtained from the plot of $\log(X/M)$ against $\log c_{\text{eq}}$. n value, which gives the degree on nonlin-

earity of the dependence adsorption on adsorbate concentration at equilibrium, is also useful in the following ways: if $n > 1$ the adsorption is a physical process, if it is < 1 the adsorption in a chemical process.

The value of the correlation coefficient was used to determine the strength of the linear relationship in the plot of $\log(X/M)$ against $\log c_{\text{eq}}$. In the plot, square of the correlation coefficient, R^2 , greater than 0.95 was considered sufficiently good.

Under equilibrium conditions, at temperature T , the change in Gibbs energy of adsorption is related to K_F according to:

$$\Delta G^\circ = -RT \ln K_F \quad (2)$$

Under the conditions in which the enthalpy and the entropy are independent of temperature, ΔG° is related to the change in enthalpy ΔH° , and the change in entropy, ΔS° , according to:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3)$$

Therefore,

$$\ln K_F = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \frac{1}{T} \quad (4)$$

A plot of $\ln K_F$ against the reciprocal of the temperature should give ΔS° from the intercept and the ΔH° can be calculated from the slope. Eq. (4) is the popular van't Hoff equation.

RESULTS AND DISCUSSION

At pH 3.10, the plot of the dependence of the percentage of dye removed at temperatures 5–30 °C as a function of the dosage of untreated corncob charcoal (UCC) is presented in Fig. 1A. The corresponding data for treated corncob charcoal (TCC) and that involving the use of the commercially available activated carbon from animal source (AC) are presented in Fig. 1B and C, respectively.

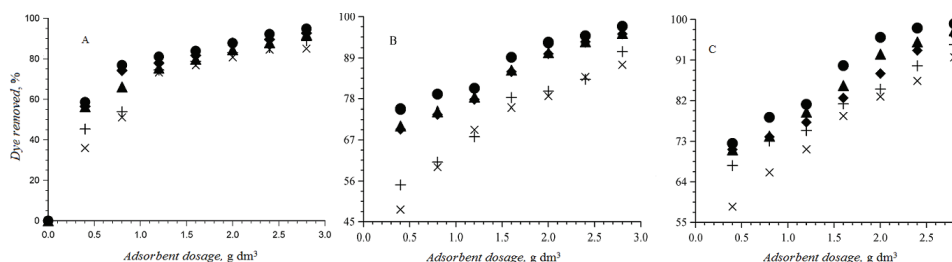


Fig. 1. The dependence of percentage malachite green removed at pH 3.10 on the dosage of: A) untreated corncob charcoal, UTC, B) 1 mol dm⁻³ sulphuric acid treated corncob charcoal, TCC, and C) commercially available activated carbon, ACC, from animal source. Symbols: × – 30; + – 25; ♦ – 20; ▲ – 10; ● – 5 °C. Initial concentration of MG = 13.6 × 10⁻⁶ mol dm⁻³.

Each data point is the mean of at least three replicate experiments subject to standard error of ~5 %.

It is seen that in each adsorbent, the percentage dye removed is highest at 5 °C compared to other temperatures at the corresponding adsorbent dosage.

Generally speaking, the results indicate that the percentage of dye removed increases with the reduction in temperature. A trend observable from the comparison of Fig. 1A, B and C indicates that the ACC removed more percentage of MG than TCC and that UCC removes the least MG, under identical conditions. This is particularly noticeable in the low dosage region.

The dependence of percentage dye removed on the adsorbent dosage at pH 5.10 for UCC, TCC and ACC are presented in Fig. 2A, B and C, respectively. It can again be seen that, as in Fig. 1, the percentage of dye removed increase with the decreasing temperature in each adsorbent and with increasing adsorbent dosage.

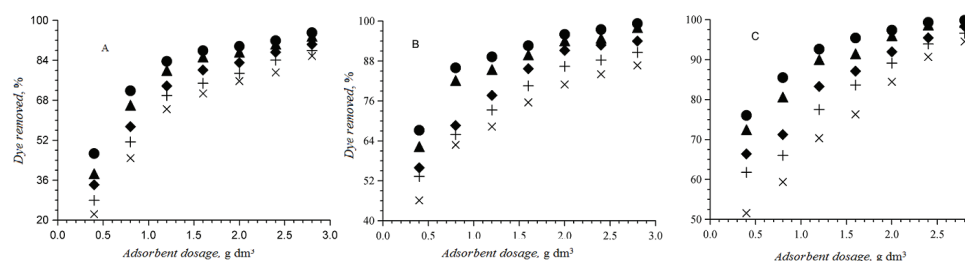


Fig. 2. The dependence of percentage Malachite Green removed at pH 5.10 on dosage of: A) untreated corncob charcoal, UCC, B) 1 mol dm⁻³ sulphuric acid treated charcoal, TCC, and C) commercially available activated carbon, ACC, from animal source. Symbols: × – 30; + – 25; ♦ – 20; ▲ – 10; ● – 5 °C. Initial concentration of MG was 13.6 × 10⁻⁶ mol dm⁻³.

The fit of the experimental data to Langmuir and Brunauer–Emmett–Teller (BET) model (not shown) were not sufficiently good as the square of the correlation coefficient R^2 of the their linearized equation plots to the experimental data were less than 0.94 in all cases, under the conditions of the experiment. The data however fitted satisfactorily to the linearized Freundlich model. Typical fits to the experimental data points for the adsorption of MG on UCC, TCC and ACC at 10 °C, pH 3.10 are shown in Fig. 3A–C, respectively. Similar plots for data collected at 25 °C, pH 5.10 for UCC, TCC and ACC are available as the Supplementary material to this paper (Fig. S-1). It can be seen that all the plots are sufficiently linear within the limits of the experimental error. Inability of the experimental data to sufficiently fit the Langmuir equation suggest that the interaction of MG with each of the adsorbent might not be monolayer or that the interaction between neighbouring MG molecules on the surface of the adsorbate might not be uniform or smooth.

An important benefit of the success achieved in fitting the experimental data to Freundlich equation lies in the potential of Freundlich constant, K_F , for determining the thermodynamic properties of adsorbent-adsorbate interaction. To the best of our knowledge, this experiment is the first to report the use of the K_F in the determination of the thermodynamic parameters of interaction. The values of

K_F were determined at different temperatures of the experiment. In doing this, we assumed that K_F , which measures the extent of adsorption of the MG to each adsorbent type is synonymous to equilibrium constant of a reaction, which measures the extent of the interaction between two reacting species in a reversible reaction at equilibrium. Here it is delineated as $K_{ad}(T)$ to show its dependence on temperature. Linear van't Hoff plot for the interaction of MG with each adsorbent should yield the values of the standard enthalpy and entropy changes, accompanying the interaction between MG and each adsorbent type.

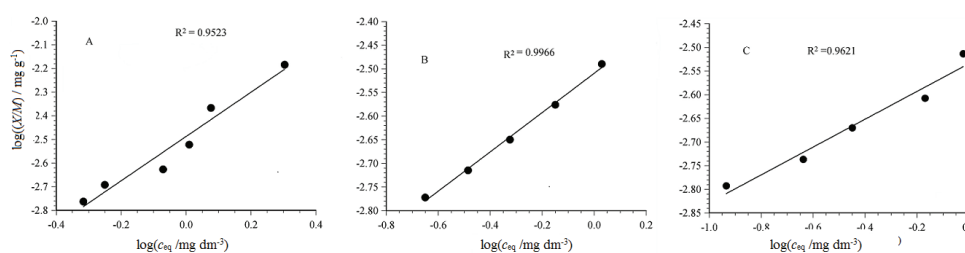


Fig. 3. Typical plots of the dependence of the logarithm to base ten of the mass of MG adsorbed per unit weight of: A) UCC, B) TCC and C) ACC against the logarithm of the concentration of MG green left in equilibrium solution according to Eq. (2) at 10 °C. After conditions pH 3.10, MG concentration and adsorbent dosage are as specified in Figs. 1 and 2. Each data point is the mean of three replicate experiments subject to 5 % standard error.

The values of $\log K_F$ obtained is the value of $\log (X/M)$ in the limit of $\log c_{eq} \rightarrow 0$, known as the intercept of the plot. $\log K_F$ is therefore obtained from plots such as presented in Fig. 3 at specified temperature. The values of $\log K_F$ at specified temperature were plotted according to van't Hoff equation to obtain the enthalpy and the entropy change of adsorption of MG on the different adsorbents with a view to determining how the treatment of the corncob and the operating pH affect the adsorptive properties of the adsorbent.

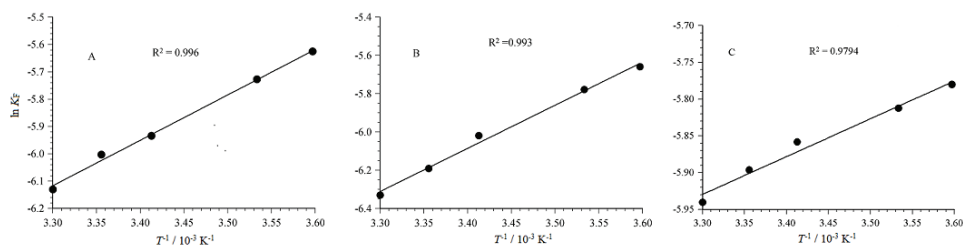


Fig. 4. The van't Hoff plot with Eq. (4) and fitting parameters of Table I, describing the adsorption of MG on: A) UCC, B) TCC and C) ACC. Conditions: concentration of MG $13.6 \times 10^{-6} \text{ mol dm}^{-3}$; pH 3.10; adsorbent dose as in Figs. 1 and 2.

Fig. 4A presents the van't Hoff plot of the UCC at pH 3.10. The corresponding data at pH 3.10 for the TCC and the ACC are presented in Fig. 4B and

C, respectively. The calculated thermodynamic parameters from these plots are reported in Table I. It can be seen that the dependence of $\ln K_F$ on the reciprocal of the T in each case is linear within experimental uncertainty. In each case the value of R^2 is greater than 0.97. This gives a strong indication that our assumption that K_F is synonymous to the equilibrium constant of an equilibrium reaction is reasonable. The enthalpy of the interaction between MG and the adsorbents increase in the order ACC < UCC < TCC (Table I).

TABLE I. Parameters of adsorption of MG at pH 3.10, obtained from van't Hoff plots and Freundlich adsorption isotherms

Adsorbent	ΔH° J mol ⁻¹	ΔS° J K ⁻¹ mol ⁻¹	n (mean \pm SD)	K_{ad} at		
				5 °C	20 °C	30 °C
UCC	-13835.7	-96.52	1.22 \pm 0.27	0.003613	0.002157	0.002205
TCC	-18747.2	-114.3	1.71 \pm 0.92	0.003564	0.0019	0.001825
ACC	-4275.75	-63.42	2.37 \pm 1.35	0.003094	0.002287	0.002656

Fig. 5A–C presents the van't Hoff plot of the adsorption of MG on UCC, TCC and ACC, respectively, using the fitting parameters of Table II at pH 5.10.

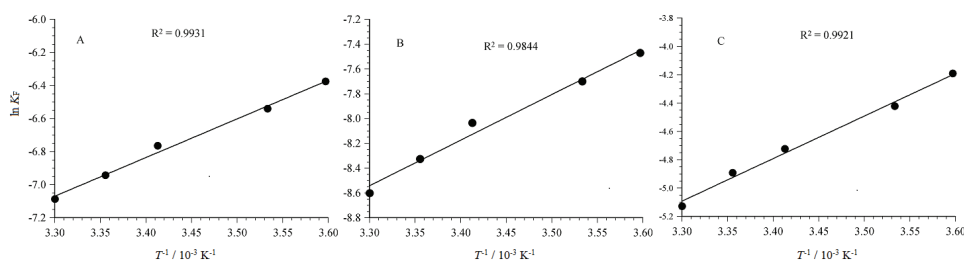


Fig. 5. The van't Hoff plot with Eq. (4) and fitting parameters of Table II, describing the adsorption of MG on: A) UCC, B) TCC and C) ACC. Conditions: concentration of MG, 13.6×10^{-6} mol dm⁻³; pH 5.10; adsorbent dose, as in Figs. 1 and 2.

TABLE II. Parameters of adsorption of MG at pH 5.10, obtained from van't Hoff plots and Freundlich adsorption isotherms; n is the reciprocal of the exponent from Eq. (1)

Adsorbent	ΔH° J mol ⁻¹	ΔS° J K ⁻¹ mol ⁻¹	n (mean \pm SD)	K_{ad} at		
				5 °C	20 °C	30 °C
UCC	-19442	-115.9	1.86 \pm 0.09	0.003972	0.002092	0.001984
TCC	-30598.4	-151.6	1.47 \pm 0.25	0.006767	0.002812	0.00227
ACC	-24972	-131.1	2.43 \pm 0.44	0.006983	0.003305	0.002864

The dependence of $\ln K_F$ on the reciprocal of the temperature is linear in a manner that suggests that the process is exothermic. In each case, the value of the square of the correlation coefficient R^2 of the linear plot is greater than 0.98. This gives a strong indication that K_F behaves very much like the equilibrium constant

of a reaction. The strong correlation also suggests that there are no other side reactions accompanying the adsorption process.

The effects of pH on adsorption under the two pH conditions are revealed by comparing the adsorption of MG at the given temperatures, as a function of the adsorbent dose. It is evident that the adsorption of MG increases with the increasing adsorbent dosage. It is also clear that the magnitude of the MG adsorbed under any particular conditions depends on the both the nature of the adsorbent and the temperature. The magnitude of the adsorption is higher at lower temperatures at a given pH and the trend of the dependence of the adsorption on the adsorbent dose is qualitatively similar at both temperatures. To avoid self-repetition, we only illustrated our findings using the data obtained at 5 °C, for each of the different adsorbents types. Comparing Fig. 1A (UCC data obtained at pH 3.10) with Fig. 2A (UCC data obtained at pH 5.10), it is clear that though at low adsorbent dosage, the percentage dye adsorbed is somewhat higher at low pH than at pH 5.10, by about 12 %. This difference decreases gradually with the increasing dosage of UCC up to UCC dosage of 2.8 g dm⁻³, the maximum adsorbent dosage of the experiment. At this dosage, the percentage MG adsorbed at low and high pH becomes essentially identical. In TCC (comparing Fig. 1B and 2B), the similar pattern was observed. At the minimum dosage of TCC (0.4 g dm⁻³), the percentage dye removed at pH 3.10 is greater than that at pH 5.10 by about 8 %. This difference also reduces with the increasing adsorbent dosage, so that at the maximum dosage of adsorbent (2.8 g dm⁻³), the percentage MG adsorbed at pH 5.10 becomes greater than at pH 3.10 by about 2 %. In the case of ACC, Figs. 1C and 2C, however, the percentage MG adsorbed is higher at pH 5.10 by about 3.5 % at low dosage (0.4 g dm⁻³). With the increasing adsorbent dosage, this difference decreases, such that the percentage MG adsorbed at high pH becomes essentially identical in value to the one at low pH at the limit of high adsorbent dosage. It is evident from this result that whereas the adsorption of MG on any particular type of adsorbent at low dosage may be significantly different at different pH, at high dosage of adsorbent the sensitivity of adsorbent to pH difference tend to disappear. The disappearance of the adsorption disparity at high dosage may have arisen because when the concentration of the adsorbate is high, there will be more site for adsorption, hence there will be less competition by the solute in solution for the adsorption site. Therefore, the discrepancy in the affinity of the adsorbent for solute (MG) becomes less obvious. The observed effect of pH on the percentage of adsorption is in qualitative agreement with the finding that the adsorption of the reactive dye brilliant blue KN-R onto functionalized resin NKY, is essentially insensitive to pH change at high dosage of adsorbent.¹⁷ Also, the adsorption of methyl orange, methyl blue, rhodamin B, congo red, methyl violet and amido black 10B, on two cellulose-based wastes (banana and orange peel), at 0.01 g dm⁻³ of adsorbent concentrations, show that their sensitivity to

pH increases in a manner which suggests that adsorption of the dye increases with the increasing pH (from pH 4.0 to a maximum at pH ~6). After the maximum is reached, depending on whether the adsorbent is banana or orange peel source, it may level off with the increasing pH, or begin to reduce with further increasing pH.¹⁸ This finding, together with our results, suggest that the changes of sensitivity of adsorbent to pH are more reliably determined in the low concentration range (less than 0.5 mg dm^{-3}).

Of importance to a physical chemist is to predict the extent of adsorption of adsorbate in solution to the adsorbent at temperature other than that at which experiments were carried out. Determination of the enthalpy change (ΔH°) and the entropy change (ΔS°) accompanying the adsorption process are therefore essential. In determining ΔH° and ΔS° , for different adsorbent, the plot of natural logarithm of the Freundlich constant ($\ln K_F$), obtained at pH 3.10 for any particular adsorbent, were plotted as a function of temperature according to Eq. (4) with the fitting parameters reported in Table I. The plots are presented in Fig. 4. It is seen that all the plots are linear. The square of the correlation coefficient is greater than 0.97 in each case. The corresponding data at pH 5.10 are presented in Fig. 5 and Table II. In Fig. 5, the square of the correlation coefficient of each plot is greater than 0.98.

It is evident that the adsorption of MG to each adsorbent is an exothermic process, suggesting the absence of dissociation of MG molecule on the adsorbent. The justification for this assertion is that the energy required to break covalent bonds would be greater than the energy of adsorption, which would have resulted in an endothermic process. The enthalpy change accompanying the adsorption of MG to UCC at pH 3.10 is about 3.2 times that of its adsorption to ACC and the enthalpy change of the adsorption of MG to TCC is 4.3 times that one of ACC (Table I). To determine the effect of the adsorbent treatment on the equilibrium constant of adsorption, K_{ad} , it was calculated at three temperatures of the experiment (Table I). In spite of the difference in the enthalpy of adsorption, the equilibrium constant of adsorption of MG to the adsorbent, calculated from the value of the free energy of the process at the specified temperature, is not significantly different for the different adsorbent. It appears that the difference in the enthalpy of the adsorption was compensated for by the entropic term of the free energy of the interaction. This suggest that at low pH, the treatment of the corn-cob does not have significant effect on the adsorptive power of the adsorbent. It is also evident from the value of n , the reciprocal of the exponent of Eq. (1) (Table I) which is between 1.22 and 2.37, values greater than 1, that neither pH change nor the adsorbent treatment changed the mechanism of adsorption. The adsorption is purely a physical process. Calculation of the equilibrium constant of adsorption at different temperatures shows that increasing the temperature of adsorption of UCC from 5 to 30 °C reduces the equilibrium constant of adsorption

by ca. 1.64-fold. The same temperature change reduces the adsorption of the dye on TCC by ca. 1.95-fold. That of ACC is reduced by a factor of ca. 1.16 when the temperature is raised from 5 to 30 °C. This suggests that the treatment of the corncob charcoal has a more significant effect on its sensitivity to temperature change at low pH.

The adsorption of MG to TCC at pH 5.10 was accompanied by the highest enthalpy change which is ca. 1.6 times that of MG adsorption to UCC (Table II). The enthalpy change accompanying the adsorption of MG to ACC is only about 1.3 times that of UCC (Table II). The reduction in entropy accompanying the adsorption of MG to TCC is ca. 1.3 times that of adsorption to UCC. The entropy change of adsorption of ACC is only ca. 1.1 times that of UCC. The adsorption of the dye to both TCC and ACC is more sensitive to temperature changes, compared to UCC (Table II). Whereas decreasing the temperature of the adsorption from 30 to 5 °C doubles the value of the equilibrium constant of adsorption of MG to UCC, it triples the value of the equilibrium constant of adsorption of MG to TCC and multiplies that of adsorption to ACC by ca. 2.4. This suggest that the acid treatment of the corncob charcoal significantly improves the adsorption properties of the charcoal at pH 5.10. This observation may be the consequence of the leaching of bound metal ions that are present in the corncob charcoal by acid, leading to the formation of more space for dye adsorption in TCC than in UCC.

An interesting finding in this work is that while the acid treatment significantly improves the ability of corncob charcoal to adsorb MG at pH 5.10 compared to UCC, at lower pH the equilibrium constant of adsorption to TCC and ACC are not significantly different from that of UCC. Increasing the pH of the solution of the MG also increases the value of the change in standard entropy accompanying the adsorption on each adsorbent to a varying degree. Whereas, the entropy change accompanying the adsorption of MG to ACC is more than double, when the pH is increased from 3.10 to 5.10, the ones of TCC and UCC are only about 1.3 and 1.2 times respectively. This result is consistent with the previous findings, which showed that the adsorption of methylene blue on activated pine cone,¹⁹ and textile vat dye on waste ash²⁰ were optimum at higher pH. This might be an indication that the adsorbing surface is slightly positively charged. If it were negatively charged, the adsorption should decrease with the increasing pH of dye solution. Since both enthalpy and entropy are state function, from our data, it is a trivial task to determine the enthalpy and entropy change accompanying the change in pH of the experiment from 3.10 to 5.10. In each adsorbent, the enthalpy and the entropy change of the interaction between MG and the adsorbent are reduced by increasing the pH from 3.10 to 5.10 (Tables I and II). This suggests that the pH of the solution play a very important role in the utilization of adsorbent for dye removal from solution. It should however be noted that the effect of pH is not significant in the UCC adsorbent, but is more

important in both TCC and AC. The strong correlation between the variation of the enthalpy values at a particular pH of the different adsorbent and the entropy under the same conditions suggest that the enthalpies measured are essentially, if not entirely, due to the consequence of physical adsorption. It is expected that adsorption process should generally result in the reduction in entropy, since the orderliness of adsorbed materials must increase as a result of adsorption.

CONCLUSIONS

The high values of the square of the correlation coefficient, R^2 of the linear fit to the Freundlich model (0.94–0.99) in all cases, suggests that the adsorption of MG on the charcoal adsorbents are well fitted with Freundlich model. This result is in good agreement with previous report,⁸ which showed that the data of the equilibrium adsorption of MG on groundnut shell activated charcoal was well fitted with the Freundlich model though it fitted also but less to BET model. An interesting finding of this work is the discovery that the Freundlich constant, K_F behaved very much like the equilibrium constant of a reversible reaction at equilibrium and provided very important thermodynamic information about the adsorption process. The treatment of the corncob charcoal with 1 mol dm^{-3} acid improved the adsorptive efficiency of the treated corncob charcoal significantly, so that the adsorption capacity compares favourably with that of commercially available animal charcoal particularly at low temperature. The efficiency of MG for the removal of dye is favoured by low temperature and pH of *ca.* 5.10. It is gratifying to note that both the enthalpy values obtained from van't Hoff plot on one hand and the Freundlich adsorption n values, on the other hand, point in the direction that the adsorption of the MG on each of the adsorbent used occur by physisorption.

SUPPLEMENTARY MATERIAL

Additional data are available electronically at the pages of journal website: <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

ИЗВОД

ТЕРМОДИНАМИКА АДОРПЦИЈЕ МАЛАХИТ ЗЕЛЕНОГ-ХИДРОХЛОРИДА НА ТРЕТИРАНОМ И НЕТРЕТИРАНОМ УГЉУ ОД КЛИПОВА КУКУРУЗА

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Потреба за развојем еколошког и јефтиног адсорбента за уклањање боја из загађених вода наметнула је захтеве за детаљним термодинамичким испитивањима уклањања боја из вештачки загађених вода. Сорпциони капацитети нетретираног угља од клипова кукуруза (УСС), третираног угља од клипова кукуруза (ТСС) и комерцијално доступног активног угља (АСС) за малахитно зелено (МГ) су одређени на рН вредностима 3,10 и 5,10 у температурском опсегу 5–30 °С при условима равнотежне адсорпције. Адсорпциони капацитет сваког адсорбента за МГ опадао је са порастом температуре што указује на егзотермни процес. Резултати добијени при адсорпционој равнотежи су

добро opisani Фројндлиховом изотермом. Промена енталпије адсорпције је већа на рН 5,10 за сваки испитивани тип адсорбента у поређењу са подацима добијеним на рН 3,10. Адсорпција МГ је највећа на активном угљу на рН 5,10. Адсорпциони процес на рН 3,10 доводи до смањења промене ентропије у случају свих адсорбената и то следећим редом $\Delta S^{\circ}_{TCC} > \Delta S^{\circ}_{UCC} > \Delta S^{\circ}_{ACC}$, пратећи исти тренд као и промена енталпије. Међутим, на рН 5,10 је $\Delta S^{\circ}_{TCC} > \Delta S^{\circ}_{ACC} > \Delta S^{\circ}_{UCC}$ и промена енталпије адсорпције МГ прати истри тренд, $\Delta H^{\circ}_{TCC} > \Delta H^{\circ}_{ACC} > \Delta H^{\circ}_{UCC}$. Вредности промене енталпије указују на доминантну физи- сорпцију у свим испитиваним случајевима.

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