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SORPTION OF TWO ORGANIC DYES AND THE MEASUREMENT OF SPECIFIC SURFACE AREA OF SORBENTS USED IN DISASTERS AND EMERGENCY SITUATIONS

SORPCIA DVOCH ORGANICKÝCH FARBÍV A MERANIA ŠPECIFICKÉHO POVRCHU SORBENTOV POUŽÍVANÝCH PRI MIMORIADNYCH SITUÁCIACH

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ABSTRACT:

The specific surface areas of kaolinite, activated charcoal and talc cover a wide range of values, which are extensively reported in literature. Therefore, these three adsorbents were used in this study for comparison of the specific surface area measurements using two molecular probes in the dye adsorption method, namely methylene blue and brilliant green. Both dyes were dissolved in MilliQ water and the batch-equilibration technique was used to measure the respective adsorption isotherms. The equilibrium data was analysed using the Langmuir isotherm and the specific surface areas were calculated using the maximum sorption capacities for methylene blue and brilliant green, as well as the literature/calculated molecular dimensions of methylene blue and brilliant green. Adsorption equilibrium of all three adsorbents was attained within the first 24 hours of contact time with both dyes, and the adsorption followed the Langmuir isotherm model which reflects the formation of a monolayer of both dyes on all three adsorbents. Use of NaOH to increase pH of methylene blue to a stable pH of 8.5 ± 0.2 was not achieved due to methylene blue exhibiting buffering properties within the first 2 hours of the adjustment. Preparation of methylene blue and brilliant green dilutions using MilliQ water only, resulted in a more stable acidic pH of 6±0.5 and 5±0.5 respectively. The pH of dye solutions has a significant effect on the adsorption process. The specific surface area values of talc (136.1 m^2/g) and kaolinite (24.22 m^2/g) determined using brilliant green dye are higher than those determined using methylene blue dye. Brilliant green was found to be more stable than methylene blue, and talc powder indicated to be a highly significant adsorbent in wastewater treatment containing brilliant green dye. Surface area results show that kaolinite and activated charcoal have high affinity for methylene blue.

KEYWORDS: *Methylene blue. Brilliant green. Sorption. Langmuir isotherm. Wastewater.*

INTRODUCTION

Specific surface area (SSA) of particle surfaces such as soils, minerals, sorbents used to contain spills during transport accidents and pharmaceutical powders has been measured using many various methods over the years. These methods include the Brunauer-Emmett-Teller method [1,2], the polar liquid adsorption methods using the ethylene glycol monoethyl ether [3,4] and the dye adsorption method [5,6]. The dye adsorption method is based on the adsorption of dye molecules from their solution in a suitable solvent (normally water) onto the surface of the sample material and the formation of a monolayer dye on the adsorbent/analysed sample's surface [5-7]. Cationic dyes such as methylene blue (MB) as molecular probes in the SSA determination [5,7]. The MB molecule is generally assumed to adsorb to the sample surfaces in a flat orientation with an area of 130 Å^2 per molecule [2,5,8]. This assumption will be used to interpret some of the data in this article. The dye adsorption method is experimentally simple, less time consuming and has minimal equipment requirements, compared with other experimental SSA methods [9–11]. In this study, we have investigated the use of an alternative molecular probe, namely brilliant green (BG).

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The adsorption process is one of the most efficient and economical method used in treatment of wastewater [12,13]. Sorbents have also been used extensively in the containment of the spills of hazardous materials [14]. Examples of the sorbents include clay minerals. The sorption and the amount of the sorbent to be used is dependent on the sorbent properties such as the SSA value. Kaolinite is tone of the most common and abundant phyllosilicate clay mineral characterised by the summary formula $Al_2Si_2O_5(OH)_4$ [12,13]. It consists of one tetrahedral silica sheet bonded to one octahedral alumina sheet through sharing of oxygen atoms and the hydrogen bonding of adjacent silica and alumina layers hold together the successive 1:1 layers. The tetrahedral sheet has a small permanent negative charge, whereas the octahedral sheet and the crystal edges have pH-dependent variable charge caused by protonation and deprotonation of surface hydroxyl groups. Therefore, kaolinite has a low cation exchange capacity and it has no interlayer surface [10,12,15,16]. Kaolinite has been reported in literature to have an SSA on the order of 17 m^2/g [12,13,16]. The removal of the of the contaminant during chemical spills only takes place on the external surface areas of the kaolinite particles.

Activated charcoal (AC) is one of the most widely used adsorbents in water treatment and purification [17–19]. It has been used in bioremediation and management of environmental spills [20]. Spills such as these can be classified as emergency situations/environmental disasters. The amount and types of surface functional groups in AC depends on precursor treatments and have significant influence on the adsorption process. AC is characterised by internal pore structure, large surface area and high adsorption capacity [18,19]; and can have the SSA values ranging from 80-2000 m^2/g [17,19,21].

Talc is a magnesium silicate mineral composed of three layers (silica-brucite-silica) and this mineral has a summary formula $Mg_3Si_4O_{10}(OH)_2$. Talc's two outer layers are composed of silicon-oxygen tetrahedrons and the middle layer consist of magnesium-oxygen/hydroxyl octahedrons [22,23]. The positive charge of brucite neutralises the two hexagonal networks of negatively charged silica tetrahedrons, resulting in a neutral three-layer structure [22]. Sheets are held together with van der Waals forces, the basal surfaces are hydrophobic and the edges are hydrophilic due to the breakage of Si-O or Mg-O bonds [22,24]. Kaolinite, AC and talc should provide a wide range of SSA values, which are extensively reported in literature. They will therefore these three materials will be used for the comparison of the SSA measurements with MB and BG as molecular probes.

In the current article, results are presented from ongoing research efforts into the development/adaptation of methods for the characterisation of materials which have applications in disaster management. Examples include the sorption capacity of materials for fuel spillage clean-ups and barriers for containment of the (localised) flooding. The accurate values and understanding of the SSA of disaster management materials provide the possibility to plan and procure the amounts/volumes of resources for preparedness and mitigation phases in the disaster management cycle. Such predictions are of critical value in of critical disaster management operations at various disaster management scales.

1. METHODOLOGY

MB was purchased from Hopkins and Williams LTD (Essex, United Kingdom). BG used was purchased from Merck Pty. Ltd. (Johannesburg, South Africa). Kaolinite and talc were obtained from local mines in Grahamstown (South Africa) and AC was purchased from Sigma-Aldrich (Johannesburg, South Africa). All solutions were prepared using MilliQ water (Millipore/Merck, Port Elizabeth, South Africa). Unless stated otherwise, the adsorbent preparation and dry weight measurements of all adsorbents were performed as reported by Moyo et al. [25]. All glassware was purchased from Sigma-Aldrich (Johannesburg, South Africa) [25]. All solid phase concentrations of MB and BG are reported as milligrams of adsorbed dye per gram of dry weight of sorbent (mg/g).

To verify the identity of individual adsorbents, the Fourier transform infrared (FTIR) spectra were measured for all adsorbent samples. These were obtained at room temperature (approximately 25 ± 2 °C) from an average of 10 individual scans using Perkin Elmer version 10.4 spectrophotometer (Perkin Elmer, Port Elizabeth, South Africa) in the spectral range of 4000 to 650 cm^{-1} (resolution of 4 cm^{-1}). All measurements were performed with the KBr disc method.

FTIR spectra of raw kaolinite and talc from 4000 to 550 cm^{-1} were recorded on a Perkin Elmer Spectrum 400 FTIR/FT-FIR Spectrometer which was coupled to an ATR attachment. In all the spectra measured, the baseline correction was performed by applying the automatic baseline correction method. The bands ranging from 3700-3400 cm^{-1} are attributed to the stretching vibrations of O-H associated with Mg (Mg-OH) in the spectrum of talc. Characteristically, the band at 3678 cm^{-1} is associated with O-H in the 3 Mg region (Mg_3-OH) of talc [26]. The peaks at 3694 and 3620 cm^{-1} exhibited the kaolinite FTIR spectra were assigned to the stretching vibrations of inner surface OH groups.

The peak at 3654 cm^{-1} is attributed to the out of phase stretching of inner O-H groups [27]. In line with literature findings, the peaks at wavenumbers of 933 and 908 cm^{-1} can be attributed to Al-OH deforming vibration and Al-OH bending vibration [27]. In the FTIR spectra of AC confirm the presence of the following functional groups: –COOH, phenolic –OH, and -C=O. Next, the signal recorded at the wavenumber of 3401 cm^{-1} can be assigned to the C–OH stretching vibrations, while a band at 1561 cm^{-1} is the result of the presence of the C–OH bending vibrations. The stretching of C–O from the lactone moieties, hydroxyl and carboxyl groups were detected as peak at 1125 cm^{-1} [28]. The broad peak stretching 3596-3024 cm^{-1} is attributed to the free and intermolecular bonded hydroxyl groups of AC [29]. Therefore, all the sorbents met the standard reported characteristics of kaolinite, talc and AC, as reported in literature previously. The identity of all sorbents used in this study is confirmed as kaolinite, talc and AC.

Calibration curves of MB and BG were determined using a UV/VIS spectrophotometer (GBC 916, Melbourne Australia). Both stock solutions had a concentration of 1000 mg/L and were prepared by dissolving an accurately weighed out amount of MB or BG on a PA214 analytical balance (0.0001g precision, OHAUS Europe GmbH, Greifensee, Switzerland). The weighed out amounts were dissolved quantitatively in MilliQ water and transferred into a 250 mL volumetric flask. The volume was made up to mark with MilliQ water. The respective dilutions were prepared in MilliQ water to obtain calibration solutions with six different concentrations for MB and six different concentrations for BG. Where applicable, pH of the dilutions was recorded before and after determining the absorbance using a pH meter (PC Tester 35 Oakton® instruments, Singapore).

The dye concentrations were determined using a UV/VIS spectrophotometer at the wave lengths of the visible maximum at 663.7 nm for MB and at 625 nm for BG [30-33]. Calibration curves were measured at six concentration levels between 0.5 and 5.0 mg/L. All calibration solutions at each concentration level were prepared in triplicate and all absorbance measurement were also performed in triplicate. The average absorbance (A_{avg}) as a function of the average dye concentration (C_{avg}) was plotted in the concentration range from and the following regression equations were obtained (MB is shown in Equation 1 and BG is shown in Equation 2):

$$A_{avg} = 0.0114 + 0.1866 \times C_{avg};\ R^2 = 0.9991 \tag{1}$$

$$A_{avg} = 0.0018 + 0.1797 \times C_{avg};\ R^2 = 0.9988 \tag{2}$$

For adsorption kinetics, the measurements were performed in a set of 100 mL Erlenmeyer flasks containing 2 g of the particular adsorbent and 50 mL of dye solutions with various initial concentrations. All measurements of adsorption kinetics were performed at 150 mg/L and this applies to both MB and BG. Unless stated otherwise, all adsorption measurements were performed in the dark at 22 ± 2 °C. The opening of each flask was sealed using Parafilm™ (Plastrip, Cape Town, South Africa) and aluminium foil before agitation. The flasks containing the samples and dye solutions were agitated using the TS-520D 220V orbital shaker (Valread enterprise Inc. Taipei Taiwan) at 160 rpm for 24 hours or 48 hours. Next, the flasks contents were allowed to stand for 30 minutes, before an aliquot of the supernatant was removed. This aliquot was then centrifuged using a Damon IEC HN-SII centrifuge (DAMON/IEC DIVISION Needham, Massachusetts) at 2000 rpm for 30 minutes. Absorbances were measured as described for the calibration curve solutions above. If the sample absorbance was higher than 1.000, the samples were diluted with MilliQ water and the measurements were repeated. The final dye concentration was obtained using the calibration curve equation and the respective dilution factor.

The main aim of the adsorption kinetics experiment was to establish when apparent equilibrium was reached. For this, the dye removal percentage and amount of dye adsorbed was calculated as shown in Equation (3). The apparent sorption equilibrium was reached when the % dye removal reached a constant value and did not further change with extension in the duration of the sorption experiments.

$$\% \text{ Dye removal} = 100\times(C_0 - C_e)/C_0 \qquad (3)$$

In equation (3), C_e and C_0 are the dissolved concentration of dye solution at equilibrium (subscript *e*) and at time zero (subscript *0*; both concentrations have mg/L as units).

Results of the adsorption kinetics experiments showed that 24 hours was a sufficient period of time for the establishment of apparent adsorption equilibrium with all three adsorbents (see Results and Discussion for details). Thus, all sorption isotherms were measured in the same fashion as the adsorption kinetics, but the incubation period was always 24 hours. Depending on the adsorbent, the initial concentrations of MB and BG ranged from 50 to 6000 mg/L.

For all experimental conditions, the solid phase concentration/sorption capacity (q_e) was calculated as shown in Equation (4).

$$q_e = V\times(C_0 - C_e)/W \qquad (4)$$

In Equation (4), C_0 and C_e have the same meaning as in Equation (3). On the other hand, V is the total volume of the liquid phase in the adsorption isotherm replicates Erlenmeyer flasks (L). W is the dry weight of the adsorbent (g). The values of q_e were calculated from the values of C_0, C_e and the mass balance of MB or BG in the adsorption experiments. The mass balance was evaluated by investigating the influence of the evaporation and the stability of the solutions of MB and BG. This was done by running the controls which were prepared as with the adsorption kinetics measurements, but no adsorbent was added to the Erlenmeyer flasks. The percentage recovery of MB was equal to 97% of the initial amount at the end of the experiment. The analogical value for BG was equal to 96.3%. Therefore, the evaporation and stability of dry probe solutions did not have any influence on the adsorption data in this study.

Langmuir isotherm was used for data evaluation generally used for data analyses. The Langmuir isotherm model assumes that a monolayer of dye molecules forms on the homogenous surface of the adsorbent. Therefore, all adsorption sites are identical in terms of adsorption energy and the adjacent and adsorbed dye molecules do not interact with each other [30,32,34,35]. For practical purposes, the linearized Langmuir isotherm is often used in the SSA determination as shown in Equation (5).

$$(C_e/q_e) = (C_e/q_m) + 1/(q_m/K_L) \qquad (5)$$

In Equation (5), majority of the terms have the same meaning and units as in Equations (3) and (4). There are two exceptions, namely q_m which represents the maximum adsorption capacity (mg/g) and K_L (L/mg) which is the adsorption partition coefficient.

The SSA of a particular adsorbent was calculated using the Langmuir isotherm data and the molecular properties of MB and BG as shown in Equation (6).

$$SSA = (q_m\times A_V\times A_D)/M \qquad (6)$$

Where q_m has the same meaning as shown in previous equations (see above) and it applies to a particular combination of a dye probe (MB or BG) and a particular adsorbent (kaolinite, AC or talc). At the same time, A_V is the Avogadro's number, i.e. $6.023\text{x}10^{23}$ mol^{-1} and A_D is the area covered by one dye molecule (MB =130 Å^2 and BG = 151.62 Å^2). The molecular dimensions of the flat conformation of MB were obtained from literature, while the BG were calculated using the molecular mechanics tools. Finally, M is the molecular weight of the respective dye probe (MB =373.9 g/mol and BG = 482.6 g/mol).

2. RESULTS AND DISCUSSION

Removal efficacy (%)

For the initial dye concentration of 150 mg/l, more than 95% adsorption has been observed at 24 hours, for both dyes and there is no significant change in percentage dye removal at 48hours. This indicates that equilibrium was attained within the first 24 hours for both MB and BG. The percentage dry weight of talc = 99.9%, kaolinite = 99.6% and activated charcoal = 98.9%.

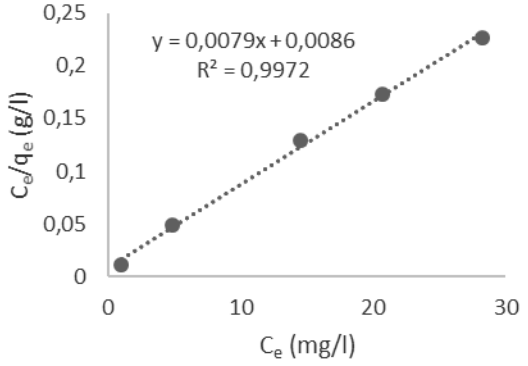
The removal efficacy of the dye molecules by kaolinite is in agreement with the studies [7,31,36] that indicate that the rate of adsorption is very fast and maximum adsorption occurs within the first 24 hours of contact time for BG and MB. The rapid electrostatic adsorption of cationic dye molecules is due to the availability of negatively charged surface of kaolinite [36]. The studies [17,18] on the application of activated carbon as adsorbent for efficient removal of MB and BG, indicate that equilibrium was quickly established within 24 hours and these results are in agreement with the present study.

The removal efficacy of activated charcoal depends mainly on its surface properties, degree of carbonisation and method of activation [19,33,37,38]. In the present study, it is observed that the adsorption equilibrium of MB and BG onto talc was attained within 24 hours as shown in figure 1b and this is in line with the literature report on removing MB from wastewater using modified talc powder [39]. Therefore, all the adsorbents used have a higher removal equilibrium rate for BG and MB cationic dyes.

Adsorption isotherms
The adsorptions of the dyes onto talc, kaolinite and activated carbon are described using the Langmuir linear isotherm equation (Table 1 and Table 2). The correlation coefficients for all the adsorbents and both dyes yield good fit of this isotherm to the experimental data (Figure 1a and 1b). The Langmuir model (Figure 1a, Table 1 and 2) reflect the formation of monolayer of both dyes and homogenous distribution of active sites on the surface of AC at equilibrium. Maximum adsorption capacity (q_e) of AC is higher for MB compared to that for BG, the difference in the size of dye molecules may have an effect on the accessibility of the internal surface of the adsorbent [38].

The interaction between carbons and MB is different depending on the nature of the carbon. The adsorption forces including hydrogen bonding, electrostatic forces, hydrophobic bonding and Van der Waals forces are involved in the adsorption of MB [17,38]. The AC have the highest maximum adsorption capacity for both dyes compared to talc and kaolin (Table 1 and 2), this confirms its high surface area, microporous structure and effectiveness in the adsorption of cationic dyes from coloured wastewater [19,21,33].

a)



b)

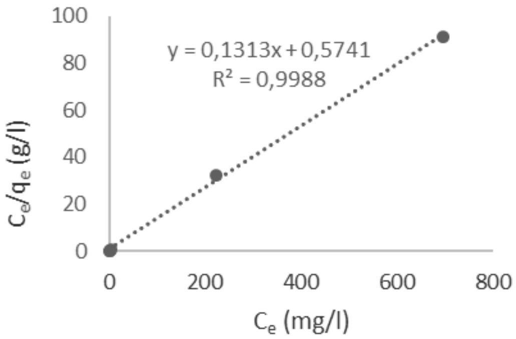


Figure 1 **Langmuir linear isotherm representing the adsorption of a) BG onto activated charcoal and b) MB onto kaolinite.**

The dye adsorption process onto kaolinite surface was well represented by the Langmuir isotherm model (Figure 1b, Table 1 and 2) indicating homogenous finite number of binding sites and the formation of monolayer on the surface of kaolinite. The maximum adsorption capacity for BG is higher than that for MB (Table 1 and 2) and significantly lower than the maximum adsorption capacity of kaolinite for BG that has been reported in literature [7,31]. The kaolinite maximum adsorption capacity value for MB in this current study is almost the same with the values that have been reported in literature for MB adsorption onto calcined pure and raw kaolinite [15,38]. Kaolinite and talc used in the current study show to have almost the same maximum adsorption capacity for MB. The absence of internal surface for kaolinite limits its dye adsorption capacity. The adsorption of MB onto kaolinite can be enhanced by purification and treatment with NaOH solution [15]. Kaolinite shows to have higher affinity for BG dye than MB dye, therefore it is a more suitable and efficient adsorbent in removal of BG from wastewater.

The adsorption of MB and BG experimental data resulted in a high fit to the Langmuir model (Table 1 and 2). The correlation coefficients close to unity suggest that monolayer was formed on a homogenous surface of talc adsorbent, however the energy adsorption constant K_L is greater than one which may imply formation of strong bonds through chemisorption. The equilibrium capacity of talc surface is higher for BG than that for MB and also significantly higher compared to the adsorption capacity of kaolinite for BG. In this current study, it is observed that talc is an efficient adsorbent in removal of BG compared to kaolinite and has a high affinity for BG compared to MB. The adsorption capacity of talc for MB is higher than the values in literature [40]. There is very limited information in literature on the adsorption of MB and BG using talc as an adsorbent. Talc has indicated to be a promising adsorbent in wastewater treatment, however there is need for further studies on modifying and enhancing its adsorption capacity.

Table 1 **Langmuir isotherm constants for the adsorption of MB onto talc, kaolinite and activated charcoal.**

			Langmuir constant		
Adsorbents	**Ce (mg/l)**	**q_e**	**q_m(mg/g)**	**K_L(l/mg)**	**R^2**
Talc	0.26-736	3.7-6.6	7.386	1.0653	0.9999
Kaolinite	0.19-695	3.8-7.6	7.616	0.2287	0.9988
Activated charcoal	71-1120	148-172	175.4	0.0813	0.9999

Table 2 **Langmuir isotherm constants for the adsorption of BG onto talc, kaolinite and activated charcoal**

			Langmuir constant		
Adsorbents	**Ce (mg/l)**	**q_e**	**q_m(mg/g)**	**K_L(l/mg)**	**R^2**
Talc	0.4-220	25-70	71.94	0.0906	0.9921
Kaolinite	0.27-513	1.2-12	12.80	0.0298	0.9897
Activated charcoal	1-28	87-124	126.58	0.9186	0.9972

Table 3 **Specific surface area for talc, kaolinite and activated charcoal determined using MB dye and BG dye**

	Talc	**Kaolinite**	**Activated carbon**
SSA_{MB} (m^2/g)	15.47	15.94	367.3
SSA_{BG} (m^2/g)	136.1	24.22	239.5

3. EXAMPLES OF APPLICATION OF CASA C-295 IN THE PROVISION OF HUMANITARIAN AID ABROAD

SSA measurements

AC has higher SSA compared to talc and kaolinite as shown in Table 3. The SSA values of talc and kaolinite determined using BG dye are higher than the SSA values determined using MB however for AC, the SSA determined using MB dye is greater than the SSA determined using BG dye. The SSA_{MB} value of kaolinite is slightly less than 17 m^2/g that has been reported in literature [12,13,15]. The SSA_{BG} value of talc is significantly high compared to the SSA_{MB} value of talc. The SSA values of AC are in line with the values that have been reported in previous studies [17,19,38]. According to Nandi et al (2009) [7] the point of zero charge (pH_{ZPC}) for kaolinite is estimated to be 7.0, below this point the kaolinite surface acquires a positive charge and the dye molecules become positive hence there an electrostatic repulsion occurs between the kaolinite and dye molecules decreasing dye adsorption. Low pH values increase the positive charge of on the surface of AC and decrease the negative charge hence the adsorption of cationic adsorbates is reduced due to repulsive forces [19,33]. A study [49] has indicated that the use of MB solution with a pH below the isoelectric point of talc will result in a positively charged surface of talcum molecules, hence repulsion between the positively charged talcum powder and the cationic dye molecules occurs.

The difference in the pH of the dye solutions thus 6±0.5 for MB and 5±0.5 for BG, has a significant effect on the deviation of SSA values. pH controls the adsorption process through changing the surface charge of adsorbent, the degree of ionisation of dye molecules and the extent of dissociation of functional groups of the adsorbent's active sites [7,37]. In this current study, the increase of the dye solution pH above the pH_{ZPC} using NaOH as a pH adjuster [13,15,17,30] did not achieve a stable basic pH for MB. A drastic decrease in pH by 2±0.5 was observed within 2 hours after adjusting the pH to 8.5±0.2 thus MB exhibit buffering properties. Preparation of MB dilutions using MilliQ water alone resulted in a more stable acidic pH of 6±0.5 and that was used in this current study.

Moreover, centrifugation and the duration of the experiment could have contributed to the deviation of the SSA values. Separation of the sample molecules and the dye solution after equilibrium has been attained using 0.5 µm PVDF hydrophobic and hydrophilic syringe filters [30,32,41] was not successful. Both types of filters absorbed the MB molecules from the aqueous phase, resulting in 70 % and 90% decrease in MB concentration using hydrophobic and hydrophilic filters respectively. Centrifugation was then used to separate the sample particles and the aqueous phase, for BG average 4% decrease in dye concentration was observed and 5% average decrease in dye concentration was observed for MB after use of a centrifuge. Therefore, the BG concentration was only influenced within the standard deviation of the individual concentration measurements. This makes BG more suitable for routine measurements of SSA, if the pH values of the sorbents measured are in the acidic or neutral range. A 2 % MB and 1.5 % BG concentration decrease was observed from the control after 24 hours, this could be due to degradation of the dye.

CONCLUSION

The amount of the dye adsorbed was found to vary between MB dye and BG dye. The adsorption equilibrium was reached within 24 hours for both dyes and data fitted the Langmuir isotherm indicating formation of a monolayer on a homogenous surface of the adsorbents. Talc and kaolinite have higher affinity for BG dye than MB dye, AC has high adsorption affinity for MB dye compared to BG dye and there is need for further studies on using talc as an adsorbent for dye removal. The pH value of the dye solutions have a great effect on the adsorption process. The use of NaOH as a pH adjuster for MB solution does not give a stable MB basic pH and MB exhibit buffering properties. MB molecules interact with hydrophilic and hydrophobic syringe filters and their use in separating sample particles from the bulk solution after equilibrium is not effective. Using a centrifuge to separate sample particles from the bulk solution after equilibrium has a negative effect on the concentration of the bulk solution. The optimised procedure developed in this article can be used for routine measurements of the SSA of materials to be used in the containment of spills in transport disasters and similar emergencies.

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