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## **Preliminary investigation of mixed adsorbents for the removal of copper and methylene blue from aqueous solutions**

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Title: Preliminary investigation of mixed adsorbents for the removal of copper and methylene blue from aqueous solutions

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Keywords: Multi-adsorbents; Wastewater; Adsorption technique; Heavy metals; Dyes

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Abstract: With most recent studies being focused on the development of advanced chemical adsorbents, this paper investigates the possibility of using two natural low-cost materials for selective adsorption. Multi-adsorbent systems containing tea waste (TW) and dolomite (DO) have been tested for their effectiveness in the removal of copper and methylene blue from aqueous solutions. The effects of contact time, solution pH and adsorption isotherms on the sorption behaviour were investigated. The Langmuir and Freundlich isotherms adequately described the adsorption of copper ions and methylene blue by both materials in different systems. The highest adsorption capacities for Cu and MB were calculated as 237.7 mg/g at pH 4.5 and 150.4 mg/g at pH 7 for DO and TW:DO respectively. Tea waste and dolomite were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy and Energy dispersive X-ray analysis. The removal of Cu and MB by dolomite was mainly via surface complexation while physisorption was responsible for most of the Cu and MB adsorption onto tea waste. Identifying the fundamental mechanisms and behaviour is key to the development of practical multi-adsorbent packed columns.

Response to Reviewers: RESPONSE TO REVIEWERS:

Authors would like to thank the reviewers for very constructive comments. We believe that addressing the reviewer's concerns has led to improvements in the manuscript.

The following explains how we handled the comments raised by reviewers.

Response to Reviewer No 1:

It is a very good study which aims the investigation of adsorption/removal of a heavy metal (copper) and a dye (methylene blue) using low-cost adsorbent. My comments are listed below.

1. Fig.1 presents the kinetic data without fitting, while Fig.2 after fitting. I recommend authors to move Fig.1 to Supporting information section.

Answer: Figure 1 has been moved to the Supplementary data as recommended.

2. Fig. 4 has 6 sub-figs without numbering. But, I think they need merging into at least 2 sub-figs and not 6.

Answer: Putting these figures in 2 sub-figures will not allow clear demonstration of the data and isotherm fitting. However, Figure 4 was split into 2 figures.

3. The major absorbencies (as described in text) should be illustrated in Fig.6, 7 (FTIR).

Answer: There are so many peaks and adding them to the figures will make it hard to notice the changes in the sample surface before and after adsorption.

4. It will be good to add a column in Table 1 (for each fitting), presenting the %change between  $Q_{e,exp}$  and  $Q_{e,cal}$ .

Answer: The  $q_{e,exp}$  and  $q_{e,cal}$  values have been discussed in the manuscript and there is no need to represent the change between them in the table.

5. Authors should illustrate (as scheme/figure) an adsorption mechanism based on their findings (FTIR, etc). It is more attractive for any reader to read and follow a figure than only text.

Answer: A new figure (Figure 6) has been added. The figure illustrates the possible removal mechanisms for copper and methylene blue onto dolomite and tea waste.

Response to Reviewer No 2:

6. In table 3 the Redlich-Peterson model capacity is not comparable with the Langmuir model capacities. This capacity must be omitted.

Answer: The Redlich-Peterson model has not been employed to describe the isotherm experimental data in this study.

7. Figure 1 gives no essential information and can be omitted.

Answer: As per Reviewer 1 suggestion, Figure 1 has been moved to the supplementary data section.

Response to Reviewer No 3:

8. There are several technical errors:

Page 6: row 129 "The Cr(VI)percentage removal...". It should be Cu(II).

There are two tables numbered as No 3. Table 3.Comparison of adsorption capacities...has to be mentioned in the text.

Answer: The manuscript was revised and all typo mistakes have been corrected.

**Dear Editor,**

On behalf of myself and my colleagues (co-authors of this work), please find attached an electronic copy of the manuscript "*Preliminary investigation of mixed adsorbents for the removal of copper and methylene blue from aqueous solutions*" submitted to "**Chemical Engineering Journal**" for possible publication.

This work is original and has not been submitted nor published anywhere else. The findings and results in this work are novel and have not been taken from any other source.

I will be really thankful if you consider this work for possible publication in this reputable Journal.

Best Regards,

*Dr Ahmad Albadarin, PhD.*

*Materials Surface Science Institute,*

*Department of Chemical and Environmental Sciences,*

*University of Limerick, Ireland*

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## RESEARCH HIGHLIGHTS:

- Multi-adsorbent systems containing tea waste (TW) and dolomite (DO) have been tested.
- The effects of contact time, solution pH and adsorption isotherms were investigated.
- Adsorption capacities for Cu and MB were calculated as 237.7 and 150.4 mg.g<sup>-1</sup> for DO and TW:DO respectively.
- Solution pH had little effect on the capacity of the TW:DO system, specifying that the system has good potential for practical use.

1 **Preliminary investigation of mixed adsorbents for the removal of copper and methylene**  
2 **blue from aqueous solutions**

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26 **Abstract**

27 With most recent studies being focused on the development of advanced chemical  
28 adsorbents, this paper investigates the possibility of using two natural low-cost materials for  
29 selective adsorption. Multi-adsorbent systems containing tea waste (TW) and dolomite (DO)  
30 have been tested for their effectiveness in the removal of copper and methylene blue from  
31 aqueous solutions. The effects of contact time, solution pH and adsorption isotherms on the  
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34 systems. The highest adsorption capacities for Cu and MB were calculated as 237.7 mg/g at  
35 pH 4.5 and 150.4 mg/g at pH 7 for DO and TW:DO respectively. Tea waste and dolomite  
36 were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy  
37 and Energy dispersive X-ray analysis. The removal of Cu and MB by dolomite was mainly  
38 via surface complexation while physisorption was responsible for most of the Cu and MB  
39 adsorption onto tea waste. Identifying the fundamental mechanisms and behaviour is key to  
40 the development of practical multi-adsorbent packed columns.

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42 **Keywords:** Multi-adsorbents; Wastewater; Adsorption technique; Heavy metals; Dyes

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## 51        **1. Introduction**

52    Dyes (very frequently methylene blue and methyl orange) and heavy metals (copper,  
53    cadmium and nickel mostly from the organo-metallic dyes) are dangerous pollutants found in  
54    large quantities in wastewaters from textile and paper industries. It is known that heavy  
55    metals are toxic and non-biodegradable [1, 2]. Heavy metals have many environmental  
56    issues such as animal and plant death, reduced rates of reproduction and the decrease of  
57    ecosystem diversity [3]. While dyes are difficult to treat as the colour tends to hold strong  
58    even after the conventional removal processes [4]. There are more than 100,000  
59    commercially available dyes with over 700,000 tons produced annually [5]. The presence of  
60    some of these dyes even in very small amounts i.e.  $< 1 \text{ mg.dm}^{-3}$  is undesirable [6, 7]. Dyes-  
61    Heavy metal loaded wastewaters are highly coloured, have a fluctuating pH and regularly  
62    contain large amounts of suspended oils. Dyes and heavy metals find their way into the  
63    environment, primarily dissolved or suspended in water everyday [8] and create serious  
64    damage to the environment by changing the biological life balance in rivers and lakes [9, 10].  
65    Adsorption is a well-established and powerful practice for the removal of dyes and heavy  
66    metal pollutants from wastewaters. For these reasons, thousands of investigations have used  
67    uncountable adsorbents to remove heavy metals [11] or dyes [12]. Most of these studies focus  
68    on single-component aqueous solutions and recently, more research papers have been  
69    published dealing with the adsorption of dyes and metals in multi-component aqueous  
70    systems [6]. Also, composite adsorbents have been established to adsorb dyes and heavy  
71    metals from wastewater such as chitosan/montmorillonite composites [13-15] and fly  
72    ash/activated carbon [16]. In previous studies, composite materials were used to selectively  
73    adsorb a particular pollutant. Ho and co-workers proved that amino functionalized silica  
74    solids can selectively adsorb dye anthraquinone blue in the presence of methylene blue,  
75    while, from the same dye mixture, carboxy-functionalized materials adsorb methylene blue

76 selectively [17]. Prediction of multicomponent adsorption is still one of the most challenging  
77 problems in the adsorption field [18]. There is little data available to provide more  
78 understanding about the interactions between adsorbents and developing design models for  
79 such practical systems is very important [19]. This is the case for many composite materials  
80 as well as adsorption processes with multi-adsorbate and multi-adsorbent systems. Dolomite,  
81 with a structure of alternative layers of calcite and magnesite, is a potential inexpensive and  
82 readily available adsorbent [20]. Many studies showed that dolomite and charred dolomite  
83 have the potential to act as adsorbents for reactive dyes and heavy metals [21]. Tea,  
84 processed leaves from *Camellia sinensis* species, is the second most common drink being  
85 consumed after water with an average daily drinking of 20 billion cups. The producers of  
86 making tea drinks face a problem in disposing of the spent tea leaves after the extraction [22,  
87 23]. The feasibility of using the richly available solid waste, spent tea leaves, for the removal  
88 of heavy metals and dyes has also been extensively investigated [24]. A good understanding  
89 of the effect of adsorbent-adsorbent interactions on selective adsorption is essential as a  
90 foundation for selecting the best adsorbent and employing it in an optimal way. Hence, the  
91 aim of this research is to clarify the chemical and physical interferences between the two  
92 materials, namely tea waste and dolomite, when used for the removal of copper and  
93 methylene blue from aqueous solutions. In this paper, the term adsorption will refer to  
94 biosorption onto tea waste (TW) and adsorption onto dolomite (DO). Copper ions and  
95 methylene blue dye adsorption onto tea waste and dolomite using different factors, such as  
96 reaction contact time and pH of solution as well as initial metal and dye concentration on  
97 selective adsorption was examined. Recognizing the fundamental mechanisms and behaviour  
98 would be useful for practical multi-adsorbent packed columns.

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## 101        **2. Materials and Methods**

### 102        **2.1. Adsorbents and adsorbents**

103        The two low cost materials used in this experiment were tea waste (TW) biosorbent and  
104        dolomite (DO) adsorbent. Fine Dolomite ( $d_p < 50\mu\text{m}$ ) was supplied by Killwaughter  
105        Chemical Company, UK. The typical chemical composition of the dolomite in the deposit  
106        was 44%  $\text{MgCO}_3$  and 53%  $\text{CaCO}_3$  (obtained by XRD analysis) [25]. The tea waste  
107        biosorbent was collected from Queen's University cafeteria; it was washed several times with  
108        hot water and dried in a conventional oven at 110 °C. The two adsorbents were  
109        comprehensively characterized in previous investigations [26, 27]. Copper(II) and Methylene  
110        Blue (MB) stock solutions were prepared by dissolving known amounts of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  
111        MB in deionised water. The stock solutions were then diluted to get various initial  
112        concentrations. All chemicals were purchased from Sigma Aldrich UK.

### 113        **2.2. Adsorption Experiment**

114        To investigate the influence of pH on Cu(II) and MB adsorption onto TW and DO, six sets of  
115        experiments were prepared: Cu(II) or MB with TW biosorbent; Cu(II) or MB with DO  
116        adsorbent and Cu(II) or MB with a mixture of 1:1 TW:DO (w/w%). Samples of 25  $\text{cm}^3$  of  
117        adsorbate solutions with  $C_o = 120$  and 100  $\text{mg}/\text{dm}^3$  of Cu and MB, respectively, were  
118        adjusted to different pH values: 2–11. The same procedures were performed to study the  
119        effect of contact time and adsorption isotherms. The initial concentrations of Cu(II) for the  
120        contact time studies was 200  $\text{mg}/\text{dm}^3$  and for MB it was 120  $\text{mg}/\text{dm}^3$ . For the adsorption  
121        isotherm studies, a concentration of:  $C_o = 10$ –100  $\text{mg}/\text{dm}^3$  for Cu(II) and  $C_o = 10$ –75  $\text{mg}/\text{dm}^3$   
122        for MB were used. An adsorbent dose of 1  $\text{g}/\text{dm}^3$  was used for all experiments at room  
123        temperature (~20 °C) and a contact time of 4 days to ensure reaching the equilibrium. There  
124        were no pH adjustments for contact time and isotherm experiments, so the experimental  
125        processes are more environmental friendly. The concentrations of Cu(II) and MB were

126 analysed using an ICP– OES Thermo Scientific IRIS and UV/Vis spectrophotometer (Perkin  
127 Elmer LAMBDA 25, UK), respectively. The amount of Cu(II) and MB adsorbed per unit  
128 mass of adsorbent  $q$  in (mg/g) and removal percentage were calculated using Eq. (1) and Eq.  
129 (2):

130 The percentage removal =  $\left[1 - \frac{C_e}{C_o}\right] \times 100\%$  (1)

131  $q = \left[\frac{C_o - C_e}{M}\right] \times V$  (2)

132 Where  $C_o$  and  $C_e$  (mg/L) are the concentration of adsorbate at initial and equilibrium,  
133 respectively,  $M$  is the mass of adsorbent (g) and  $V$  is the volume ( $\text{dm}^3$ ).

### 134 2.3. Infrared and SEM measurement

135 The FT-IR analyses for TW and DO surfaces before and after Cu(II) and MB adsorption were  
136 carried out on a Perkin Elmer Spectrum 100 within the range of  $400\text{--}4000\text{ cm}^{-1}$ . For the  
137 SEM analysis and Energy dispersive X-ray (EDX) analysis, TW and DO samples were  
138 coated with carbon and vacuumed (5–10 min) for electron reflection prior to analysis on a  
139 JEOL-JSM 6400 scanning microscope.

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### 147 3. Results and Discussion

#### 148 3.1. Effect of contact time

149 Figures S1 (a) and (b) are the plots of Cu(II) and MB removal against time for TW and DO  
150 materials, respectively. It can be seen that Cu(II) and MB were almost completely  
151 removed by dolomite and tea waste after 6 hrs at room temperature (20 °C). The adsorption of  
152 Cu(II) and MB dye was fast in the initial stage due to the large number of available binding  
153 sites, resulting in a concentration gradient [28]. The removal rate gradually declined with  
154 time until equilibrium was achieved. The maximum removal efficiencies of copper ions and  
155 MB onto TW and DO were approx. 90% at pH of 5–7. The adsorption capacities of Cu(II)  
156 and MB were reduced when the two materials were mixed together; this reduction was more  
157 significant in the case of Cu(II). The adsorption capacity of the mixed adsorbent (TW:DO)  
158 was reduced to approx. 45% and 85% for Cu and MB, respectively. This reduction is  
159 attributed to the change in the sorbent and solution properties such as  $pH_{PZC}$  and  $pH_{equilibrium}$   
160 [29]. However, results indicate that these pollutants can still be efficiently removed with high  
161 selectivity onto the mixed adsorbents.

#### 162 3.2. Kinetics Modelling

163 The adsorption mechanism can be investigated using various adsorption kinetics models.  
164 The pseudo first- [30] and pseudo second-order [31] models (Eq. 3 and Eq. 4) have been  
165 employed to examine the experimental data for the adsorption of Cu(II) and MB by nonlinear  
166 regression. The pseudo first-order model equation is given as follow:

$$167 \quad q_t = q_e (1 - e^{-k_1 t}) \quad (3)$$

168 The pseudo second-order equation is given as;

$$169 \quad q_t = \frac{k_2 q_e^2}{(1 + k_2 q_e t)} t \quad (4)$$

170 The second-order rate constants were used to calculate the initial sorption rate given by:

171  $h = k_2 q_e^2$  (5)

172 where  $k_1$  (1/min) and  $k_2$  (g/mg min) are the rate constants for first order and second-order  
173 models.

174 The plots of  $q_t$  versus  $t$  and values of the constants of kinetic models obtained from the plots  
175 are given in Figure 1 and Table 1. From Table 1, the pseudo first- and pseudo second-order  
176 models fit the kinetic data with adequate accuracy ( $R^2 > 0.897$ ). However, the experimental  
177 data demonstrated more agreement with the pseudo second-order model in terms of closer  
178  $q_{e,cal}$  values to  $q_{e,exp}$  and higher correlation coefficients than the pseudo first-order model.  
179 This indicates that the chemical adsorption was the main control process for the TW and DO  
180 materials and the uptake capacity is proportional to the number of active sites [32]. Similar  
181 trends were reported for the removal of copper onto chitosan-coated sludge [33] and  
182 methylene blue onto magnetic graphene-carbon nanotube composite and polyaniline  
183 nanotubes base/silica [34, 35]. The rate constants ( $k_1$  and  $k_2$ ) for both Cu(II) and MB sorption  
184 onto the TW biosorbent are higher than that for the DO adsorbent. This indicates that it is  
185 faster for Cu(II) and MB–TW systems to reach a specific fractional uptake. Initial adsorption  
186 rate ( $h$ ) values for Cu(II) and MB sorption followed the same trends (Cu(II) (89.07– 110.9  
187 mg/g min) and MB (17.56– 56.65 mg/g min). Also, the Elovich equation was used to  
188 evaluate the kinetic sorption data. The linear form of the Elovich equation is given in Eq. 6  
189 below:

190  $q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t)$  (6)

191 where  $\alpha$  is the initial adsorption rate (mg/g min), whilst  $\beta$  is the extent of surface coverage  
192 (g/mg) and activation energy of the process.

193 As can be seen in Table 1, the initial sorption rate ( $\alpha$ ) is lower in the case of sorption onto the  
194 DO system, similar to that of rate constants and initial sorption rate ( $h$ ) in the pseudo second-

195 order model. The Elovich equation did not fit the experimental data very well with the  
196 regression coefficient,  $R^2$ , within 0.659–0.877, suggesting that sorption systems of this study  
197 are maybe homogeneous.

### 198 **3.3. Effect of solution pH**

199 The pH parameter is associated with the adsorption mechanisms onto the adsorbent/biomass  
200 surfaces from water and determines the magnitude of the electrostatic charges [36]. From  
201 Figure 2, it can be observed that the uptake of Cu(II) onto the DO is significantly increased  
202 from 39% of removal at pH 2 to a maximum removal of 89% at pH 4.5. At this pH value, the  
203 main species of copper are Cu(II) free ions which are primarily involved in the removal  
204 process. With a pH value greater than 6, immediate precipitation of copper hydroxide takes  
205 place especially for high concentration of Cu(II) ions hindering the adsorption or biosorption  
206 processes [37]. The adsorption capacity of Cu(II) onto TW was notably lower at pH 4.5 with  
207 a maximum percentage removal of 39% at pH 5.5. The relatively lower Cu(II) removal onto  
208 TW can be attributed to the surface chemistry properties of TW such as; the surface point of  
209 zero charge. The PZC was previously determined to be  $\text{pH} = 4$  [27] and had an important  
210 effect on the equilibrium ( $\text{pH}_{\text{equilibrium}}$ ). For example, the Cu(II) solution with a  $\text{pH}_0 = 5.5$   
211 decreased to  $\text{pH}_{\text{eq}} = 4.2$  after being put in contact with TW for 4 days. Similar trends were  
212 observed for the biosorption of Cd(II) onto sawdust [1]. Also, it was found that the  
213 equilibrium pH for MB solution at  $\text{pH}_0 = 10$  was reduce to  $\text{pH}_{\text{eq}} = 8.8$  when using the TW:DO  
214 mixed adsorbent. However, MB was efficiently removed by TW over the pH range studied,  
215 which is attributable to the electrostatic attraction between the negatively charged TW surface  
216 and the cationic MB dye molecules [38]. These results demonstrated that pH had little effect  
217 on the capacity of the TW:DO system, indicating that the system has good potential for  
218 practical use.

## 219 **3.4. Equilibrium modelling**

### 220 **3.4.1. Langmuir Isotherm**

221 The Langmuir isotherm assumes that the surface of the adsorbent is homogeneous, the  
222 adsorption energy is constant over all sites and each site can accommodate only one molecule  
223 or atom [39]. The Langmuir adsorption isotherm is given as [40]:

$$224 \quad q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (7)$$

225 where  $q_{\max}$  (mg/g) and  $b$  (dm<sup>3</sup>/mg) are Langmuir constants associated with the capacity and  
226 energy of adsorption.

227 The fundamental characteristics of the Langmuir isotherm can be expressed by a  
228 dimensionless separation factor,  $R_L$ , defined by:

$$229 \quad R_L = \frac{1}{1 + (q_{\max} \times b) C_o} \quad (8)$$

230 The  $R_L$  parameter indicates the shape of the isotherm as follows:  $R_L > 1$ , unfavourable;  $R_L = 1$ ,  
231 linear;  $0 < R_L < 1$ , favourable;  $R_L = 0$ , irreversible.

### 232 **3.4.2. Freundlich Isotherm**

233 The Freundlich isotherm explains a particular phenomenon when the adsorption takes place  
234 on a heterogeneous surface [41]. The Freundlich isotherm model is given in Eq. 9:

$$235 \quad q_e = K_F C_e^n \quad (9)$$

236 where  $K_F$  and  $n$  are the Freundlich constants.

237 The Langmuir and Freundlich isotherm constants obtained from non-linear regression fitting  
238 are revealed in Table 2. The Langmuir and Freundlich isotherms were able to represent  
239 adsorption of copper ions and methylene blue by both materials in different systems (Figure 3  
240 & 4). The adsorption capacity of DO for Cu is significantly higher than TW and the trend is

241 reversed for MB. It can also be observed that the combination of TW and DO adsorbents will  
242 reduce the adsorption capacity towards Cu, while increasing the MB adsorption capacity  
243 (Table 2). In general, the sorption capacities were higher for MB than Cu, which may be due  
244 to the isotherm experiment being carried out without any pH adjustment. The dimensionless  
245 separation factor ( $R_L$ ) values were close to zero in all cases. This indicates that the adsorption  
246 processes of Cu and MB were favourable at the investigated conditions. The  $R_L$  values  
247 approached zero when TW:DO systems were used demonstrating that the uptake of the Cu  
248 and MB in these systems was more favourable. The Freundlich constant,  $n$  values in the  
249 range of 1.061–3.764 confirmed the process is classified as favourable adsorption [42]. The  
250 closer  $1/n$  is to zero, the greater the heterogeneity of the adsorbent [43].

### 251 3.5. Surface Characteristics of TW and Dolomite

#### 252 3.5.1. SEM and EDX

253 The SEM images of the TW and DO samples before and after adsorption of Cu and MB are  
254 shown in (Figure 5); experimental conditions:  $C_0$ : MB = 120 at pH 7 and Cu = 200 at pH 4.4  
255 and 6 hrs contact time). From Figure 5 (b) and (c), it can be noticed the formation of crystals  
256 at the surface of the DO sample after adsorption with Cu and MB. The presence of  $\text{CuCO}_3$  is  
257 confirmed with the presence of small and abundant crystals on the surface of DO. The  
258 development of crystals in the case of the DO– MB sample also suggests the implication of  
259 surface precipitation in the case of MB removal by DO. Similar processes were identified by  
260 Walker et al. with the removal of  $\text{Cu}^{2+}$  by half charred dolomite where surface complexation  
261 and precipitation were identified as the main removal route (See Figure 6 (a)) [25]. Surface  
262 precipitation of dye was reported in other studies and accounted for nearly 70% of dye  
263 removal when using lime treatment [44]. For the TW material, very little changes were  
264 observed between the samples before and after adsorption of MB and Cu. The absence of  
265 obvious surface structure change indicates that no surface precipitation is involved in the

266 removal of both pollutants by TW. The metal ions and dye molecules may bound to the  
267 active sites of the biosorbent through electrostatic attraction or hydrogen bonding (Figure 6  
268 (b)). Heavy metals removal by TW is very often accounted to chemisorption while dyes  
269 removal by biosorbents or activated carbon is mainly described through physisorption with  
270 minor contribution from chemisorption mechanisms [27, 45]. Table 3 presents the EDX  
271 results obtained for the exhausted adsorbents after kinetic experiments. The area analysed  
272 was the one presented in Figure 5, focusing on the crystals formed in the case of DO-Cu or  
273 DO-MB or on the possibly larger area for the TW-Cu and TW-MB. The thin carbon layer  
274 required in the technique shifted all the results obtained for the C content. However, it can be  
275 seen that TW samples are carbon rich as expected and DO contains a substantial amount of  
276 C, partly accounted for the  $\text{CO}_3^{2-}$  groups. The EDX method shows that Cu is present in the  
277 crystals formed at the surface of DO confirming the surface precipitation phenomenon. The  
278 presence of sulphur is probably due to the sulphate groups present in the Cu salt used in the  
279 experiment. The EDX technique cannot differentiate between the crystals formed and those  
280 in the DO structure. However, due to the experimental conditions, the nature of the copper  
281 crystals precipitated are identified as copper hydroxide crystals  $\text{Cu}(\text{OH})_2$  with potential  
282 existence of sulphate or carbonate groups [46]. The blue macroscopic colour of the DO  
283 sample after adsorption of copper confirms this identification. In the case of MB adsorption  
284 onto DO, the relatively high amount of sulphur can be accounted to the sulphur atoms present  
285 in the MB molecule. As the analysis area is focusing only on the crystals visible in Figure 5  
286 (c), the value of nearly 7% sulphur has to be balanced. Regarding the TW-Cu sample, the  
287 presence of 4.3% Cu at the surface of the sample is equivalent to 43 mg/g of Cu adsorption  
288 capacity, which is very close to the adsorption capacity calculated in the kinetic experiments  
289 (Table 1). The EDX analysis in the present case was carried out over the total surface of the  
290 sample from Figure 5 (e) as no surface precipitation was noticed. The very low content of

291 sulphur on the TW-Cu sample indicates that the sulphate groups from the copper salt are not  
292 adsorbed by the biosorbents. The copper sorption onto the TW surface is therefore very  
293 selective. The higher content of sulphur on the surface of the TW–MB sample confirms the  
294 adsorption of MB. The EDX technique confirmed the precipitation of both Cu and MB onto  
295 the surface of DO and suggested that the sorption of these pollutants onto TW was either due  
296 to chemisorption or physisorption.

### 297 3.5.2. FTIR analysis

298 Figure 7 illustrates the FTIR analysis of the DO samples before and after adsorption of MB  
299 and Cu. The spectrum of the DO sample shows several peaks around  $1400\text{ cm}^{-1}$  which are  
300 related to the  $\text{CO}_3^{2-}$  groups and are attributed to the C-O bonds present in the sample [26].  
301 Bands around  $2500\text{ cm}^{-1}$  are assigned to water molecules bonded to the sample [36]. The net  
302 peaks detected after the adsorption of MB found around  $3414\text{ cm}^{-1}$  are attributed to  $\text{OH}^-$   
303 bonds and thus show the hydration of the DO sample and possible links with MB molecules  
304 through chemisorption. The relatively high peak at  $3430\text{ cm}^{-1}$  confirms the presence of  
305 hydroxyl groups and the formation of  $\text{Cu}(\text{OH})_2$  complexes. A sharp peak observable at  $714$   
306  $\text{cm}^{-1}$  after Cu sorption was also noticed by Ippolito et al. and attributed to the presence of  
307 CaO [47]. The formation of complexes in the form of  $\text{Ca}/\text{Cu}-(\text{OH})_x$  is thus highly probable. A  
308 partial ion-exchange mechanism between  $\text{Ca}^{2+}$  and  $\text{Cu}^{2+}$  in the removal of copper from  
309 wastewater was also reported by Walker et al. [25]. The FTIR analysis for the TW sample  
310 shown in Figure 8, demonstrated major peaks indicating many functional groups such as  
311  $-\text{NH}_2$  and  $-\text{OH}$  groups of proteins and glucose;  $-\text{CH}$  stretching and  $>\text{C}=\text{O}$  ester stretching  
312 vibration of triglycerides; this stretching mode conjugated with the  $\text{NH}_2$  (amide 1 band) [27].  
313 After MB adsorption onto TW two main peaks can be seen at  $1383$  and  $1337\text{ cm}^{-1}$  and most  
314 of the peaks already present are enhanced. The FTIR peaks characteristic of MB molecules  
315 overlap with peaks from the TW sample as most chemical groups present in MB are present

316 in TW. The broad peak visible around 3230– 3270  $\text{cm}^{-1}$  is linked to the N-H bonding from  
317 MB. The peaks around 1737 and 1160  $\text{cm}^{-1}$  account for the sulphate groups and are naturally  
318 present on the TW sample [48]. It is thus interesting to note that after Cu adsorption this peak  
319 is relatively high, thus indicating a sorption of the sulphate groups from the copper salt as  
320 well. Negatively charged ions are necessary to counter-balance the sorption of  $\text{Cu}^{2+}$  onto TW,  
321 also  $\text{SO}_4^{2-}$  is involved in this process. The sorption of both anions and cations is  
322 characteristics of physisorption where both ions co-habit in the diffuse layer [49]. EDX  
323 analysis coupled with FTIR investigation showed that surface complexation was the main  
324 route of removal for Cu and MB by DO. Using data from the pH study it can be concluded  
325 that physisorption was responsible for most of Cu and MB adsorption onto TW even if  
326 chemisorption was also contributing to the removal of MB by TW.

### 327 **3.6. Comparison of adsorption capacity with composite adsorbents**

328 A comparison was carried out between the results of the adsorption capacities of tea waste  
329 and dolomite multi-adsorbent system dyes and chemically prepared composite adsorbents  
330 towards copper ions and methylene blue (Table 4). Ignoring the different experimental  
331 conditions used, it can be seen that the adsorption capacities obtained in this study are  
332 comparable with those reported by other researchers. This indicates that tea waste and  
333 dolomite multi-adsorbents can be classified as one of the effective adsorption systems for this  
334 purpose. The two substances in this investigation were physically mixed without any  
335 chemical modifications. Once more, this implies that environmentally friendly composite  
336 adsorbents can be produced at low cost and very little effort without any chemical alterations.

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341 **4. Conclusion**

342 The selectivity of tea waste and dolomite for copper and methylene blue and the influence of  
343 contact time, solution pH and initial pollutant concentration on adsorption capacities was  
344 examined. The adsorption kinetics could be explained by the pseudo-second-order model.  
345 The maximum removal capacity of Cu onto both adsorbents was achieved at pH = 4.5, while  
346 MB was optimally removed over the pH range studied with removal percentages of over  
347 90%. The present investigation indicated that tea waste and dolomite can concurrently be  
348 effectively used to remove copper and methylene blue from aqueous solution. Further studies  
349 are required to examine the effect of the chemistry of solution and the design and scale-up of  
350 fixed-bed adsorption columns.

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366 **5. References**

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1 **Preliminary investigation of mixed adsorbents for the removal of copper and methylene**  
2 **blue from aqueous solutions**

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26 **Abstract**

27 With most recent studies being focused on the development of advanced chemical  
28 adsorbents, this paper investigates the possibility of using two natural low-cost materials for  
29 selective adsorption. Multi-adsorbent systems containing tea waste (TW) and dolomite (DO)  
30 have been tested for their effectiveness in the removal of copper and methylene blue from  
31 aqueous solutions. The effects of contact time, solution pH and adsorption isotherms on the  
32 sorption behaviour were investigated. The Langmuir and Freundlich isotherms adequately  
33 described the adsorption of copper ions and methylene blue by both materials in different  
34 systems. The highest adsorption capacities for Cu and MB were calculated as 237.7 mg/g at  
35 pH 4.5 and 150.4 mg/g at pH 7 for DO and TW:DO respectively. Tea waste and dolomite  
36 were characterized by Fourier transform infrared spectroscopy, scanning electron microscopy  
37 and Energy dispersive X-ray analysis. The removal of Cu and MB by dolomite was mainly  
38 via surface complexation while physisorption was responsible for most of the Cu and MB  
39 adsorption onto tea waste. Identifying the fundamental mechanisms and behaviour is key to  
40 the development of practical multi-adsorbent packed columns.

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42 **Keywords:** Multi-adsorbents; Wastewater; Adsorption technique; Heavy metals; Dyes

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51        **1. Introduction**

52 Dyes (very frequently methylene blue and methyl orange) and heavy metals (copper,  
53 cadmium and nickel mostly from the organo-metallic dyes) are dangerous pollutants found in  
54 large quantities in wastewaters from textile and paper industries. It is known that heavy  
55 metals are toxic and non-biodegradable [1, 2]. Heavy metals have many environmental  
56 issues such as animal and plant death, reduced rates of reproduction and the decrease of  
57 ecosystem diversity [3]. While dyes are difficult to treat as the colour tends to hold strong  
58 even after the conventional removal processes [4]. There are more than 100,000  
59 commercially available dyes with over 700,000 tons produced annually [5]. The presence of  
60 some of these dyes even in very small amounts i.e.  $< 1 \text{ mg.dm}^{-3}$  is undesirable [6, 7]. Dyes-  
61 Heavy metal loaded wastewaters are highly coloured, have a fluctuating pH and regularly  
62 contain large amounts of suspended oils. Dyes and heavy metals find their way into the  
63 environment, primarily dissolved or suspended in water everyday [8] and create serious  
64 damage to the environment by changing the biological life balance in rivers and lakes [9, 10].  
65 Adsorption is a well-established and powerful practice for the removal of dyes and heavy  
66 metal pollutants from wastewaters. For these reasons, thousands of investigations have used  
67 uncountable adsorbents to remove heavy metals [11] or dyes [12]. Most of these studies focus  
68 on single-component aqueous solutions and recently, more research papers have been  
69 published dealing with the adsorption of dyes and metals in multi-component aqueous  
70 systems [6]. Also, composite adsorbents have been established to adsorb dyes and heavy  
71 metals from wastewater such as chitosan/montmorillonite composites [13-15] and fly  
72 ash/activated carbon [16]. In previous studies, composite materials were used to selectively  
73 adsorb a particular pollutant. Ho and co-workers proved that amino functionalized silica  
74 solids can selectively adsorb dye anthraquinone blue in the presence of methylene blue,  
75 while, from the same dye mixture, carboxy-functionalized materials adsorb methylene blue

76 selectively [17]. Prediction of multicomponent adsorption is still one of the most challenging  
77 problems in the adsorption field [18]. There is little data available to provide more  
78 understanding about the interactions between adsorbents and developing design models for  
79 such practical systems is very important [19]. This is the case for many composite materials  
80 as well as adsorption processes with multi-adsorbate and multi-adsorbent systems. Dolomite,  
81 with a structure of alternative layers of calcite and magnesite, is a potential inexpensive and  
82 readily available adsorbent [20]. Many studies showed that dolomite and charred dolomite  
83 have the potential to act as adsorbents for reactive dyes and heavy metals [21]. Tea,  
84 processed leaves from *Camellia sinensis* species, is the second most common drink being  
85 consumed after water with an average daily drinking of 20 billion cups. The producers of  
86 making tea drinks face a problem in disposing of the spent tea leaves after the extraction [22,  
87 23]. The feasibility of using the richly available solid waste, spent tea leaves, for the removal  
88 of heavy metals and dyes has also been extensively investigated [24]. A good understanding  
89 of the effect of adsorbent-adsorbent interactions on selective adsorption is essential as a  
90 foundation for selecting the best adsorbent and employing it in an optimal way. Hence, the  
91 aim of this research is to clarify the chemical and physical interferences between the two  
92 materials, namely tea waste and dolomite, when used for the removal of copper and  
93 methylene blue from aqueous solutions. In this paper, the term adsorption will refer to  
94 biosorption onto tea waste (TW) and adsorption onto dolomite (DO). Copper ions and  
95 methylene blue dye adsorption onto tea waste and dolomite using different factors, such as  
96 reaction contact time and pH of solution as well as initial metal and dye concentration on  
97 selective adsorption was examined. Recognizing the fundamental mechanisms and behaviour  
98 would be useful for practical multi-adsorbent packed columns.

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101 **2. Materials and Methods**

102 **2.1. Adsorbents and adsorbates**

103 The two low cost materials used in this experiment were tea waste (TW) biosorbent and  
104 dolomite (DO) adsorbent. Fine Dolomite ( $d_p < 50\mu\text{m}$ ) was supplied by Killwaughter  
105 Chemical Company, UK. The typical chemical composition of the dolomite in the deposit  
106 was 44%  $\text{MgCO}_3$  and 53%  $\text{CaCO}_3$  (obtained by XRD analysis) [25]. The tea waste  
107 biosorbent was collected from Queen's University cafeteria; it was washed several times with  
108 hot water and dried in a conventional oven at  $110\text{ }^\circ\text{C}$ . The two adsorbents were  
109 comprehensively characterized in previous investigations [26, 27]. Copper(II) and Methylene  
110 Blue (MB) stock solutions were prepared by dissolving known amounts of  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$  and  
111 MB in deionised water. The stock solutions were then diluted to get various initial  
112 concentrations. All chemicals were purchased from Sigma Aldrich UK.

113 **2.2. Adsorption Experiment**

114 To investigate the influence of pH on Cu(II) and MB adsorption onto TW and DO, six sets of  
115 experiments were prepared: Cu(II) or MB with TW biosorbent; Cu(II) or MB with DO  
116 adsorbent and Cu(II) or MB with a mixture of 1:1 TW:DO (w/w%). Samples of  $25\text{ cm}^3$  of  
117 adsorbate solutions with  $C_o = 120$  and  $100\text{ mg/dm}^3$  of Cu and MB, respectively, were  
118 adjusted to different pH values: 2–11. The same procedures were performed to study the  
119 effect of contact time and adsorption isotherms. The initial concentrations of Cu(II) for the  
120 contact time studies was  $200\text{ mg/dm}^3$  and for MB it was  $120\text{ mg/dm}^3$ . For the adsorption  
121 isotherm studies, a concentration of:  $C_o = 10\text{--}100\text{ mg/dm}^3$  for Cu(II) and  $C_o = 10\text{--}75\text{ mg/dm}^3$   
122 for MB were used. An adsorbent dose of  $1\text{ g/dm}^3$  was used for all experiments at room  
123 temperature ( $\sim 20\text{ }^\circ\text{C}$ ) and a contact time of 4 days to ensure reaching the equilibrium. There  
124 were no pH adjustments for contact time and isotherm experiments, so the experimental  
125 processes are more environmental friendly. The concentrations of Cu(II) and MB were

126 analysed using an ICP-OES Thermo Scientific IRIS and UV/Vis spectrophotometer (Perkin  
127 Elmer LAMBDA 25, UK), respectively. The amount of Cu(II) and MB adsorbed per unit  
128 mass of adsorbent  $q$  in (mg/g) and removal percentage were calculated using Eq. (1) and Eq.  
129 (2):

130 The percentage removal =  $\left[1 - \frac{C_e}{C_o}\right] \times 100\%$  (1)

131  $q = \left[\frac{C_o - C_e}{M}\right] \times V$  (2)

132 Where  $C_o$  and  $C_e$  (mg/L) are the concentration of adsorbate at initial and equilibrium,  
133 respectively,  $M$  is the mass of adsorbent (g) and  $V$  is the volume ( $\text{dm}^3$ ).

### 134 2.3. Infrared and SEM measurement

135 The FT-IR analyses for TW and DO surfaces before and after Cu(II) and MB adsorption were  
136 carried out on a Perkin Elmer Spectrum 100 within the range of  $400\text{--}4000\text{ cm}^{-1}$ . For the  
137 SEM analysis and Energy dispersive X-ray (EDX) analysis, TW and DO samples were  
138 coated with carbon and vacuumed (5–10 min) for electron reflection prior to analysis on a  
139 JEOL-JSM 6400 scanning microscope.

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147 **3. Results and Discussion**

148 **3.1. Effect of contact time**

149 Figures S1 (a) and (b) are the plots of Cu(II) and MB removal against time for TW and DO  
150 materials, respectively. It can be seen that Cu(II) and MB were almost completely  
151 removed by dolomite and tea waste after 6 hrs at room temperature (20 °C). The adsorption of  
152 Cu(II) and MB dye was fast in the initial stage due to the large number of available binding  
153 sites, resulting in a concentration gradient [28]. The removal rate gradually declined with  
154 time until equilibrium was achieved. The maximum removal efficiencies of copper ions and  
155 MB onto TW and DO were approx. 90% at pH of 5–7. The adsorption capacities of Cu(II)  
156 and MB were reduced when the two materials were mixed together; this reduction was more  
157 significant in the case of Cu(II). The adsorption capacity of the mixed adsorbent (TW:DO)  
158 was reduced to approx. 45% and 85% for Cu and MB, respectively. This reduction is  
159 attributed to the change in the sorbent and solution properties such as  $pH_{PZC}$  and  $pH_{equilibrium}$   
160 [29]. However, results indicate that these pollutants can still be efficiently removed with high  
161 selectivity onto the mixed adsorbents.

162 **3.2. Kinetics Modelling**

163 The adsorption mechanism can be investigated using various adsorption kinetics models.  
164 The pseudo first- [30] and pseudo second-order [31] models (Eq. 3 and Eq. 4) have been  
165 employed to examine the experimental data for the adsorption of Cu(II) and MB by nonlinear  
166 regression. The pseudo first-order model equation is given as follow:

167 
$$q_t = q_e (1 - e^{-k_1 t}) \quad (3)$$

168 The pseudo second-order equation is given as;

169 
$$q_t = \frac{k_2 q_e^2}{(1 + k_2 q_e t)} t \quad (4)$$

170 The second-order rate constants were used to calculate the initial sorption rate given by:

171  $h = k_2 q_e^2$  (5)

172 where  $k_1$  (1/min) and  $k_2$  (g/mg min) are the rate constants for first order and second-order  
173 models.

174 The plots of  $q_t$  versus  $t$  and values of the constants of kinetic models obtained from the plots  
175 are given in Figure 1 and Table 1. From Table 1, the pseudo first- and pseudo second-order  
176 models fit the kinetic data with adequate accuracy ( $R^2 > 0.897$ ). However, the experimental  
177 data demonstrated more agreement with the pseudo second-order model in terms of closer  
178  $q_{e,cal}$  values to  $q_{e,exp}$  and higher correlation coefficients than the pseudo first-order model.  
179 This indicates that the chemical adsorption was the main control process for the TW and DO  
180 materials and the uptake capacity is proportional to the number of active sites [32]. Similar  
181 trends were reported for the removal of copper onto chitosan-coated sludge [33] and  
182 methylene blue onto magnetic graphene-carbon nanotube composite and polyaniline  
183 nanotubes base/silica [34, 35]. The rate constants ( $k_1$  and  $k_2$ ) for both Cu(II) and MB sorption  
184 onto the TW biosorbent are higher than that for the DO adsorbent. This indicates that it is  
185 faster for Cu(II) and MB-TW systems to reach a specific fractional uptake. Initial  
186 adsorption rate ( $h$ ) values for Cu(II) and MB sorption followed the same trends (Cu(II)  
187 (89.07-110.9 mg/g min) and MB (17.56-56.65 mg/g min). Also, the Elovich equation was  
188 used to evaluate the kinetic sorption data. The linear form of the Elovich equation is given in  
189 Eq. 6 below:

190  $q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t)$  (6)

191 where  $\alpha$  is the initial adsorption rate (mg/g min), whilst  $\beta$  is the extent of surface coverage  
192 (g/mg) and activation energy of the process.

193 As can be seen in Table 1, the initial sorption rate ( $\alpha$ ) is lower in the case of sorption onto the  
194 DO system, similar to that of rate constants and initial sorption rate ( $h$ ) in the pseudo second-

195 order model. The Elovich equation did not fit the experimental data very well with the  
196 regression coefficient,  $R^2$ , within 0.659–0.877, suggesting that sorption systems of this study  
197 are maybe homogeneous.

### 198 **3.3. Effect of solution pH**

199 The pH parameter is associated with the adsorption mechanisms onto the adsorbent/biomass  
200 surfaces from water and determines the magnitude of the electrostatic charges [36]. From  
201 Figure 2, it can be observed that the uptake of Cu(II) onto the DO is significantly increased  
202 from 39% of removal at pH 2 to a maximum removal of 89% at pH 4.5. At this pH value, the  
203 main species of copper are Cu(II) free ions which are primarily involved in the removal  
204 process. With a pH value greater than 6, immediate precipitation of copper hydroxide takes  
205 place especially for high concentration of Cu(II) ions hindering the adsorption or biosorption  
206 processes [37]. The adsorption capacity of Cu(II) onto TW was notably lower at pH 4.5 with  
207 a maximum percentage removal of 39% at pH 5.5. The relatively lower Cu(II) removal onto  
208 TW can be attributed to the surface chemistry properties of TW such as; the surface point of  
209 zero charge. The PZC was previously determined to be  $\text{pH} = 4$  [27] and had an important  
210 effect on the equilibrium ( $\text{pH}_{\text{equilibrium}}$ ). For example, the Cu(II) solution with a  $\text{pH}_o = 5.5$   
211 decreased to  $\text{pH}_{\text{eq}} = 4.2$  after being put in contact with TW for 4 days. Similar trends were  
212 observed for the biosorption of Cd(II) onto sawdust [1]. Also, it was found that the  
213 equilibrium pH for MB solution at  $\text{pH}_o = 10$  was reduce to  $\text{pH}_{\text{eq}} = 8.8$  when using the TW:DO  
214 mixed adsorbent. However, MB was efficiently removed by TW over the pH range studied,  
215 which is attributable to the electrostatic attraction between the negatively charged TW surface  
216 and the cationic MB dye molecules [38]. These results demonstrated that pH had little effect  
217 on the capacity of the TW:DO system, indicating that the system has good potential for  
218 practical use.

### 219 3.4. Equilibrium modelling

#### 220 3.4.1. Langmuir Isotherm

221 The Langmuir isotherm assumes that the surface of the adsorbent is homogeneous, the  
222 adsorption energy is constant over all sites and each site can accommodate only one molecule  
223 or atom [39]. The Langmuir adsorption isotherm is given as [40]:

$$224 \quad q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (7)$$

225 where  $q_{\max}$  (mg/g) and  $b$  (dm<sup>3</sup>/mg) are Langmuir constants associated with the capacity and  
226 energy of adsorption.

227 The fundamental characteristics of the Langmuir isotherm can be expressed by a  
228 dimensionless separation factor,  $R_L$ , defined by:

$$229 \quad R_L = \frac{1}{1 + (q_{\max} \times b) C_o} \quad (8)$$

230 The  $R_L$  parameter indicates the shape of the isotherm as follows:  $R_L > 1$ , unfavourable;  $R_L = 1$ ,  
231 linear;  $0 < R_L < 1$ , favourable;  $R_L = 0$ , irreversible.

#### 232 3.4.2. Freundlich Isotherm

233 The Freundlich isotherm explains a particular phenomenon when the adsorption takes place  
234 on a heterogeneous surface [41]. The Freundlich isotherm model is given in Eq. 9:

$$235 \quad q_e = K_F C_e^n \quad (9)$$

236 where  $K_F$  and  $n$  are the Freundlich constants.

237 The Langmuir and Freundlich isotherm constants obtained from non-linear regression fitting  
238 are revealed in Table 2. The Langmuir and Freundlich isotherms were able to represent  
239 adsorption of copper ions and methylene blue by both materials in different systems (Figure 3  
240 & 4). The adsorption capacity of DO for Cu is significantly higher than TW and the trend is

241 reversed for MB. It can also be observed that the combination of TW and DO adsorbents will  
242 reduce the adsorption capacity towards Cu, while increasing the MB adsorption capacity  
243 (Table 2). In general, the sorption capacities were higher for MB than Cu, which may be due  
244 to the isotherm experiment being carried out without any pH adjustment. The dimensionless  
245 separation factor ( $R_L$ ) values were close to zero in all cases. This indicates that the adsorption  
246 processes of Cu and MB were favourable at the investigated conditions. The  $R_L$  values  
247 approached zero when TW:DO systems were used demonstrating that the uptake of the Cu  
248 and MB in these systems was more favourable. The Freundlich constant,  $n$  values in the  
249 range of 1.061–3.764 confirmed the process is classified as favourable adsorption [42]. The  
250 closer  $1/n$  is to zero, the greater the heterogeneity of the adsorbent [43].

### 251 **3.5. Surface Characteristics of TW and Dolomite**

#### 252 **3.5.1. SEM and EDX**

253 The SEM images of the TW and DO samples before and after adsorption of Cu and MB are  
254 shown in (Figure 5); experimental conditions:  $C_0$ : MB = 120 at pH 7 and Cu = 200 at pH 4.4  
255 and 6 hrs contact time). From Figure 5 (b) and (c), it can be noticed the formation of crystals  
256 at the surface of the DO sample after adsorption with Cu and MB. The presence of  $\text{CuCO}_3$  is  
257 confirmed with the presence of small and abundant crystals on the surface of DO. The  
258 development of crystals in the case of the DO–MB sample also suggests the implication of  
259 surface precipitation in the case of MB removal by DO. Similar processes were identified by  
260 Walker et al. with the removal of  $\text{Cu}^{2+}$  by half charred dolomite where surface complexation  
261 and precipitation were identified as the main removal route (See Figure 6 (a)) [25]. Surface  
262 precipitation of dye was reported in other studies and accounted for nearly 70% of dye  
263 removal when using lime treatment [44]. For the TW material, very little changes were  
264 observed between the samples before and after adsorption of MB and Cu. The absence of  
265 obvious surface structure change indicates that no surface precipitation is involved in the

266 removal of both pollutants by TW. The metal ions and dye molecules may bound to the  
267 active sites of the biosorbent through electrostatic attraction or hydrogen bonding (Figure 6  
268 (b)). Heavy metals removal by TW is very often accounted to chemisorption while dyes  
269 removal by biosorbents or activated carbon is mainly described through physisorption with  
270 minor contribution from chemisorption mechanisms [27, 45]. Table 3 presents the EDX  
271 results obtained for the exhausted adsorbents after kinetic experiments. The area analysed  
272 was the one presented in Figure 5, focusing on the crystals formed in the case of DO–Cu or  
273 DO–MB or on the possibly larger area for the TW–Cu and TW–MB. The thin carbon layer  
274 required in the technique shifted all the results obtained for the C content. However, it can be  
275 seen that TW samples are carbon rich as expected and DO contains a substantial amount of  
276 C, partly accounted for the  $\text{CO}_3^{2-}$  groups. The EDX method shows that Cu is present in the  
277 crystals formed at the surface of DO confirming the surface precipitation phenomenon. The  
278 presence of sulphur is probably due to the sulphate groups present in the Cu salt used in the  
279 experiment. The EDX technique cannot differentiate between the crystals formed and those  
280 in the DO structure. However, due to the experimental conditions, the nature of the copper  
281 crystals precipitated are identified as copper hydroxide crystals  $\text{Cu}(\text{OH})_2$  with potential  
282 existence of sulphate or carbonate groups [46]. The blue macroscopic colour of the DO  
283 sample after adsorption of copper confirms this identification. In the case of MB adsorption  
284 onto DO, the relatively high amount of sulphur can be accounted to the sulphur atoms present  
285 in the MB molecule. As the analysis area is focusing only on the crystals visible in Figure 5  
286 (c), the value of nearly 7% sulphur has to be balanced. Regarding the TW–Cu sample, the  
287 presence of 4.3% Cu at the surface of the sample is equivalent to 43 mg/g of Cu adsorption  
288 capacity, which is very close to the adsorption capacity calculated in the kinetic experiments  
289 (Table 1). The EDX analysis in the present case was carried out over the total surface of the  
290 sample from Figure 5 (e) as no surface precipitation was noticed. The very low content of

291 sulphur on the TW–Cu sample indicates that the sulphate groups from the copper salt are not  
292 adsorbed by the biosorbents. The copper sorption onto the TW surface is therefore very  
293 selective. The higher content of sulphur on the surface of the TW–MB sample confirms the  
294 adsorption of MB. The EDX technique confirmed the precipitation of both Cu and MB onto  
295 the surface of DO and suggested that the sorption of these pollutants onto TW was either due  
296 to chemisorption or physisorption.

### 297 **3.5.2. FTIR analysis**

298 Figure 7 illustrates the FTIR analysis of the DO samples before and after adsorption of MB  
299 and Cu. The spectrum of the DO sample shows several peaks around  $1400\text{ cm}^{-1}$  which are  
300 related to the  $\text{CO}_3^{2-}$  groups and are attributed to the C–O bonds present in the sample [26].  
301 Bands around  $2500\text{ cm}^{-1}$  are assigned to water molecules bonded to the sample [36]. The net  
302 peaks detected after the adsorption of MB found around  $3414\text{ cm}^{-1}$  are attributed to  $\text{OH}^\square$   
303 bonds and thus show the hydration of the DO sample and possible links with MB molecules  
304 through chemisorption. The relatively high peak at  $3430\text{ cm}^{-1}$  confirms the presence of  
305 hydroxyl groups and the formation of  $\text{Cu}(\text{OH})_2$  complexes. A sharp peak observable at  $714$   
306  $\text{cm}^{-1}$  after Cu sorption was also noticed by Ippolito et al. and attributed to the presence of  
307 CaO [47]. The formation of complexes in the form of  $\text{Ca/Cu}-(\text{OH})_x$  is thus highly probable. A  
308 partial ion-exchange mechanism between  $\text{Ca}^{2+}$  and  $\text{Cu}^{2+}$  in the removal of copper from  
309 wastewater was also reported by Walker et al. [25]. The FTIR analysis for the TW sample  
310 shown in Figure 8, demonstrated major peaks indicating many functional groups such as  
311  $-\text{NH}_2$  and  $-\text{OH}$  groups of proteins and glucose;  $-\text{CH}$  stretching and  $>\text{C}=\text{O}$  ester stretching  
312 vibration of triglycerides; this stretching mode conjugated with the  $\text{NH}_2$  (amide 1 band) [27].  
313 After MB adsorption onto TW two main peaks can be seen at  $1383$  and  $1337\text{ cm}^{-1}$  and most  
314 of the peaks already present are enhanced. The FTIR peaks characteristic of MB molecules  
315 overlap with peaks from the TW sample as most chemical groups present in MB are present

316 in TW. The broad peak visible around 3230–3270  $\text{cm}^{-1}$  is linked to the N-H bonding from  
317 MB. The peaks around 1737 and 1160  $\text{cm}^{-1}$  account for the sulphate groups and are naturally  
318 present on the TW sample [48]. It is thus interesting to note that after Cu adsorption this peak  
319 is relatively high, thus indicating a sorption of the sulphate groups from the copper salt as  
320 well. Negatively charged ions are necessary to counter-balance the sorption of  $\text{Cu}^{2+}$  onto TW,  
321 also  $\text{SO}_4^{2-}$  is involved in this process. The sorption of both anions and cations is  
322 characteristics of physisorption where both ions co-habit in the diffuse layer [49]. EDX  
323 analysis coupled with FTIR investigation showed that surface complexation was the main  
324 route of removal for Cu and MB by DO. Using data from the pH study it can be concluded  
325 that physisorption was responsible for most of Cu and MB adsorption onto TW even if  
326 chemisorption was also contributing to the removal of MB by TW.

### 327 **3.6. Comparison of adsorption capacity with composite adsorbents**

328 A comparison was carried out between the results of the adsorption capacities of tea waste  
329 and dolomite multi-adsorbent system dyes and chemically prepared composite adsorbents  
330 towards copper ions and methylene blue (Table 4). Ignoring the different experimental  
331 conditions used, it can be seen that the adsorption capacities obtained in this study are  
332 comparable with those reported by other researchers. This indicates that tea waste and  
333 dolomite multi-adsorbents can be classified as one of the effective adsorption systems for this  
334 purpose. The two substances in this investigation were physically mixed without any  
335 chemical modifications. Once more, this implies that environmentally friendly composite  
336 adsorbents can be produced at low cost and very little effort without any chemical alterations.

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341 **4. Conclusion**

342 The selectivity of tea waste and dolomite for copper and methylene blue and the influence of  
343 contact time, solution pH and initial pollutant concentration on adsorption capacities was  
344 examined. The adsorption kinetics could be explained by the pseudo-second-order model.  
345 The maximum removal capacity of Cu onto both adsorbents was achieved at pH = 4.5, while  
346 MB was optimally removed over the pH range studied with removal percentages of over  
347 90%. The present investigation indicated that tea waste and dolomite can concurrently be  
348 effectively used to remove copper and methylene blue from aqueous solution. Further studies  
349 are required to examine the effect of the chemistry of solution and the design and scale-up of  
350 fixed-bed adsorption columns.

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Table 1: Pseudo first-order and pseudo second-order model constants for Cu(II) and MB sorption onto tea waste and dolomite at different systems.

Adsorbent		Pseudo first-order model				Pseudo second-order model			Elovich equation		
		$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	$k_1$ (1/min)	$R^2$	$q_{e,cal}$ (mg/g)	$k_2$ (g/mg min)	$R^2$	$\alpha$	$\beta$	$R^2$
<b>Cu</b>	<b>TW</b>	60.80	55.68	0.221	0.901	59.26	0.005	0.967	0.532	5.376	0.853
	<b>DO</b>	186.5	177.9	0.011	0.897	193.8	0.001	0.910	0.019	29.12	0.823
	<b>TW + DO</b>	82.09	74.23	0.480	0.908	79.34	0.009	0.947	0.438	5.135	0.837
<b>MB</b>	<b>TW</b>	111.6	109.4	0.407	0.995	112.8	0.007	0.999	0.598	15.12	0.659
	<b>DO</b>	67.75	57.70	0.126	0.896	62.65	0.003	0.963	0.108	10.90	0.877
	<b>TW + DO</b>	107.7	102.6	0.486	0.991	105.3	0.010	0.997	0.689	14.13	0.661

Table 2: The Langmuir and Freundlich isotherm constants for Cu(II) and MB sorption onto tea waste and dolomite at different systems.

Adsorbent		Langmuir isotherm model				Freundlich isotherm model		
		$q_{\max}$ (mg/g)	$b$ (dm <sup>3</sup> /mg)	$R_L (\times 10^3)$	$R^2$	$K_F$ (mg/g)(dm <sup>3</sup> /mg) <sup>1/n</sup>	$n$	$R^2$
<b>Cu</b>	<b>TW</b>	77.31	0.015	8.549	0.960	2.402	1.492	0.979
	<b>DO</b>	237.7	0.022	1.883	0.990	6.607	1.244	0.983
	<b>TW + DO</b>	38.2	0.239	1.094	0.984	12.69	3.764	0.922
<b>MB</b>	<b>TW</b>	130.5	0.271	0.376	0.946	28.02	1.564	0.912
	<b>DO</b>	113.3	0.018	6.493	0.901	4.256	1.520	0.925
	<b>TW + DO</b>	150.4	0.262	0.338	0.967	30.92	1.445	0.944

Table 3: EDX analysis results expressed in % w/w.

<b>Elemental composition in % w/w</b>						
	<b>C</b>	<b>O</b>	<b>Mg</b>	<b>S</b>	<b>Ca</b>	<b>Cu</b>
<b>DO-Cu</b>	22.80	29.88	2.77	4.33	14.55	25.66
<b>DO-MB</b>	18.42	43.33	6.64	6.21	25.40	-
<b>TW-Cu</b>	65.41	29.82	-	0.46	-	4.31
<b>TW-MB</b>	71.60	27.00	-	1.40	-	-

Table 4: Comparison of adsorption capacities of the TW:DO system with composite adsorbents in literature.

<b>Adsorbents</b>	<b>Pollutant</b> <b>(Cu or MB)</b>	<b>Adsorption</b> <b>capacity (mg/g)</b>	<b>Max conc.</b> <b>Studied</b>	<b>Best fit isotherm</b>	<b>Ref.</b>
<b>Bentonite–polyacrylamide</b>	Cu(II)	32.8	15 ppm	Langmuir	[2]
<b>Ligand modified composite</b>	Cu(II)	182.1	60 ppm	Langmuir	[14]
<b>Alginate/Mauritanian clay (Na-ZS26)</b>	Cu(II)	15.1	200 ppm	Langmuir	[15]
<b>Tea waste + Dolomite</b>	Cu(II)	38.1	100 ppm	Langmuir	Current study
<b>Alumina-carbon</b>	MB	1152.3	420 ppm	Redlich-Peterson	[10]
<b>Magnetic graphene-carbon nanotube</b>	MB	65.79	35 ppm	Langmuir	[34]
<b>Polyaniline nanotubes base/silica</b>	MB	10.3	10 ppm	Langmuir	[35]
<b>Tea waste + Dolomite</b>	MB	150.4	75 ppm	Langmuir	Current study

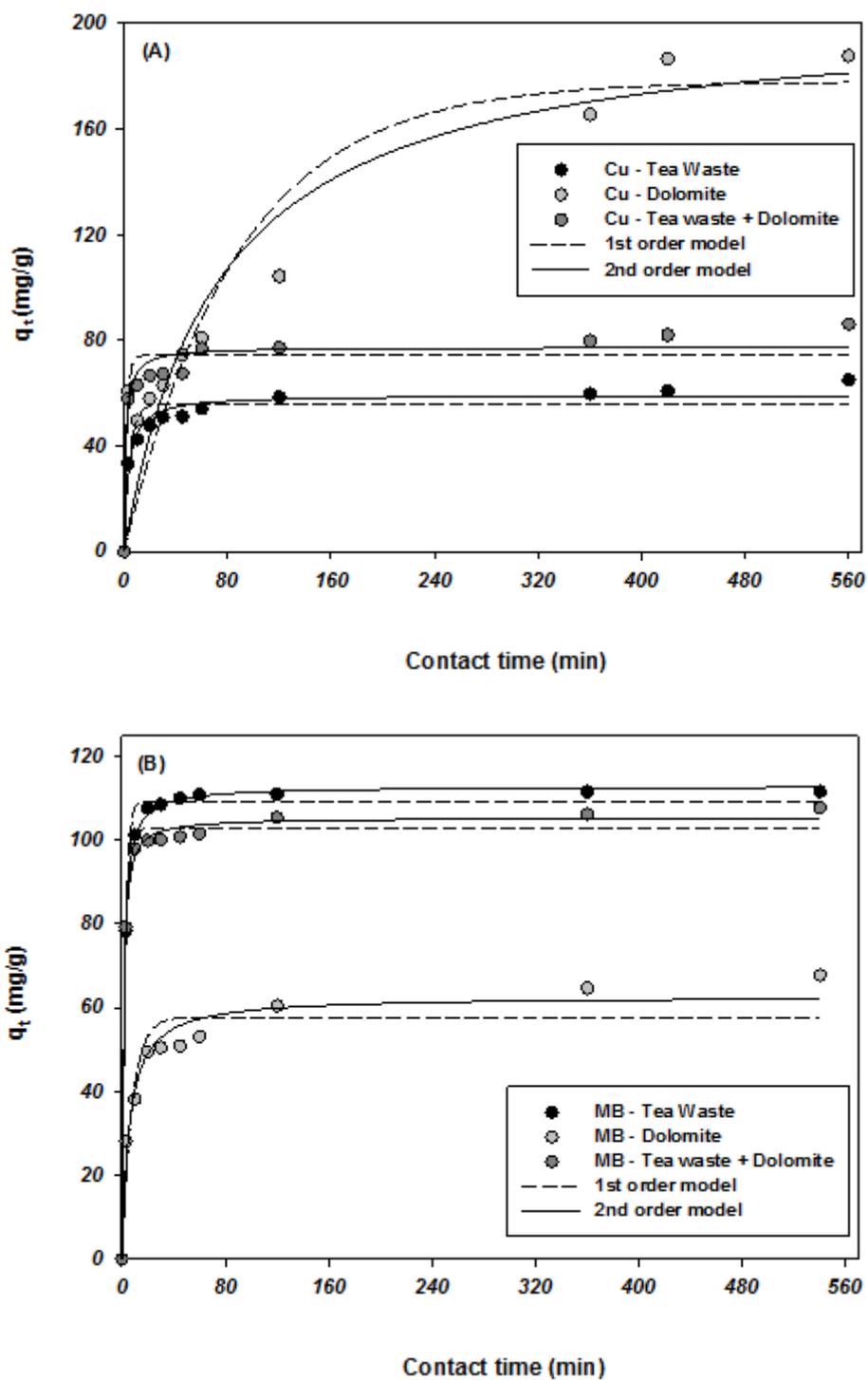


Figure 1: The fitting of pseudo first- and second-order models for Cr(II) and MB removal onto TW and DO.

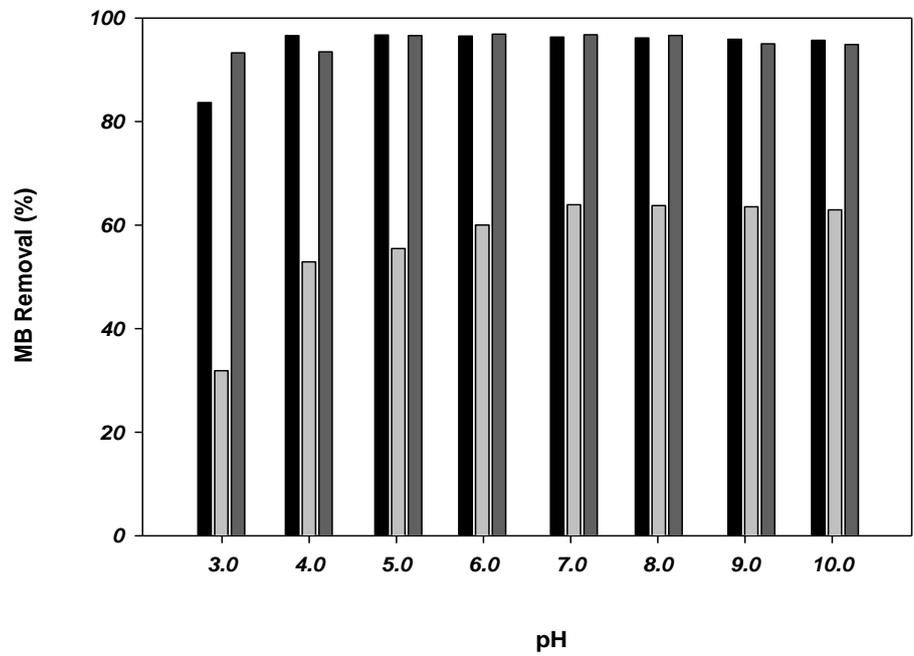
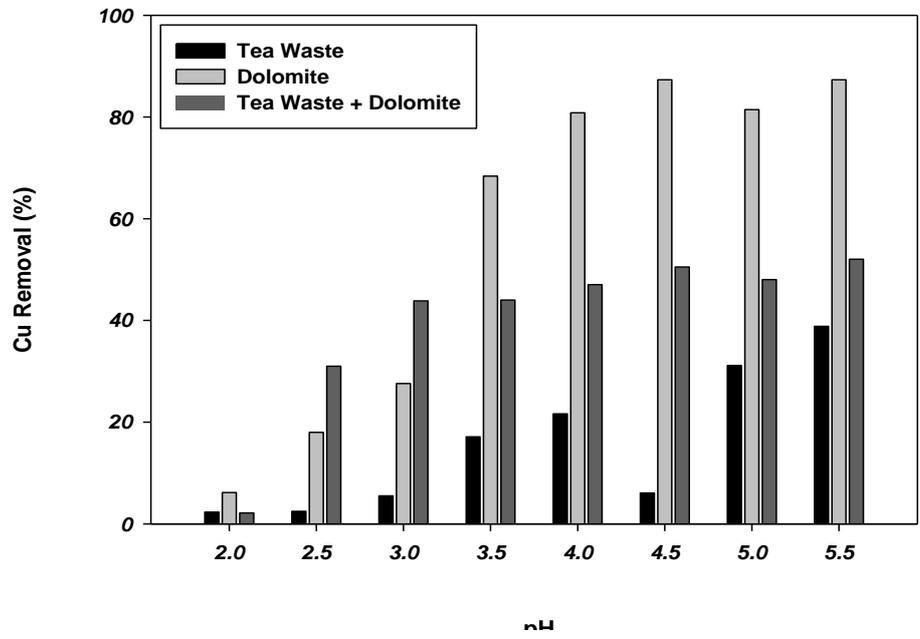


Figure 2: Effect of pH on the removal of Cu(II) and MB onto TW and DO.

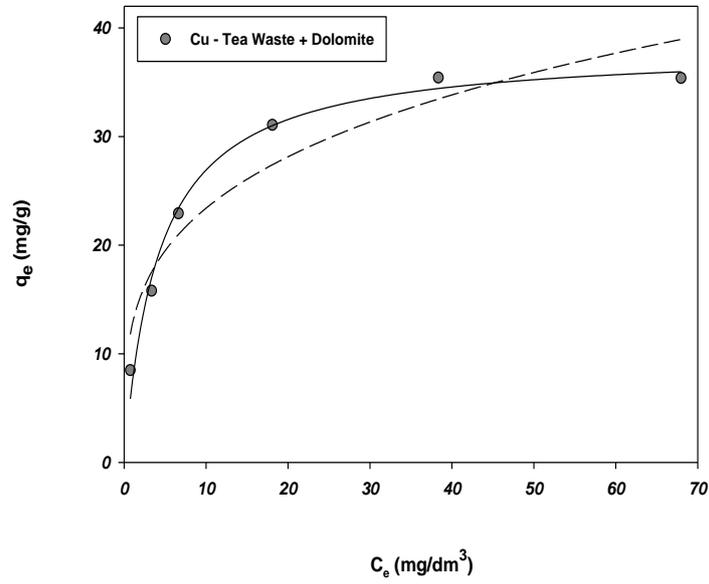
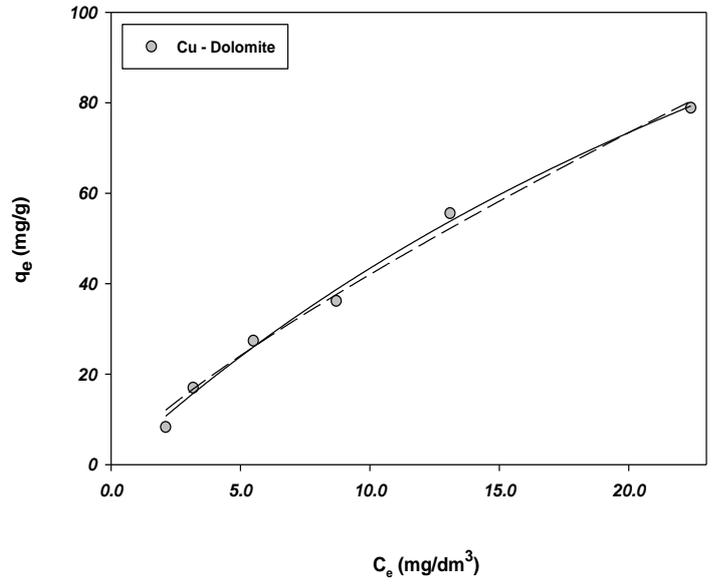
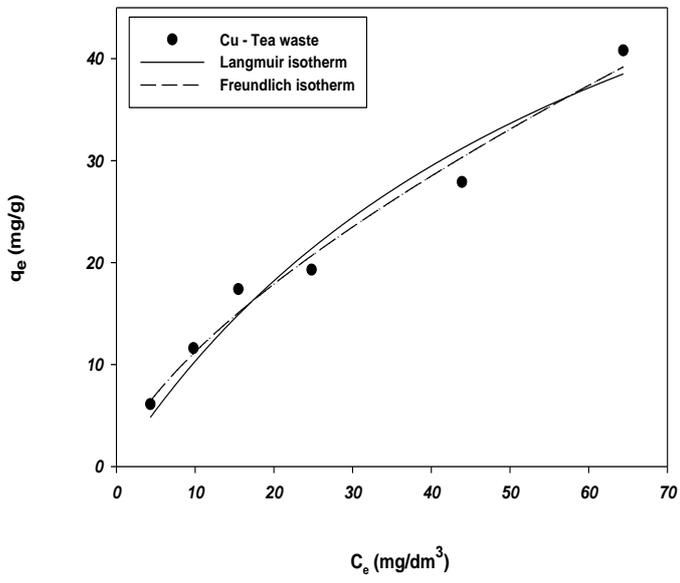


Figure 3: Non-linear forms of Langmuir and Freundlich adsorption isotherm plots of Cu adsorption onto Tea Waste (TW) and Dolomite (DO).

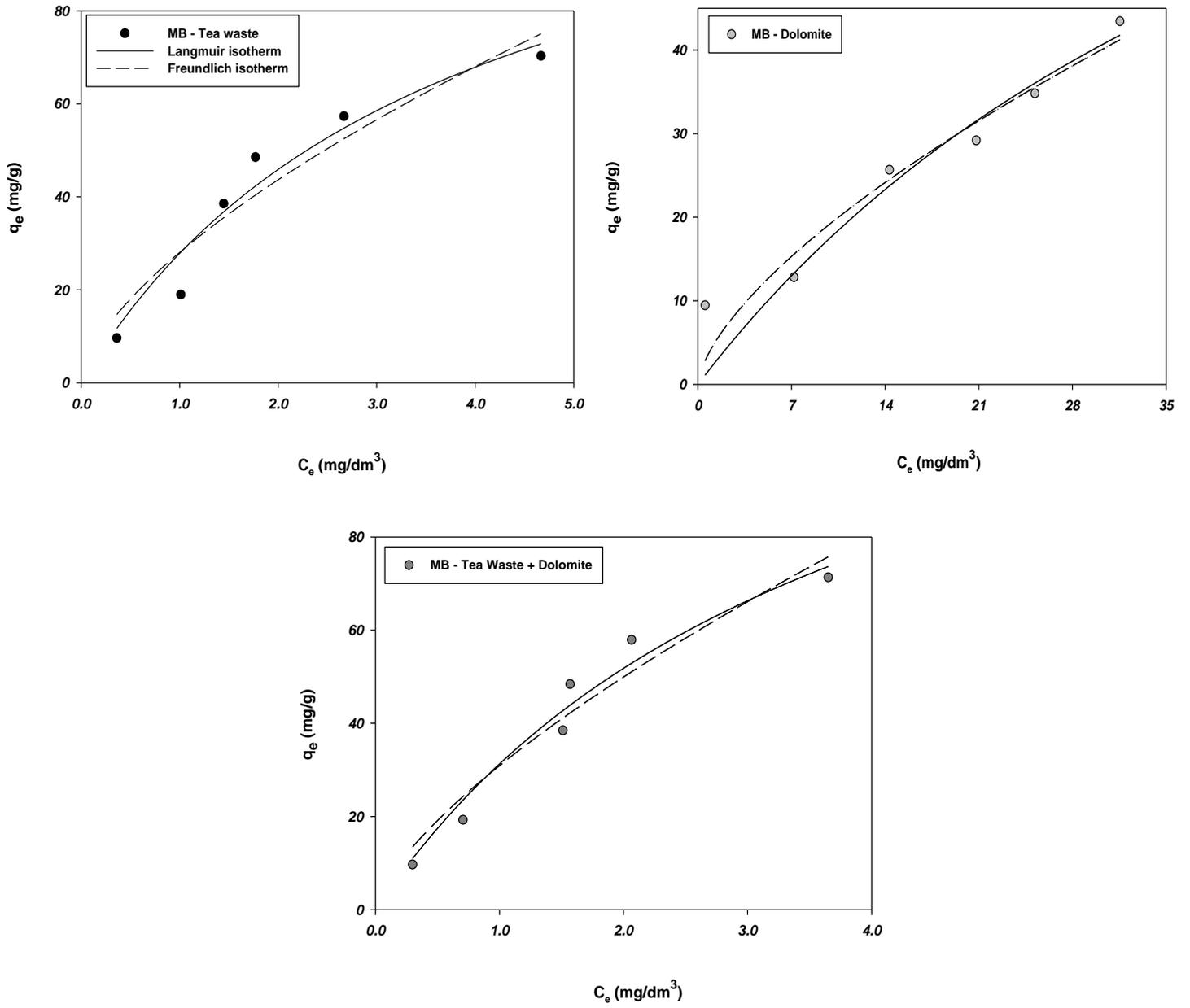


Figure 4: Non-linear forms of Langmuir and Freundlich adsorption isotherm plots of MB onto Tea Waste (TW) and Dolomite (DO).

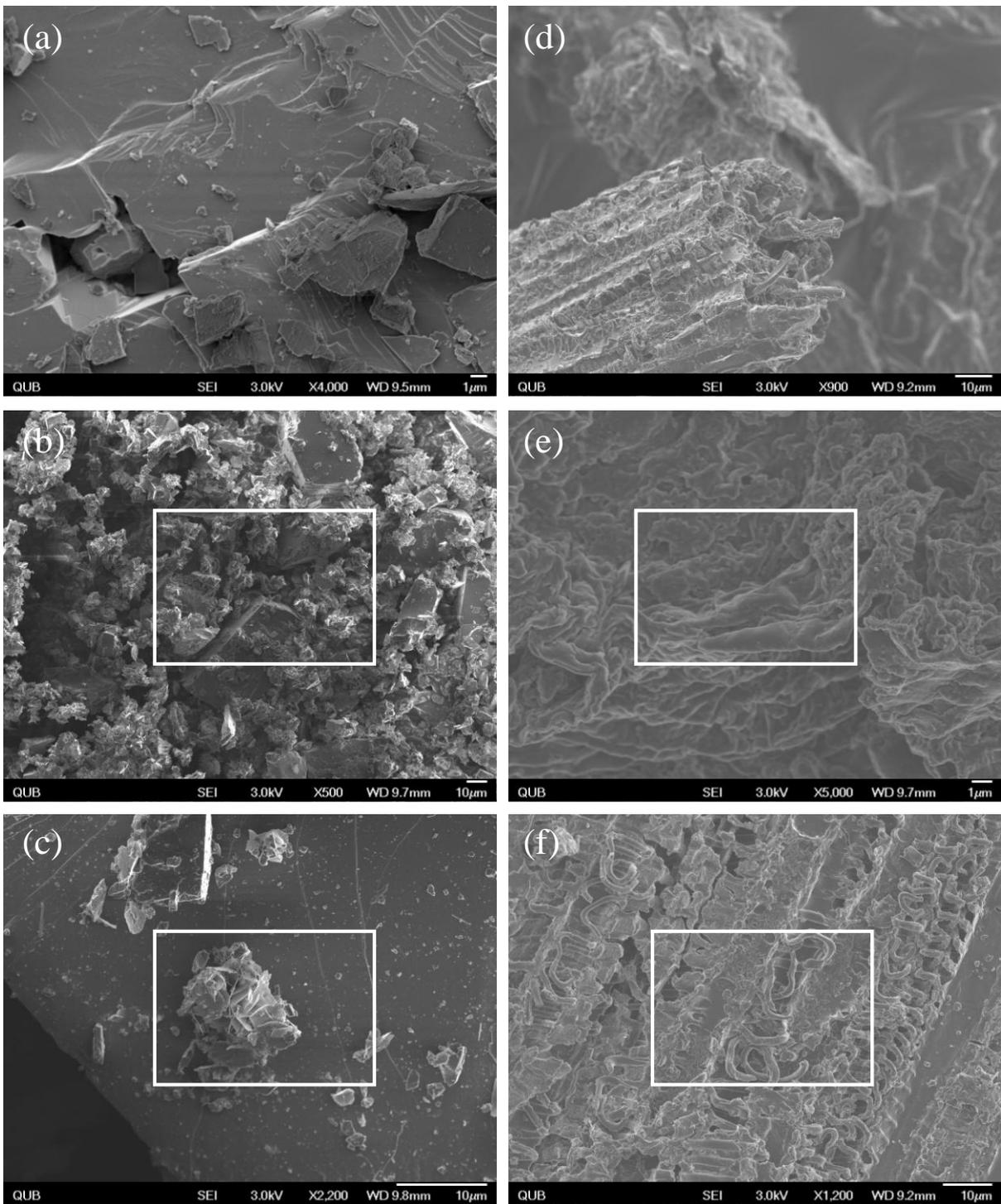


Figure 5: SEM images of Dolomite and Tea Waste before adsorption experiments (a) and (d), after Cu adsorption (b) and (e) and after MB adsorption (c) and (f) respectively.

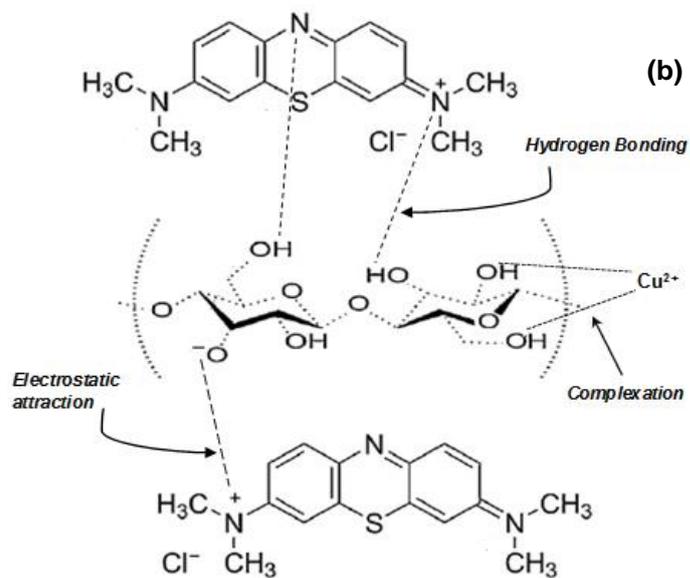
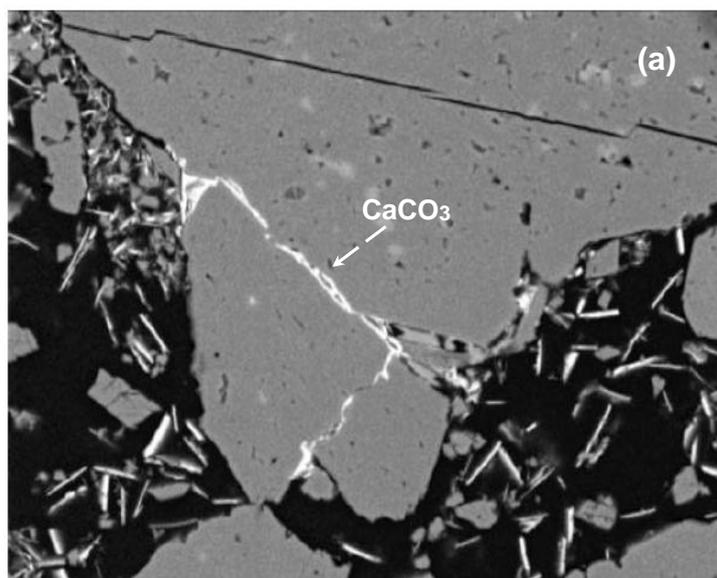


Figure 6: (a) Copper surface precipitation within cracks on dolomite (After Ref [25]) and (b) Metal ions and dye molecule removal through electrostatic attraction and hydrogen bonding (After Ref [45]).

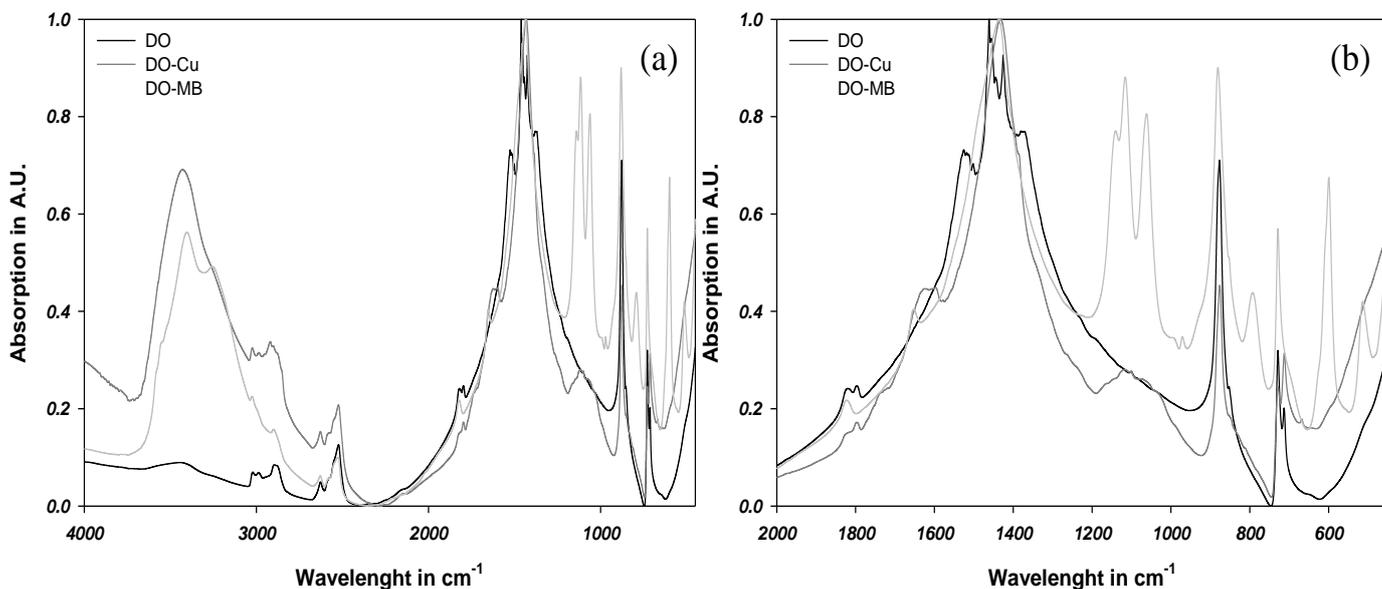


Figure 7: FTIR spectra of DO before and after adsorption with Cu and MB, (a) full spectrum and (b) close up onto the 2000 to 450  $\text{cm}^{-1}$  region. The spectra are normalised and un-shifted.

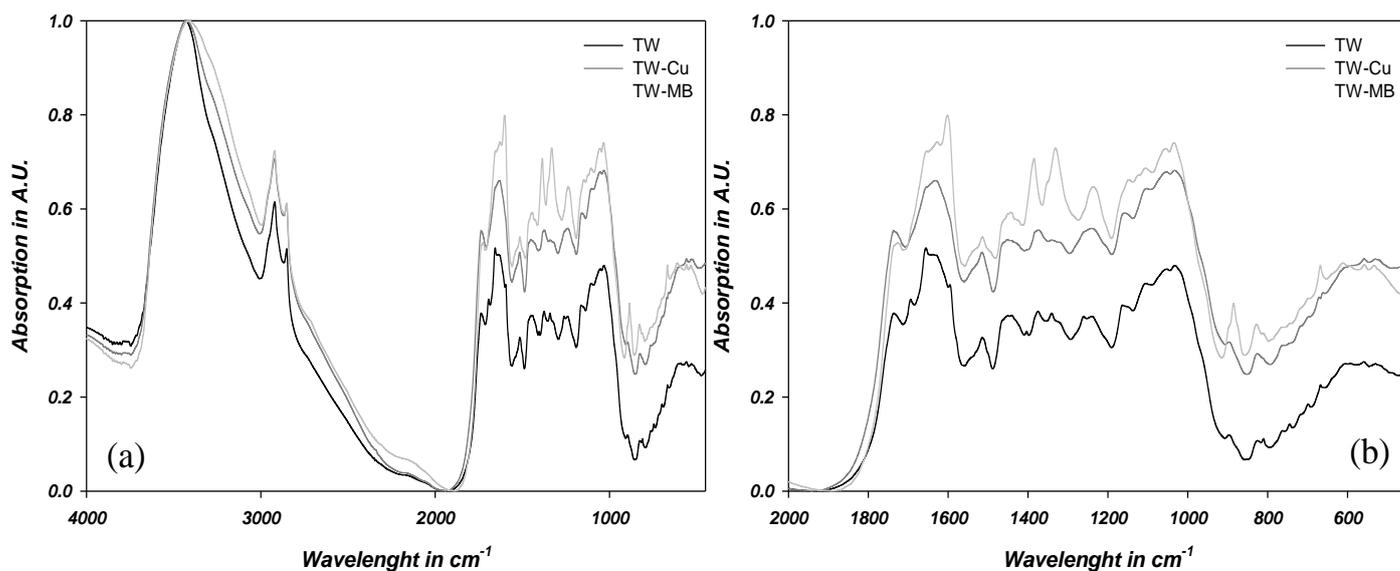


Figure 8: FTIR spectra of TW before and after adsorption with Cu and MB, (a) full spectrum and (b) close up onto the 2000 to 450  $\text{cm}^{-1}$  region. The spectra are normalised and un-shifted.

**Supplementary Material**

[Click here to download Supplementary Material: SUPPLEMENTARY MATERIAL FIGURE S1.docx](#)