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Hajar Farzaneh
  Hamad Bin Khalifa University College of Science and Engineering

Jayaprakash Saththasivam
  Qatar Environment and Energy Research Institute

Gordon McKay
  Hamad Bin Khalifa University College of Science and Engineering

Prakash Parthasarathy (✉ prakrock@gmail.com)
  Hamad Bin Khalifa University College of Science and Engineering   https://orcid.org/0000-0003-2635-4416

Research Article

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Hajar Farzaneh[1], Jayaprakash Saththasivam[2], Gordon McKay[1]*, Prakash Parthasarathy[1]*

[1]Division of Sustainable Development, College of Science and Engineering, Hamad Bin Khalifa University, Education City, Qatar Foundation, Doha, Qatar.

[2]Qatar Energy and Environment Research Institute, Hamad Bin Khalifa University, Education City, Qatar Foundation, Doha, Qatar.

*Corresponding author: gmckay@hbku.edu.qa, prakrock@gmail.com, pparthasarathy@hbku.edu.qa

Abstract

Pharmaceutical products in water, frequently referred to as personal pharmaceutical products, PCPPs are regarded as problematic emerging pollutants with the potential to cause damaging health and environmental impacts to several ecosystems. In this study, an acid activated carbon has been produced from waste date stones, the waste product obtained from the seedless date products manufacturing industry. This material has been used to remove the pharmaceutical compound ibuprofen from water with a high adsorption capacity of 126 mg ibuprofen per g waste date stone derived activated carbon. In order to optimise the use of the activated carbon, a design study has been performed to minimise the quantity of carbon needed using a two-stage batch adsorption system. Several variables have been inputted into the design model to test the model and compare the quantities of adsorbent required in the two-stage and the single stage systems under various conditions.

Keywords: pharmaceutical adsorption; high removal capacity; waste date stone derived carbon; adsorbent usage minimisation; two-stage batch adsorber optimisation.

1. Introduction

In recent decades, a myriad of, PPCPs, pharmaceutical personal care products and endocrine-disrupting substances (EDCs), has been frequently identified in the aquatic environment and various water bodies such as treated sewage effluents, surface water, groundwater and drinking water (Tran et al. 2014; De Vargas et al. 2021). The presence of these emerging contaminants, despite in trace amounts, is a growing concern due to their potential adverse toxic effects on aquatic organisms and human health (Nassiri Koopaei and Abdollahi 2017; Gallego-Ríos et al. 2021). One of the primary pathways for these compounds to enter and contaminate potable water resources is via treated sewage effluents (Schröder et al. 2016). As the majority of wastewater treatment plants are designed to remove waste solids, carbon, nitrogen and phosphorus, the conventional treatment processes deployed in these plants are only capable of partially eliminating emerging contaminants as some of these compounds are not biodegradable, highly stable, resist precipitation and remain soluble in the effluent stream (Mestre et al. 2009; Badmus et al. 2018). Studies have indicated that estrogenic compounds found in treated sewage effluents led to the feminization of fish and amphibians (Rathner et al. 2017). It has also being reported that estrogenic compounds could negatively affect and alter the self-endocrine regulation of human (Kishor et al. 2021). Another serious concern caused by emerging contaminants is the development of antibiotic-resistant bacteria and genes (Rodriguez-Mozaz et al. 2015; Kumar and Pal 2018) that could pose a severe health risk to humans and animals.

Advanced tertiary treatment processes, namely, advanced oxidation operations, membrane filtration and adsorption, can be used to enhance the removal of contaminants of emerging concern such as PPCPs and EDCs. Advanced oxidation processes such as ozone, ozone-hydrogen peroxide and UV-hydrogen peroxide have been reported as one of the effective processes in removing emerging contaminants (Westerhoff et al. 2005; Ponnusamy et al. 2019), but these operations may incur higher capital and operating cost for full-scale operation (Borikar et al. 2014; Farzaneh et al. 2020). Formation of by-products of higher toxicity is another concern that is often associated with the usage of advanced oxidation processes (Kudlek 2018). Membrane filtration processes using nanofiltration and reverse osmosis membranes are also capable of removing emerging contaminants. However, the removal efficiency of membrane technologies is greatly governed by the properties of the membrane (molecular weight cutoff (MWCO), hydrophobicity, and surface charge) and the contaminants (MW distribution, hydrophobic /hydrophilic and charge groups of organic material) (Shon et al. 2006). The high membrane fouling potential due to the presence of organic matter is another drawback of using membranes technologies. Adsorption is another

50 efficient treatment process that can remove organic contaminants and does not produce any toxic by-products

51 (Golovko et al. 2020; Sadraei 2020).

52   In this study, ibuprofen is used as a reference compound to evaluate the performance of activated carbon

53 synthesized from local date stones. Almanassra *et al.* (Almanassra et al. 2020) reported that carbide-derived carbon

54 (CDC) can be effectively used as an adsorbent for the removal of ibuprofen from deionized water and treated

55 sewage effluent. Guedidi *et al.* (Guedidi et al. 2013) claimed that surface modification of commercial granular

56 activated carbon using hydrogen peroxide as an oxidant, led to the formation of carbonyl groups that aid the

57 adsorption uptake of ibuprofen. Another investigation by Guedidi *et al.* (Guedidi et al. 2017) that investigated the

58 performance of an activated carbon cloth in removing ibuprofen, showed adsorption kinetics of ibuprofen was

59 higher at lower pH. An investigation by Baccar *et al.* (Baccar et al. 2012) that studied the removal of ibuprofen

60 along with other pharmaceuticals such as ketoprofen, naproxen and diclofenac using olive-waste cake waste derived

61 activated carbon revealed that contaminant removal efficiency was lower at alkaline pH. In a comparative study

62 applying activated carbon obtained from local plant waste, Mestre *et al.* (Mestre et al. 2011) reported that ibuprofen

63 had a higher removal efficiency than paracetamol. This was attributed to the electrostatic interactions between the

64 ibuprofen and surface charges of the carbon. Many other studies have reported high quality activated carbons and

65 chars have been produced from waste biomass and other wastes, including: olive stones (Saleem et al. 2019) ,

66 bagasse (Chen et al. 2001), chitosan (Wong et al. 2004), waste bamboo furniture/scaffolding (Mui et al. 2010b) and

67 vehicle tyres (Mui et al. 2010a). Palm kernel shell was used to investigate the adsorption of three pharmaceuticals

68 (To et al. 2017), namely, atenolol, acebutolol and carbamazepine with adsorption capacities of 154, 165 and 154

69 mg/g respectively. Some studies have reported the production of activated carbons from date stones often termed

70 date pits (Merzougui et al. 2011; Danish et al. 2014) using phosphoric acid (Girgis and El-Hendawy 2002), zinc

71 chloride (Cherik and Louhab 2017) and carbon dioxide (Suresh Kumar Reddy et al. 2013). The methodologies of

72 converting date stones into activated carbons have yielded a variety of pollutant removal applications for this

73 material, such as, pesticides (Hameed et al. 2009; Hassan et al. 2020), dyes (Al-Ghouti et al. 2010; Bouchemal et al.

74 2012; Messaoudi et al. 2016), heavy metals (Al-Ghouti et al. 2010; Bouhamed et al. 2012; Mangwandi et al. 2020)

75 and pharmaceuticals (Belhamdi et al. 2016; Darweesh and Ahmed 2017).

76   In the current study the activated carbon has been produced by thermally treating phosphoric acid impregnated

77 powdered waste date stone chars (by pyrolysis at 350-600°C) at 550°C for two hours. This carbon has been tested

78 experimentally for its adsorption capacity towards ibuprofen and the experimental equilibrium data were analyzed

79 using seven isotherm models. Finally, a model was developed and applied to determine the to optimum use of the

80 activated carbon using a design study performed to minimise the quantity of carbon required using a two-stage batch

81 adsorption system. Several variables have been inputted into the design model to test the model and compare the

82 quantities of adsorbent required in the two-stage and the single stage systems under various conditions.

83 **2. Materials and Experimental**

84 **2.1. Raw materials treatment**

85 Dates stones were provided by a stoneless date food products manufacturer (Bateel Ltd. Qatar). The raw date

86 stones were washed twice with water to remove the soluble impurities from the stones. These washed stones were

87 immersed in nitric acid (0.1 M) for 1 hour, and then in methyl alcohol for 60 min. in order to remove the organic and

88 inorganic material from the date stone surface. This processed date stone material was dried at 140°C for 12 hours,

89 crushed/powdered using a hammer mill and then segregated by sieving using BSS-25 sieves followed by storage in a

90 dessicator. Following this step it is suitable for charring and activation. This treated date stone was used as the raw

91 material for the preparation of the activated carbons.

92 The production methods of activated carbons from the date stones has been reviewed (Hijab et al. 2020) and

93 the particular activation method of the current date stone powder has been described previously (Hijab et al. 2020).

94 The waste date stone derived activated carbon used in the present study was based on a modified phosphoric acid

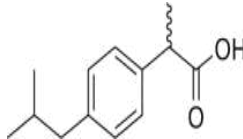95 activation (PAA) process used by Hijab *et al*. (Hijab et al. 2020).

96 The first stage treatment was thermal treatment to produce a char product. This was followed by the chemical

97 activation of the charred date stone powdered material by 30 % (w/w) orthophosphoric acid using a 1:1 (w/w) ratio

98 of acid: date stone char.

99 **2.2. Ibuprofen**

100 Ibuprofen (IBU) obtained from Sigma-Aldrich company was used in the preparation of 40 mg/L

101 concentration stock solution in Type I ultrapure water (PW) having a resistivity value 18.0 MΩ.cm. The

102 characteristic properties of the pharmaceutical are shown in **Table 1**. The stock solution of ibuprofen, IBU, was

103 prepared using sonication for one hour at 60°C, and HPLC analysis was performed to measure and confirm the

104 concentration of the ibuprofen stock solution. The concentrations of all ibuprofen solutions in this study were

105 measured and calibrated using IBU standard solutions prepared in 100 % methanol. The stock solutions were

106 maintained and stored at 4°C.

107
108

Table 1. Ibuprofen properties

Property	Ibuprofen
Chemical formula	$C_{13}H_{18}O_2$
Chemical structure	
Molecular weight	206.28 g/mol
Physical state[*]	Solid
Melting point	76°C
Boiling point	157°C
pKa	4.91
log K_{ow}	3.97
Water solubility[a]	21 mg/L

*measured at 25°C.

109

110

2.3. Derived date stone adsorbents preparation

112 The product was based on an acidified date stone powder being activated by thermal treatment - heating at

113 550°C. The initial treatment stage was the thermal treatment of the raw date stone powder in the range of 350 to

114 600°C to produce an intermediate char product using a Carbolite furnace purged with nitrogen. Next chemical

115 activation was performed by adding 30 % (w/w) orthophosphoric acid in a 1:1 (w/w) ratio of acid: date stone char

116 followed by heating the acid/char mix in an inerted muffle furnace, supplied by Carbolite, and purged with nitrogen

117 at 100 cm³/min. The acid activation process generates a high surface area and places H+ ions on the surface of the

118 date stone carbon. This effect then attracts negatively charged species but it repels positive basic charged species,

119 however, at a higher pH, the H+ ions at the surface can diffuse into the solution generating some available sites with

120 a surplus negative charge to attract the positively charged basic species. Nitrogen gas was flowed through the system

121 for 30 min. prior to pyrolysis. The furnace was cooled to ambient temperature after the activation step while the flow

122 of nitrogen was in operation. The acid activated material was water washed to remove any excess phosphoric acid

123 until the residual wash water achieved pH 6.5-7.5. The washed material was now filtered and left in an air- drying

124 oven overnight at 115°C.

2.4. Microwave and thermally treated date stone characterisation

126 In order to investigate if the raw date stone was suitable as a precursor material for activated carbon

127 production, a thermo-gravimetric analysis, TGA, was carried out with a TA instrument supplied by New Castle, DE,

128 USA, and has been discussed in a previous paper (Hijab et al. 2018). Furthermore, the pore volume and BET surface

129 area of the raw date stones were measured in order to compare and assess the effect of the phosphoric acid activation

130 at 550°C on these characteristic properties. The characterization of the phosphoric acid activated carbon product was

131 performed by a Micromeritics ASAP 2020 surface area analyser (Micromeritics, USA) and the nitrogen based pore

132 volume and specific surface area were obtained and these values were compared with the raw feed date stone data.

133 The IBU adsorption capacities were determined by measuring the ibuprofen in solution concentrations by HPLC

134 analysis as previously mentioned in section 2.3.

2.5. Equilibrium isotherm studies

136 The experimental equilibrium isotherms were carried out at 20±2°C in a temperature-controlled water bath

137 shaker by the addition of accurately weighed quantities of date stone derived activated carbon to the solutions of the

138 adsorbate IBU containing specific concentrations in plastic jars. The agitation speed of the shaker was set at 250 rpm

139 and the initial and final concentrations of IBU in solution were determined by HPLC.

140 All adsorption studies were undertaken at 20°C under controlled temperature conditions by adding 5 mg date

141 carbon to 100 mL IBU solution of specified concentration in the plastic jars. The shaker agitation speed was set at

142 250 rpm. As previous, both final and initial sample solution concentrations were determined. The quantity of IBU

143 adsorbed was determined from the material balance equations (1) and (2). The IBU adsorbed is equal to the quantity

144 of pharmaceutical removed from the initial solution concentration, C_0. That is:

Quantity of IBU adsorbed on carbon = Quantity of IBU removed from solution (1)

$$m\,(q_0 - q_e) = -V\,(C_0 - C_e) \tag{2}$$

145 Rearranging the equation for q_e:

$$q_e = \frac{V}{m}\,(C_0 - C_e) \tag{3}$$

146 where, q_e is the quantity IBU adsorbed on the solid carbon at equilibrium in mg/g, q_0 is the quantity adsorbed

147 on carbon at time zero, t = 0, this is equal to 0, C_0 and Ce represent the initial and the final (equilibrium) IBU

148 solution concentrations (mg/L) respectively, V is the volume of IBU solution in litres, L, and m is mass of carbon

149 adsorbent, g. The IBU removal effectiveness increases with increasing contact time until the equilibrium/saturation

150 capacity on the adsorbent is reached. The quantity of adsorbed IBU on the activated carbon surface rises quickly in

151 the early phase of the process and then decreases continually slowing down, eventually reaching a plateau in the

152 final stage. The duration of the IBU-activated carbon adsorption process to achieve equilibrium was monitored and

153 found to be 12 h. However, the isotherm experiments were continued for a 24 h cycle to make sure that equilibrium

154 was achieved. The ibuprofen concentration range under investigation varied between 1 to 20 mg/L.

155 **3.   Equilibrium Isotherms**

156 **3.1. Isotherm Models**

157 Equilibrium isotherm equations provide a mathematical description of the correlation between q_e (mg/g), the

158 quantity of IBU pollutant/solute removed/adsorbed onto the date stone activated carbon adsorbent material, and C_e

159 (mg/L), the IBU pollutant/solute remaining in the aqueous phase at equilibrium. For treatment system design

160 purposes, an effective adsorption correlation/model must be developed based on the actual equilibrium experimental

161 data. It is important to test a range of isotherm correlations to determine the most appropriate best fitting isotherm

162 correlation to predict the most accurate design capacity and develop the optimisation equations for both batch and

163 column adsorption processes. In the present study, the experimental data were tested and correlated using seven of

164 the widely accepted isotherm model equations and the best fit parameters were evaluated based on error analyses

165 using the sum of the square of the errors (SSE) method to determine the best fitting equilibrium model and the

166 isotherm constants. The data are presented in **Table 3** and the isotherm model equations are presented.

167 **3.1.1.   Langmuir Isotherm Model**

168 In the Langmuir isotherm (Langmuir 1916) it is assumed that there is a constant energy of adsorption and it is

169 independent of the surface coverage. In addition, any interactions between adjacent adsorbed species are assumed to

170 be independent between adjacent adsorbed species; and finally, the maximum adsorption capacity or saturation

171 capacity takes place due to the adsorbent surface being occupied by a monolayer of the adsorbate species. The

172 amount of adsorbed IBU at the equilibrium point, q_e, is given by equation (4):

$$q_e = \frac{q_m b_L C_e}{1 + b_L C_e}$$ (4)

173   q_e, mg IBU/g, is the amount of IBU adsorbed per g date carbon at equilibrium, C_e, mg IBU/L solution, is

174   the equilibrium concentration of the IBU adsorbed pharmaceutical in the liquid phase. The constant q_m represents

175   the maximum quantity IBU adsorbed in the Langmuir model, and is usually called the monolayer capacity, and b

176   (L/mg) is the energy the adsorption process, respectively.

177   To evaluate the Langmuir model constants, Equation (4) can be transposed into the linear expression and is

178   presented in Equation (5):

$$\frac{C_e}{q_e} = \frac{1}{q_m b_L} + \frac{C_e}{q_m}$$ (5)

179   A plot of q_e versus C_e for the linearised Langmuir equation format showing the plateau as a point defining the

180   equilibrium monolayer capacity value at which no further adsorption will occur because of the absence of free

181   surface sites.

3.1.2.   Freundlich Isotherm Model

183   Freundlich (Freundlich 1906) developed an isotherm correlation to explain the heterogeneous nature and

184   behavior in adsorbents. The Freundlich equation has been widely applied for heterogeneous systems and has been

185   frequently found to explain adsorption of many organic molecules with different interactions onto heterogeneous

186   surface sites. In the Freundlich equation (6) the ratio of the amount of adsorbate adsorbing onto a specific mass of

187   date carbon adsorbent to the IBU solute concentration in solution is not constant with varying increasing adsorbate

188   solution concentrations, that implies, there is no monolayer formation. Freundlich developed this multi-site

189   equilibrium correlation for application to heterogeneous adsorption processes and the mathematical form of this

190   model is shown in equation (6):

$$q_e = K_F C_e^{1/n}$$ (6)

191   In equation (6), q_e is the quantity of IBU adsorbing on the solid date carbon adsorbent at the equilibrium

192   condition (mg/g), C_e is the IBU concentration in solution at equilibrium (mg/L), K_F is the Freundlich coefficient or

193   constant (L/g) and 1/n is the Freundlich isotherm exponent. The Freundlich equation is empirical in form and it

194   describes the non-ideal case of adsorption and is logarithmic in nature. It may be used in the case of multilayer

195   adsorption having a non-uniform energy distribution pattern. The quantity of adsorbed material represents the

196   adsorption which occurs at all sites and accounts for the range of individual bond energies. The adsorption energy

197 values decrease in an exponential manner until the adsorption step is finished. Consequently, the Freundlich model

198 has proved popular for heterogeneous adsorption, where the potential forces and enthalpies of adsorption are varying

199 along the surface of the adsorbent, and the slope of the linearised equation designates the heterogeneity level; its

200 linear form is shown in equation (7):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{7}$$

201 For this equation, K_F (L/g) and 1/n are indicators of the capacity of the adsorbent and the surface heterogeneity,

202 respectively. The exponential term, 1/n ranges between 0, for the more heterogeneous cases, and 1, for the more

203 homogeneous systems.

204 **3.1.3. Redlich-Peterson Isotherm Model**

205 Redlich and Peterson (Redlich and Peterson 1959) developed their three parameter empirical isotherm

206 equation which comprises a numerator term with a linear dependence on Ce, as in the Langmuir model; and an

207 exponential function in the denominator term demonstrating an exponential dependence on Ce, in the form Ce^{bR}, as

208 in the Freundlich expression. Thus, this model involves incorporating features of both the Freundlich and Langmuir

209 isotherms and therefore, the Redlich-Peterson expression in equation (8) represents a hybrid model mechanism.

$$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^{bR}} \tag{8}$$

210 In equation (8) q_e and C_e are defined as previously. K_{RP} is the Redlich-Peterson equilibrium constant term (L/g),

211 a_{RP} is an isotherm constant (L/mg) and b_{RP} is the Redlich-Peterson exponential parameter, which lies between must

212 fall in the range of 0 to 1. When b_R =1, it becomes the Langmuir equation; when b_R =0, it becomes Henry's law.

213 **3.1.4. Langmuir-Freundlich or SIPS Isotherm Model**

214 This isotherm model, termed the Langmuir-Freundlich correlation, is frequently referred to as the SIPS

215 correlation (Sips 1948). Again, this model is a combination comprising the Langmuir and Freundlich expressions to

216 include heterogeneous system mechanisms which are not as extreme than the Freundlich process. The Langmuir-

217 Freundlich isotherm reduces to the Freundlich equation format at low concentrations, however, moving to higher

218 concentrations, the model, and its parameters approximate more towards the monolayer Langmuir model isotherm.

219 The SIPS or Langmuir-Freundlich isotherm is presented in Equation (9) and substituting for the equilibrium constant,

220 K_{LF}, equation (10) is obtained:

9

$$q_e = \frac{q_s a_s C_e^{n_{LF}}}{1 + a_s C_e^{n_{LF}}}$$ (9)

$$q_e = \frac{K_{LF} C_e^{n_{LF}}}{1 + a_{LF} C_e^{n_{LF}}}$$ (10)

221 C_e and q_e are defined as before; q_s (L/g) and a_s (L/mg) are the Langmuir-Freundlich isotherm capacity and

222 isotherm constant, whereas K_{LF} is an equilibrium constant and n_{LF} is the isotherm exponent. Also $q_s a_s = K_{LF}$, the

223 Langmuir-Freundlich equilibrium constant.

224 **3.1.5.   Temkin Isotherm Model**

225 The Temkin isotherm was developed to explain hydrogen adsorption during electrolysis in acidic solutions.

226 Consequently, the Temkin isotherm became a preferential isotherm to describe gas-phase equilibrium, but has not

227 been applied much for liquid processes. The Temkin equation assumption is that the heat of adsorption decreases in

228 a linear manner with adsorbate surface coverage as a result of adsorbent/adsorbate interactions (Temkin and Pyzhev

229 1940). The model is not suitable for the more extreme concentrations both for low and high values. It assumes that

230 the binding energies between the adsorbate and adsorbent are evenly distributed. The Temkin isotherm can be

231 represented by Equations (11) and (12):

$$q_e = \left(\frac{RT}{b}\right) \ln(K_{Te} C_e)$$ (11)

$$q_e = \frac{RT}{b_T} ln K_{Te} + \frac{RT}{b_T} ln C_e$$ (12)

232 where, K_{Te} (L/g) is the isotherm binding constant at equilibrium, b_T is the Temkin constant, R is the universal

233 gas constant (8.314 kJ/mol.K) and T is the absolute temperature at 298 K.

234 **3.1.6.   Toth Isotherm model**

235 A modification of the Langmuir equation was proposed by Toth (Toth 1971) and comprised a linear Ce

236 dependent term in the numerator in the Langmuir format, and having an exponential term in the denominator as per

237 the Freundlich expression. The Toth modelcan be represented by Equation (13):

$$q_e = \frac{K_t C_e}{(a_t + C_e^t)^{1/t}}$$ （13）

238 Where K_t, a_t, and t are Toth constants.

3.1.7. Dubinin-Radushkevic Isotherm Model

Another model, particularly useful for isotherms of a high degree of rectangularity, such as ion exchange, has been developed by Dubinin and Radushkevich. The Dubinin-Radushkevich isotherm (Dubinin 1960) is based on the potential theory and is expressed in equation (14) as:

$$q_e = q_s \exp(-B_{DR}\varepsilon^2) \tag{14}$$

Where ε can be expressed as:

$$\varepsilon = RT ln(1 + \frac{1}{C_e}) \tag{15}$$

Substituting equation (15) into equation (14) produces equation (16):

$$q_e = q_m \exp\left(\frac{\left(RT ln\left(1 + \frac{1}{C_e}\right)\right)^2}{-2E^2}\right) \tag{16}$$

By taking the logarithm of equation (16) yields equation (17):

$$ln q_e = ln q_s - B_{DR}R^2T^2\left[ln(1 + \frac{1}{C_e})\right]^2 \tag{17}$$

and substituting K_{DB} into $B_{DR}R^2T^2$, equation (14) becomes equation (18):

$$ln q_e = ln q_s - K_{BR}\left[ln(1 + \frac{1}{C_e})\right]^2 \tag{18}$$

R is the universal gas constant and T is the absolute temperature; B_{DR} is a constant depending on, ε, the mean free energy of sorption per adsorbate molecule transferred to the surface of the solid from infinity in the solution. The free energy is evaluated using equation (15) and B_{DR} is obtained by rearranging equation (19):

$$\varepsilon = \frac{1}{\sqrt{2B_{DR}}} \tag{19}$$

3.2 Error Analysis

3.2.1. Sum of Squared Error Analysis Method (SSE)

The sum of the square of the errors, SSE, is one of the most popular and widely applied error functions by many researchers to evaluate the optimum or best fitting equilibrium relationship correlation (Kumar and Sivanesan 2006) and this SSE method is based on evaluating the sum of the squares for the residuals. The method incorporates both variance and the variance bias in its solution. In the present application, the SSE is based on comparing the square of

256 the correlation between the experimental and the calculated adsorbed data values and can be expressed by equation

257 (20):

$$SSE = \sum_{i=1}^{N} (q_{e,exp} - q_{e,iso})_i^2 \qquad (20)$$

258 The subscripts "exp" and "iso" stand for the experimental and calculated adsorbed capacity values, respectively.

259 The results of the SSE analysis demonstrated that the SIPS, that is, the Langmuir-Freundlich isotherm describes the

260 experimental data extremely accurately. Consequently, the Langmuir–Freundlich model is the preferred equation for

261 application in the adsorbent minimisation model presented in section 3.3.

262 **3.2.2.   Akaike information criterion (AIC)**

263 The AIC, Akaike information criterion (Akaike 1998), can measure the benefit of a particular isotherm model in

264 comparison with other isotherm model equations, primarily by taking into account the different number of

265 parameters and the relationship is shown in equation (21)

$$AIC = 2K - 2\log(L(\hat{\theta}|y)) \qquad (21)$$

266 The lowest of the AIC values, the more superior is the model fitting, where, K represents the number of

267 estimated parameters and $\log(L(\hat{\theta}|y))$ is the log-likelihood value at the maximum point. However, the data set and

268 the same number of points were used in all the models so the AIC analysis is not required as the trend would be the

269 same as the SSE analysis results.

270 **4.   Results and Discussion**

271 **4.1. Adsorbent Characterization**

272 A previous TGA study (Hijab et al. 2018) has showed that date stones have a low moisture content,<10%,

273 and high contents of cellulose and hemicellulose The char experimental yield values were confirmed by the TGA

274 studies, which showed a steady decrease with increasing pyrolysis temperatures, with yields finally reaching about

275 25% w/w. Consequently, raw date stones possess considerable potential to be successfully activated, requiring only

276 a small amount of energy for drying. A number of publications have reported the results of activating date stones

277 with various activating agents and at various temperatures (Girgis and El-Hendawy 2002; Merzougui et al. 2011;

278 Suresh Kumar Reddy et al. 2013; Danish et al. 2014; Cherik and Louhab 2017). In order not to duplicate previous

279 work and focus this study on the water treatment application, optimum literature criteria were selected to provide a

280 high surface area at a relatively low temperature for keeping energy costs low. In this study, the date pits were

281 impregnated with a mass ratio of 2:1 of phosphoric acid to date stone char, activated at 550°C for 2 hours with a

282 nitrogen flow of 100 mL/min. The resulting activated carbon had a yield of 30 %, a BET-N_2 surface area of 727

283 m^2/g, a pore volume 0.70 cm^3/g and a mean pore diameter size = 3.89 nm. The raw date stone possessed a

284 relatively low surface area of 86.0 m^2/g and a pore volume of 0.22 cm^3/g, proving the beneficial suitability of the

285 activation method.

286   The BET surface area studies show a similar trend with data retrieved from literature by Girgis and El-

287 Hendawy (2002), who obtained the highest surface area using phosphoric acid treated date stone as 740 m^2/g. A

288 higher impregnation ratio of 2:1 utilised in this study yielded a similar surface area value. The results of the TGA

289 analysis indicated a moisture content of 8 % (w/w), a residual solids content of 22 % (w/w) and the soluble

290 extractive components of 7% (w/w). The most rapid and main mass loss occurred at 250°C to 350°C, which was

291 representative of a large percentages of cellulose and hemicellulose. Furthermore, in the region of 400°C, 70 % of

292 the mass has been lost. In the range 400°C to 600°C, the mass loss rate decreased significantly due to the slow

293 breakdown of the large lignin compounds as seen in **Table 2** (char yield at various temperatures). Consequently,

294 date stones have demonstrated a strong potential to be successfully applied in activation and pyrolysis.

295
296

Table 2. Char yield at different temperatures

Temperature (°C)	Yield (%)
350	55.1
400	36.9
450	28.6
500	27.3
550	26.2
600	25.1

297

298   The char product yields decrease as the pyrolysis temperature increases. At the lower temperatures, the

299 differences in the product yields are significantly higher. It can be observed that the extent of mass loss decreased

300 with increasing temperature and is much lower at the high temperatures because of the large lignin molecules which

301 are difficult to fracture.

302 **4.2. Equilibrium studies**

303   The Langmuir-Freundlich or SIPS isotherm provides the best correlation to the experimental equilibrium data

304 values based on the SSE and correlation coefficient (R^2) values in **Table 3**. The type of isotherm gives an indication

305 regarding the type and nature of the adsorption mechanism. In the case of phosphoric acid treated date stone chars,

in this study, the SIPS or Langmuir-Freundlich is the best fit equilibrium isotherm. The Freundlich and Tempkin

isotherm equations were excluded for the remainder of the analysis due to their large SSE values. The Langmuir

model is based on monolayer adsorbate coverage so that the isotherm reaches a plateau, when the maximum

equilibrium capacity is achieved, and when the adsorption stage takes place on one kind of surface site only, which

all have an equal adsorption energy. The Langmuir-Freundlich model indicates the variance on this mechanism,

showing some degree of heterogeneous adsorption, but still the site energy levels are similar. The two curves in

Figure 1 indicate the formation of a plateau by the last few high concentration data values showing the date stone

derived activated carbon has achieved saturation. The results show a significant increase in the capacity of IBU

adsorption onto date stones after the phosphoric acid treatment. The maximum IBU adsorption capacity for the

phosphoric acid activated date stone carbon is 126 mg/g based on the Langmuir isotherm, extrapolating the

experimental data also provides a value of 125±3 mg/g, and the best fit Langmuir-Freundlich isotherm also yields a

capacity value of 126 mg/g. Therefore this is the maximum adsorption capacity used in further discussions and the

design modelling.

Table 3. Isotherm Parameters and SSE of IBU adsorption on date stone activated carbon

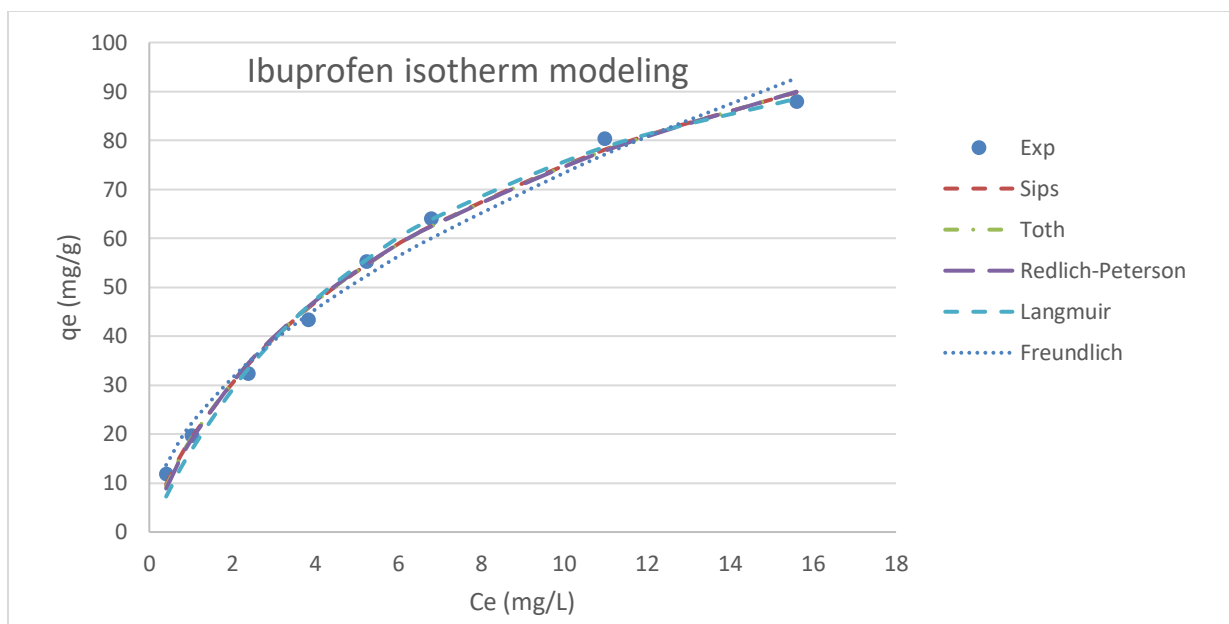|	Langmuir	Freundlich	Temkin	DR	Redlich-Peterson	SIPS/ LF	Toth
SSE	42.1	72.3	317.0	727.0	33.0	25.0	30.0
Parameter	K_L = 19.0, a_L = 0.151, q_m = 126	K_F = 22.0, n_F = 1.91	B = 2.74, A_T = 112	Q_m = 83.4, E = 550	K_{RP}= 27.6, a_{RP}= 0.428, b_{RP} = 0.776	K_{LF} = 16.4, n_{LF} = 1.24, a_{LF} = 0.130	Q_m = 216, K_T = 2.84, n = 0.552

Figure 1. Five isotherm models compared with the experimental IBU equilibrium data.

Other studies (see **Table 4**.) for the adsorption of IBU using various adsorbents obtained a wide range of capacities; for carbide derived carbon (Almanassra et al. 2020), commercial activated carbon (Guedidi et al. 2013) and olive waste cake derived activated carbon (Baccar et al. 2012) the IBU adsorption capacities were 367, 160 and 14.4 mg IBU/g adsorbent. Two of the values are very high but they were performed at very acidic pH to optimise the capacity. In practice, the effluents and treated sewage waters, where these emerging pollutants are prominent generally have pH values in the range of 6 to 8.5. The capacity of our phosphoric acid activated date stone carbon at 64.7 mg/g, is lower, but still in the same range of magnitude but the treatment process was performed at a pH value of 7.

Table 4. IBU adsorption capacities on various materials

Adsorbent	Surface area (m^2/g)	Isotherm	Equilibrium time (h)	IBU concentration (mg/L)	Maximum IBU adsorption capacity (mg/g)	Ref.
CDC	1054	Langmuir	24	1-20	367 at pH 3, 293 K	(Almanassra et al. 2020)
Commercial granular AC	800	Langmuir-Freundlich	67	5-100	160 at pH 3, 298 K	(Guedidi et al. 2013)
Olive waste cake AC	793	Langmuir	26	10	14.4 at pH 4.1, 298 K	(Baccar et al.

335

4.3. Optimization procedure for minimizing the quantity of adsorbent in a two-stage batch process

337   Our optimisation study is based on minimising the amount of activated date stone carbon adsorbent using a two-

338   stage batch process represented in the schematic in **Figure 2.** The IBU capacities will be determined using the best

339   fit equilibrium isotherm for the phosphoric acid treated date stone activated carbon, and the concentration, Ce, or C_2,

340   is the IBU concentration in the treated effluent, to be discharged from the two-stage process. Typically this

341   concentration value is important because it is the maximum or effluent pollutant concentration limit allowed by the

342   legislative authorities in their effluent discharge limits for process licensing to be allowed into receiving waters. It is

343   of the utmost importance to determine the adsorbent IBU uptake capacity at this C_e/C_2 value – because it is this

344   capacity that is controlling the quantity of adsorbent required in the operating wastewater facility. It is almost certain

345   that this corresponding q_e value will not correspond to the maximum isotherm adsorption capacity, q_{max}, because its

346   value is determined by C_2 and the system operating line gradient. The isotherm equation representing the adsorbate

347   uptake mass balance, provides the corresponding adsorption capacity value at C_2. Consequently, it becomes of great

348   significance to evaluate this design capacity at the plant design stage, because the mass of adsorbent will be less than

349   the $q_{e,max}$ capacity and therefore the adsorber plant units sizes will need to be increased .

350   Optimization analyses and design calculations have been performed for the IBU removal treatment systems

351   by adsorption processes for two-stage batch and single-stage batch operations. The batch adsorption stage is

352   typically utilized for the removal of pollutants produced by industrial operations at a relatively small scale. However,

353   the application of single-stage batch adsorption processes has difficulty meeting the required legislative effluent

354   limit discharge value, although the single-stage batch operation is highly flexible. This is due to the stringent and

355   steadily intensifying final low level discharge concentrations imposed by the environmental legislation authorities,

356   because it implies very large quantities of the adsorbent, as shown later in this study. The system modelling for the

357   two-stage batch adsorber is now presented. The process schematic for the two-stage batch adsorber unit is presented
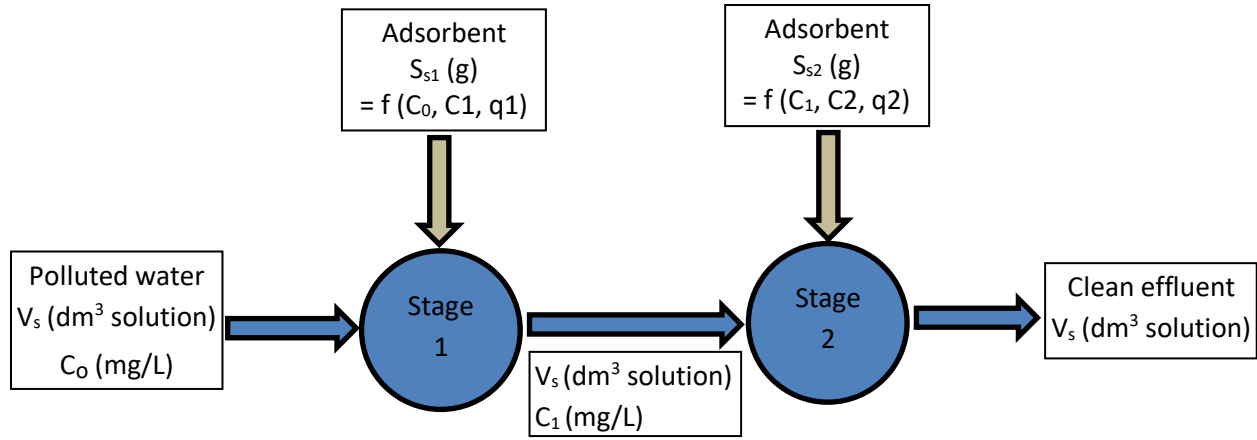
358   in **Figure 2**.

359

362   **Figure 2.** Schematic figure of a two-stage system

363

364   A two-stage adsorption scheme is presented in **Figure 2**, showing S_{s1} and S_{s2} are the quantities of the

365   adsorbent in each adsorber vessel, namely, stage 1 and stage 2 respectively; hence, the total date stone carbon

366   adsorbent, which is required, is $S_{s1} + S_{s2}$. To estimate the minimum total quantity adsorbent to be applied for

367   achieving the final effluent discharge concentration leaving stage 2, that is C_2. Then, it is required to minimize this

368   quantity, namely, $S_{s1} + S_{s2}$, and this value may be obtained from, $d(S_{s1}+S_{s2})Vs/dC_1$ and equating to zero to for the

369   maximum or minimum values. The derived solution equation then provides the interstage intermediate concentration,

370   C_1, to be obtained; and using this value, the two adsorbers required carbon quantities can be determined using

371   equations (22) and (24).

372   Using the most accurate isotherm correlation, namely, Langmuir-Freundlich, as being the best fit isotherm,

373   the general mass balance equation for adsorber stage 1 is:

$$\frac{S_{s1}}{V_s} = \frac{C_0 - C_1}{q_1 - q_0} \tag{22}$$

374   Substituting the isotherm equation for q_1 and since $q_0 = 0$, then equation (22) becomes equation (23) (23):

$$\frac{S_{s1}}{V_s} = \frac{(C_0 - C_1)(1 + a_{LF}C_1^{b_{LF}})}{K_{LF}C_1^{b_{LF}}} \tag{23}$$

375   For the stage 2 adsorber unit, represented by equation (24):

$$\frac{S_{s2}}{V_s} = \frac{C_1 - C_2}{q_2 - q_0} \tag{24}$$

376   By an analogous substitution as before, but for q_2, then equation (24) becomes equation (25):

17

$$\frac{S_{s2}}{V_s} = \frac{(C_1 - C_2)(1 + a_{LF}C_2^{b_{LF}})}{K_{LF}C_2^{b_{LF}}} \tag{25}$$

377   The total amount of adsorbent used is given by equation (26):

$$\frac{S_{S1} + Ss_2}{V_s} = \frac{1}{K_{LF}}\left(\frac{(C_0 - C_1)\left(1 + a_{LF}C_1^{b_{LF}}\right)}{C_1^{b_{LF}}} + \frac{(C_1 - C_2)\left(1 + a_{LF}C_2^{b_{LF}}\right)}{C_2^{b_{LF}}}\right) \tag{26}$$

Now this differential term,

378      $\frac{d[(S_{S1}+S_{s2})/V_s]}{dC_1}$ is set equal to zero in order to determine the minimum total adsorbent required. Rearranging, and

379   (26) becomes equation (27):

$$0 = \frac{1}{K_{LF}}\left[\frac{b_{LF}-1}{C_1^{b_{LF}}} - \frac{b_{LF}C_0}{C_1^{b_{LF}+1}} + \frac{1}{C_2^{b_{LF}}}\right] \tag{27}$$

380   Multiplying by $C_1^{b_{LF}}$ and rearranging, produces equation (28):

$$0 = \left(\frac{C_1}{C_2}\right)^{b_{LF}} - b_{LF}\left(\frac{C_0}{C_1} - 1\right) - 1 \tag{28}$$

381   The intermediate concentration, C_1, may be evaluated by solving Equation (28) and applying the Microsoft

382   Excel solver function. Consequently, the optimised value for the minimum quantity of date stone activated carbon

383   required for each unit can be obtained using Equations (23) and (25). In section 4.4, various limitations for the

384   extent of IBU removal have been applied as percentage removal and also in terms of absolute final concentrations of

385   IBU in the effluent, eg. similar to fixing effluent limit discharge values. This allows the eventual comparison of the

386   quantity of date stone carbon required for the single stage process with the amount required for a two-stage adsorber

387   in section 4.5.2. This adsorbent quantification has been undertaken to evaluate the optimised minimum adsorbent

388   amounts for the phosphoric acid treated date stone.

389   **4.4. Model Results and Discussion**

390   The first target was to assess the amount of phosphoric acid treated date stone carbon required in order to

391   achieve the final discharge limit values in terms of percentage removals of IBU for 0.5 % C_0, 1 % C_0, 2 % C_0, and

392   5% C_0; and the second target was to determine the quantities of this carbon necessary to achieve certain fixed set

393   discharge concentration limits of IBU to meet the set values of 0.5, 1, 2 and 5 mg/g, have been analyzed. The

394   Langmuir-Freundlich (Sips) isotherm parameters, as the best fitting equation data, were applied for modelling the

395   process optimization and minimizing the quantity of the acid activated date stone carbon, which was used in the

model to optimize the system by minimizing the total date carbon to be used. **Table 5** is the summary of the optimized amounts of the acid activated date carbon required when the final effluent concentration of IBU is 0.5 % of the initial concentration, C_0. The tables for the other four percentages are presented in the Supplementary Information tables **S.1** for 5.0 % C_0, **S.2** for 2.0 % C_0 and **S.3** for 1.0 % C_0.

Table 5. Minimum total quantity of phosphoric acid treated date stone activated carbon to remove IBU using the Langmuir-Freundlich model to achieve C_2=0.5 % C_0 for 1000L of solution

C_0 (mg/L)	C_2 (mg/L)	C_1 (mg/L)	S_{s1} (kg)	S_{s2} (kg)	$S_{s1}+S_{s2}$ (kg)
1	0.005	0.084	1.19	3.41	4.60
2	0.010	0.169	1.02	2.88	3.90
3	0.015	0.253	0.931	2.62	3.55
4	0.020	0.337	0.880	2.45	3.32
5	0.025	0.421	0.841	2.32	3.16
6	0.030	0.506	0.813	2.22	3.03
7	0.035	0.590	0.792	2.14	2.93
8	0.040	0.674	0.776	2.07	2.85
10	0.050	0.843	0.753	1.97	2.72
12	0.060	1.012	0.738	1.88	2.62
14	0.070	1.180	0.728	1.82	2.54
15	0.075	1.264	0.725	1.79	2.51
16	0.080	1.349	0.723	1.76	2.48
18	0.090	1.517	0.720	1.71	2.43
20	0.100	1.686	0.719	1.67	2.39

The trends in **Table 5** and the Supplementary Information files, **Tables S.1** to **S.3**, are similar but with different individual amounts of date activated carbon adsorbent requirements. All the data values are plotted in **Figure 3** to enable a comparison.
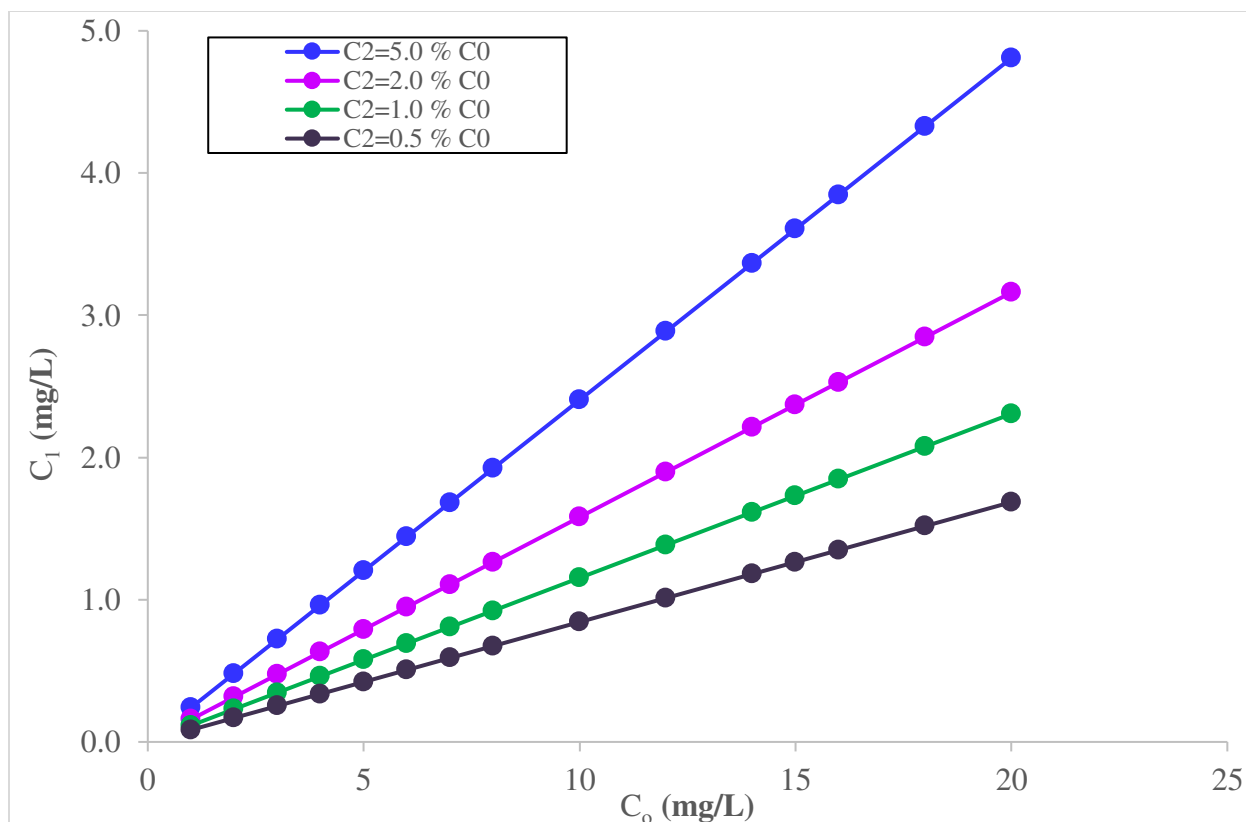
Figure 3. Interstage concentrations, C1, to remove different fixed % C_0 IBU using the Langmuir-Freundlich model.

In **Table 5**, it cab be observed that more date stone activated carbon is required for the second stage adsorber, S_2, than in the case of the first adsorber stage, S_1. For example at Co = 1 mg/L and the removal target is 0.05 % C_0, then S_1 = 1192 g and S_2 = 3408 g. In all the cases tested, the ratio of the adsorbent used, namely, S_2:S_1 is in the range of 2.0 to 2.5. Furthermore, for the same initial concentrations the target % C0 removal significantly affects the total quantity of date carbon required. This requirement occurs because the final concentration, C2, required to be achieved is steadily increasing as the % C0 increases; therefore, the percentage change in the C2 discharge is also being relaxed as C2 is allowed to increase. Consequently, the percentage decrease requirement in the IBU concentration is larger in the first condition (total carbon requirement = 4600 g adsorbent for 0.5 % C0 at C_0 = 1 mg/L); than that in the second condition (total carbon requirement = 2700 g adsorbent for 1.0 % C0 at C_0 = 1 mg/L); and third stage (total carbon requirement = 1570 g adsorbent for 2.0 % C0 at C_0 = 1 mg/L); and finally the fourth condition (total carbon requirement = 746 g adsorbent for 5.0 % C0 at C_0 = 1 mg/L); as the % Co increases therefore allowing an increase in C2 and consequently, relaxing on the total amount of adsorbent needed. The trend is seen in

20

423   **Figure 3** for the four % Co changes at a range of C_0 values. The variation in the total adsorbent quantity required as

424   a function of the intermediate concentration, C_1, between the two stages, is shown in **Figure 4**. It is interesting to

425   note that there is a levelling out in the total adsorbent mass required at each % C_0 target discharge level at around C_1
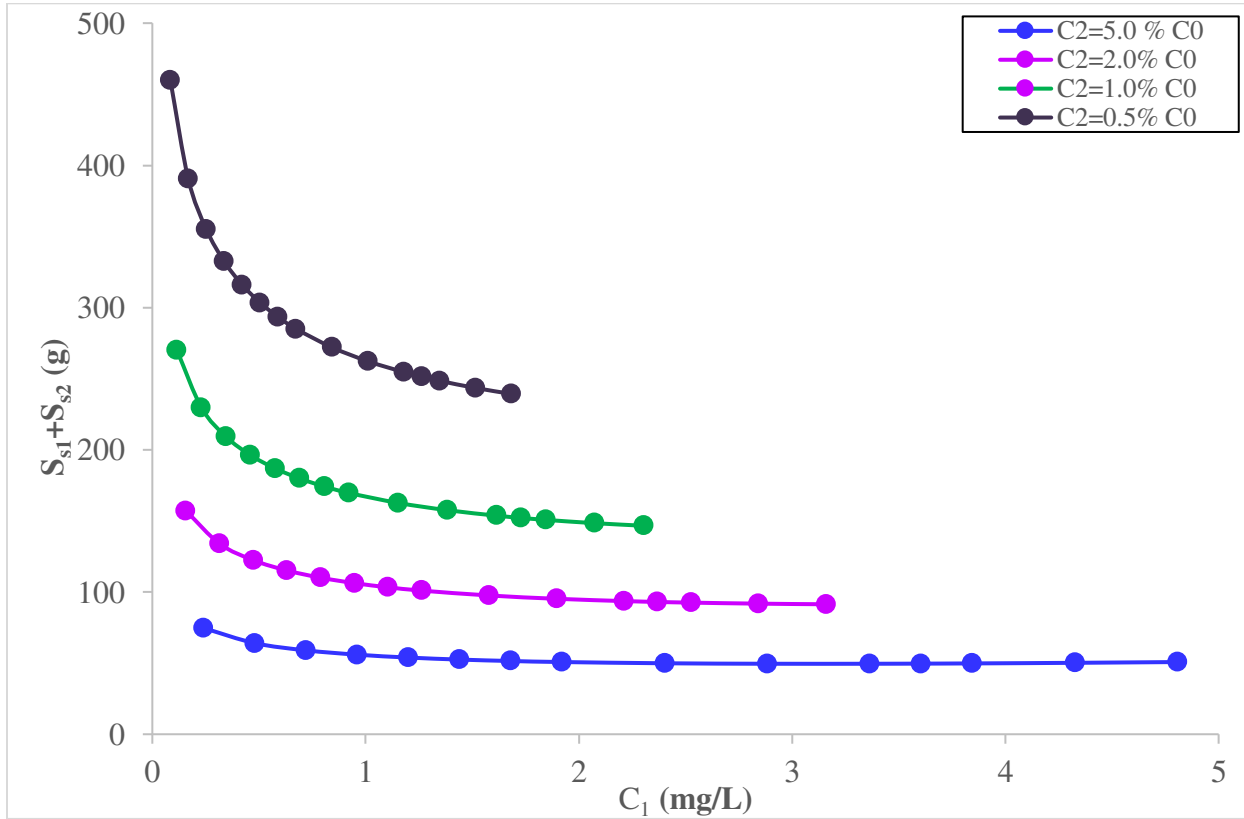
426   = 2 mg/L.

427
428   **Figure 4**. Minimum quantity of acid treated date stone activated carbon, S_1+S_2, against the interstage
429   concentrations, C_1, to remove IBU using the Langmuir-Freundlich model for different removal values, % C0.

430   A further correlation of particular interest to the water treatment plant design engineer is the relationship

431   between the total quantity of date carbon required and the initial concentration, C_0, of the pollutant material. **Figure**

432   **5** presents the curves for the present system of S1+S2 against C_0 for the range of final discharge levels based on %

433   C_0 for IBU removal using the waste date stone derived activated carbon. Again the figure shows an interesting trend

434   by levelling out at relatively constant fixed adsorbent quantities at C_0 = 10 mg/L at the individual % C_0 removal
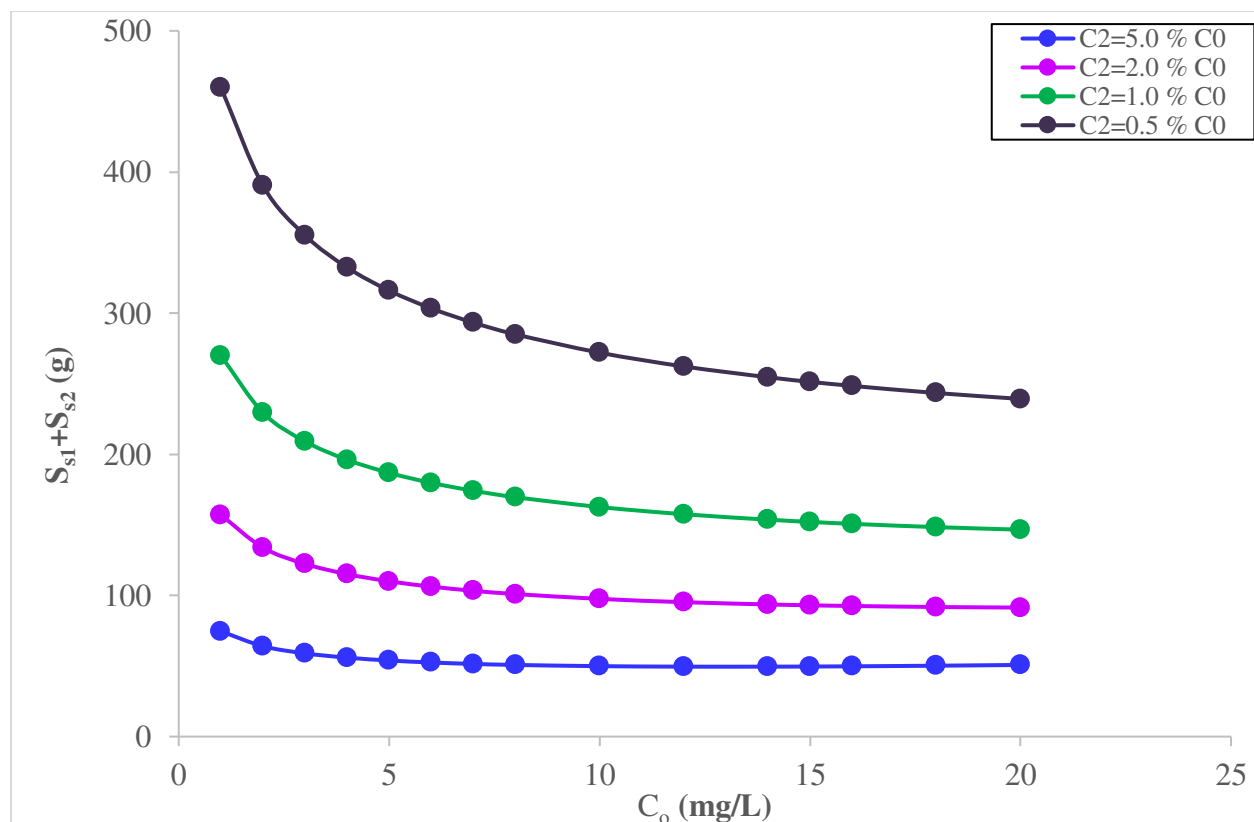
435   values.

436

21

Figure 5. Minimum total quantity of acid treated date stone activated carbon, S_1+S_2, against the initial IBU concentration, C_0, to remove a fixed % C_0 IBU using the Langmuir-Freundlich model.

Table 6 summarises the optimum amounts of the date acid activated carbon (S_1+S_2) neede to achieve a final effluent concentration, C_2, when the C_2 IBU is 0.20 mg/L for a range of initial IBU concentrations from $C_0 = 1.0$ to 20 mg/L. The tables for the other three specified final discharge concentrations, namely, $C_2 = 0.10$, 0.050 and 0.10 mg/L concentrations percentages are presented in the Supplementary Information tables **S.4** for 0.5 % C_0, **S.5** for 0.20 mg/L, and **S.6** for 0.10 mg/L. The trends in **Table 6** and the Supplementary Information files are similar to the general trends in **Table 5** and its associated but with different individual amounts of date carbon adsorbent requirements. All the data values are plotted in **Figure 6** to enable a comparison due to the effect of the initial discharge concentration C0 and its influence on the mass of adsorbent required for a fixed final treated effluent discharge concentration of 0.20 mg/L.

Table 6. Minimum total quantity of date stone acid treated activated carbon to remove IBU using the Langmuir-Freundlich model to achieve C_2=0.20 mg/L

C_0 (mg/L)	C_2 (mg/L)	C_1 (mg/L)	S_{s1} (kg)	S_{s2} (kg)	$S_{s1}+S_{s2}$ (kg)
1	0.20	0.458	0.089	0.117	0.206

2	0.20	0.663	0.145	0.209	0.353
3	0.20	0.824	0.184	0.281	0.465
4	0.20	0.962	0.216	0.343	0.559
5	0.20	1.085	0.244	0.399	0.643
6	0.20	1.197	0.269	0.450	0.718
7	0.20	1.302	0.292	0.497	0.789
8	0.20	1.400	0.313	0.541	0.854
10	0.20	1.580	0.353	0.622	0.975
12	0.20	1.745	0.389	0.690	1.09
14	0.20	1.898	0.423	0.766	1.19
15	0.20	1.971	0.440	0.799	1.24
16	0.20	2.042	0.455	0.831	1.29
18	0.20	2.178	0.486	0.892	1.38
20	0.20	2.307	0.516	0.950	1.47

453

454
455 **Figure 6.** Minimum total quantuty of acid treated date stone carbon, S_1+S_2, to remove IBU applying the Langmuir-
456 Freundlich model at different initial IBU concentrations, C_0, for different set values of final IBU concentrations, C_2,
457 in the effluent

458

459   In **Figure 6**, the required total quantity of date activated carbon increases either with increasing initial IBU

460 concentration or with the lower the IBU concentration in the final solution discharge, C_2. The optimization results

461 for the total quantity of acid treated date stone carbon for removing the IBU to comply with certain set values of C_2

462 provides an important reference point, for example, when there is a legislative or imposed effluent discharge

463 standard for treating the effluent, containing IBU, that must be achieved.

464 Inspection of **Table 6**, shows that more adsorbent is needed for the second stage adsorber, S2, than for the

465 first stage adsorber, S1, for example at Co = 10 mg/L and the removal target is 0.20 mg/L, then S1 = 353.0 g and S2

466 = 622.5 g. In all the cases tested, the ratio of the adsorbent used, namely, S2:S1 is in the range of 1.4 to 2.0.

467 Furthermore, for the same initial concentrations the discharge concentration, C_2, significantly affects the total

468 quantity of date carbon required. This requirement occurs because the final discharge concentration, C_2, is

469 decreasing from 0.20 to 0.01 mg/L and the total amount of adsorbent required is steadily increasing as C_2 is

470 decreasing. Consequently, the change/decrease taking place in the IBU concentration (C_0-C_2) at a set C_0 is lowest for

471 the highest C_2 (total carbon requirement = 975.5 g adsorbent for C_2 = 0.20 mg/L at C_0 = 10 mg/L); and in the second

472 highest initial concentration (total carbon requirement = 1626.2 g adsorbent for C_2 = 0.10 mg/L at C_0 = 10 mg/L);

473 and the third highest value of C_2 = 0.05 mg/L (total carbon requirement = 2720.0 g adsorbent for C_2 = 0.05 mg/L at

474 C_0 = 10 mg/L); and finally the fourth and lowest discharge condition of C_2 = 0.01 mg/L and requiring the highest

475 mass at this (total carbon requirement = 9082.1 g adsorbent for C_2 = 0.05 mg/L at C_0 = 10 mg/L); as the C_2 design

476 value decreases, therefore an increase in the total adsorbent mass, S_1+S_2, is required. The trend is seen in **Figure 5**

477 for the four C_2 changes at a range of C_0 values.

478 The variation in the total adsorbent quantity required as a function of the interstage concentration, C_1,

479 between the two stages, is shown in **Figure 7**, for the four different set effluent IBU discharge values for the final

480 IBU concentrations in the effluent, C_2. It is interesting to observe that there is an almost linear trend in the total

481 adsorbent mass required at each C_2 discharge level value. the minimum total quantity of acid treated date stone,

482 S_1+S_2, to remove IBU against the interstage IBU concentration, C_1, using the Langmuir-Freundlich model for the

483 four different fixed IBU permitted discharge concentration values in the final effluent, C_2.
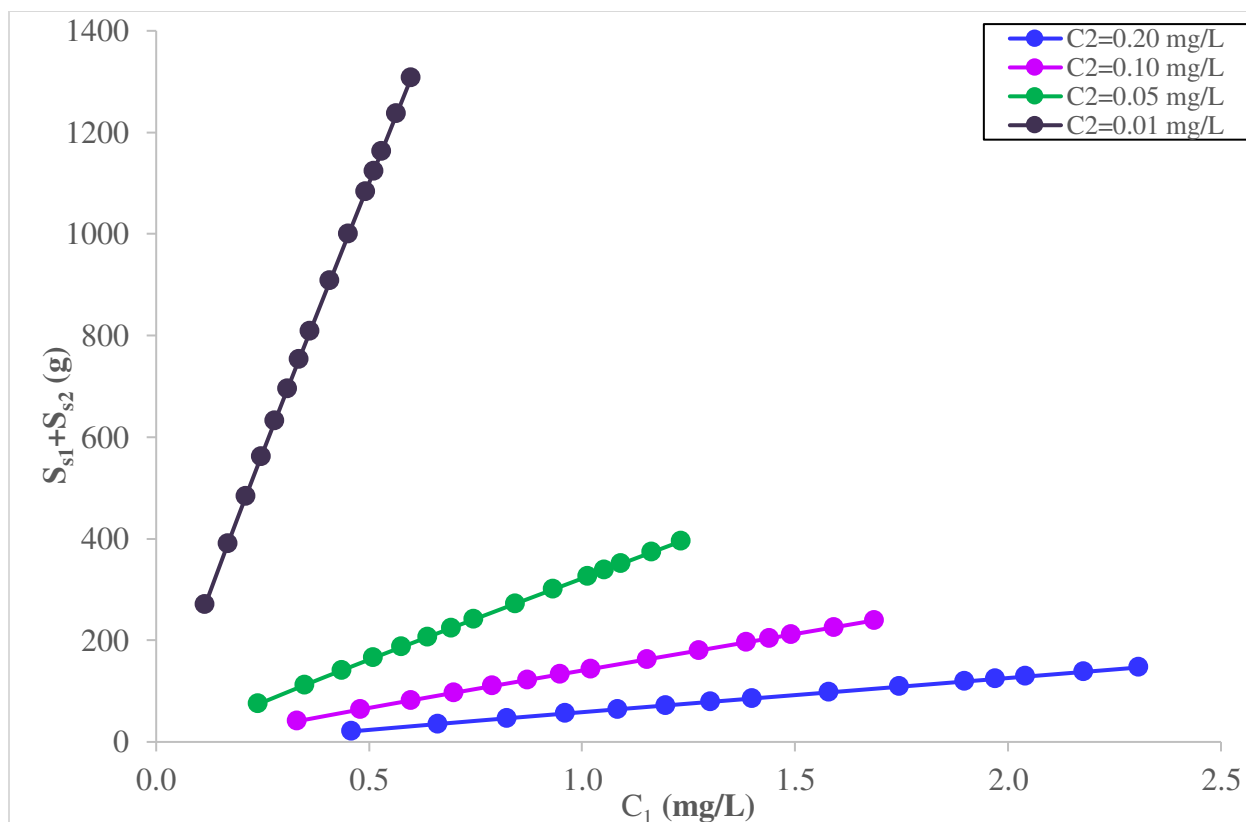
484

Figure 7. Minimum quantity of acid treated date stone carbon, S_1+S_2, to remove IBU against the interstage IBU concentration, C_1, using the Langmuir-Freundlich model for the set values of final IBU concentrations in the effluent, C_2.

Two data tables only, **Table 5** and **6**, are shown and presented in this manuscript, the remaining tables are presented in the Supplementary Information (**S.7** and **S.8**), however, all the consolidated results are depicted in the **Figures 3 to 7.**

Figure 7 shows interstage concentrations, C_1, for acid treated date stone carbon to remove IBU using the Langmuir-Freundlich model for different initial IBU concentrations, C_0, for different fixed final IBU concentrations, C_2.

4.5. Some Economic Implications

To a large extent the benefits or disadvantages of the system described is strongly based on the balance between the costs associated with the adsorbent savings versus the additional capex and opex costs of installing the two stage adsorption reactors with a corresponding reduction in the adsorption time.

4.5.1.   Plant equipment costs

In the case of the multistage adsorption system, smaller adsorber vessel reactors would be involved *e.g.* these vessel units would contain the activated adsorbent and incorporate an interstage filter unit in order to separate the spent adsorbent material. Hence, from a practical viewpoint, the multistage plant is better enhancing the process efficiency by minimizing the total amount of adsorbent to be applied and reducing the overall bath processing time. Therefore making the multistage process potentially attractive in economic terms. The larger the number of stages, the greater will be the saving in adsorbent costs, but the total capital equipment costs – for multiple units – will increase and the handling costs will also be increased. Due to these competing influencing factors, the number of batch stages is usually limited to two or three in order to optimize the economic benefits. For this reason, it is usually required to evaluate the minimum quantity of adsorbent in a two-stage process and the associated savings.

4.5.2.   Adsorbent Savings

On the basis of the adsorbent quantities and the data listed in **Tables 5** and **6,** the quantity of the date stone based carbon that can be conserved by the application of the two-stage adsorber batch reactor versus a single-stage batch adsorber. The total adsorbent quantity applied for the two-stage optimization adsorber based on 99.5 % IBU removal and initial IBU concentrations of 1.0, 2.0, 5.0, 10.0 and 20.0 mg/L – the amount of activated carbon falls in the range of 4.60 to 2.39 kg adsorbent as shown in **Table 7** for the treatment of 1000L, 1 m3, of solution. For a single-stage adsorption unit the quantity of the treated date stone carbon required is in the range of 43.3 to 21.2 kg as shown in **Table 7** using equations (6) and (22):

$$\frac{S_S}{V_S} = \frac{C_0 - C_2}{q_2 - q_0} \tag{29}$$

The extra quantity of adsorbent necessary to perform for the single stage treatment ranges from 9.4 to 8.8 times more than the optimized two-stage batch adsorber amount – this is quite substantial.

Table 8. presents the total quantity of date stone derived activated carbon applied for the two-stage batch optimized system to produce a fixed treated effluent limit concentration value of 0.20 mg/L IBU removal for initial

521 IBU concentrations of 1.0, 2.0, 5.0, 10.0 and 20.0 mg/L – the quantities of the derived activated carbon adsorbent

522 are 0.206, 0.353, 0.643, 0.976 and 1.47 kg for 1000 L of solution.

523 For the single-stage batch system equivalency, the quantity of date stone carbon is 9.04, 4.47, 2.19, 0.822

524 and 0.365 kg using equations (6) and (21). The additional quantity of the activated carbon adsorbent necessary for

525 the single-stage batch adsorption system ranges 6.1 times to 1.8 times, demonstrating the advantages for a two-stage

526 process over a single-stage process in terms of adsorbent utilization.

527
528 **Table 7.** Minimum total amount of acid activated date stone carbon for the 99.5 % removal of ibuprofen in single
529 (S_S) and two-stage ($S_{S1} + S_{S2}$) operations for C_0 values and 1000L of solution

Variable (C_0) (mg/L)	1.0	2.0	5.0	10.0	20.0
Effluent (C_2) (mg/L)	0.005	0.010	0.025	0.050	0.100
Single Stage (S_S) (kg)	43.3	36.7	29.4	25.0	21.2
Two-Stage ($S_{S1}+S_{S2}$) (kg)	4.60	3.90	3.16	2.72	2.39
q_e for single stage (mg/g)	0.0230	0.0543	0.169	0.398	0.937

530
531 **Table 8.** Minimum total amount of phosphoric acid activated date stone carbon for an IBU effluent concentration of
532 0.20 mg/L in both a single (S_S) and a two-stage ($S_{S1}+S_{S2}$) system for various C_0 values for 1000 L solution

Variable (C_0) (mg/L)	1.0	2.0	5.0	10.0	20.0
Effluent (C_2) (mg/L)	0.20	0.20	0.20	0.20	0.20
Single Stage (S_S) (kg)	0.365	0.822	2.19	4.47	9.04
Two-Stage ($S_{S1}+S_{S2}$) (kg)	0.206	0.353	0.643	0.976	1.47
q_e for Single Stage (mg/g)	2.19	2.19	2.19	2.19	2.19

533

534 In **Table 8**, the effect of a lower effluent discharge concentration has a major impact on the additional

535 amount of adsorbent required in the case of the single stage batch adsorption process, that is, at a discharge limit

536 concentration of 0.005 mg/L, then 43.3 kg adsorbent are required, that is, 9.4 times the quantity required for the

537 optimized two stage system. In **Table 8**, the influence of initial concentration is demonstrated and shows that the

538 higher the initial IBU concentration then the greater is the extra amount of carbon: 6.1 times more at C_0 = 20 mg/L

539 and C_e = 0.20 mg/L and only 1.8 times the amount of additional carbon at C_0 = 1.0 mg/L and Ce = 0.20 mg/L.

540 **4.6 Regeneration**

541   Regeneration tests have not been performed due to the problem of available time but conventional regeneration

542   technologies could be applicable for a number of pharmaceuticals which are often recalcitrant in nature. studies were

543   not undertaken in the time available but standard regeneration methods could be considered for this type of

544   recalcitrant compound. IBU does not have any nitrogen or halogen groups therefore regeneration by combustion

545   burning off the pharmaceutical directly is feasible. However, combustion has the inherent disadvantages associated

546   with it including: energy/fuel requirements, greenhouse gas emmissions since carbon dioxide is produced and so

547   contributing to global warming, typically there is a loss of carbon from carbon based adsorbents of the order of 10-

548   12 % and the destruction/loss of the adsorbed IBU. Steam or hot gas stripping has gained popularity enabling

549   volatile organic solvents to be recovered and recycled but the high boiling and melting point of the pharmaceutical

550   IBU would render this technique almost impossible. The treatment by the use of a microbial slurry to biodegrade the

551   IBU is a possible alternative approach but IBU is microbiologically reasonably stable against the majority of micro-

552   organisms, in addition, this methodology takes quite a lengthy period of time to implement and complete. Solvent

553   extraction seems to be a reasonable approach by using a volatile alcohol having a high solubility for IBU. Then, by

554   making use of one of the on-site batch adsorber units for dissolving the IBU followed by pumping the IBU solution

555   to a vacuum driven evaporation system or vacuum driven stripping column recovering the solvent for recycling and

556   recovering the IBU for recycling too. Several toxic loaded adsorbents are disposed of in hazardous landfill sites

557   frequently after stabilisation by encapsulation or by vitrification although this procedure is expensive and there is no

558   recovery of the adsorbent and the IBU. Longer term detrimental effects of hazardous landfilling include the

559   production of landfill leachate creating environmental problems in-situ site anaerobic degradation to produce

560   methane biogas emissions. Consequently, the application of a volatile solvent extraction stage incorporating solvent

561   recovery, adsorbent regeneration and re-use with potential IBU recovery, offers the most attractive technology

562   opportunity for further investigation.

563   **5.   Conclusion**

564   Phosphoric acid has been used to treat waste date stone derived char and heated to 550°C to produce activated

565   carbon. The BET-N$_2$ surface area of this date stone derived activated carbon is 727 m^2/g, a pore volume of 0.70

566   cm^3/g and a pore diameter size = 3.89 nm. The adsorption capacity the active carbon was tested for the adsorption of

567   the ibuprofen and the maximum adsorption capacity carbon product was 126 mg/g, which compared favourably with

568   the very few reported IBU capacities in the literature. Experimental equilibrium data have been modelled applying

569 seven isotherm equations, namely, Langmuir, Freundlich, Langmuir-Freundlich, Redlich-Peterson, Temkin,

570 Dubinin-Radushkevic and Toth isotherm models. The Langmuir-Freundlich isotherm provided the optimised best fit

571 correlation based on the application of an SSE error analysis. This correlation was then applied for minimising the

572 amount of date carbon adsorbent needed in designing a two-stage batch adsorber system for the removal of IBU.

573 The quantity of the date stone derived activated carbon was determined for a two-stage batch adsorber and for an

574 equivalent single stage process. The quantity of activated carbon adsorbent require was greatly reduced in the two-

575 stage system, sometimes by a factor of more than 9-fold. This optimization study also demonstrated the amount of

576 adsorbent strongly depends on both the IBU concentration and especially the effluent discharge limit value adopted

577 or imposed. The results demonstrate the potential at an industrial scale for designing and performing economic and

578 technical feasibility studies on two-stage and multi-stage batch adsorption process units for the treatment of

579 emerging pollutants.

580 **Declarations**

581 **Ethics approval and consent to participate-** Not applicable

582 **Consent for publication-** Not applicable

583 **Availability of data and materials**

584 All data generated or analysed during this study are included in this published article [and its supplementary

585 information files].

586 **Competing interests**

587 The authors declare that they have no competing interests" in this section.

594 **Authors' contribution**

595 **HF**- Investigation, Validation, Writing - Original Draft.

596 **JS**- Conceptualization, Project administration, Methodology, Writing - Review & Editing.

604   **Authors' information**

Name	Email	Contact address
Hajar Farzaneh	hajfarzaneh@hbku.edu.qa	Division of Sustainable Development, College of Science and Engineering, Hamad Bin Khalifa University (HBKU), Qatar Foundation (QF), Doha, Qatar.
Dr. Jayaprakash Saththasivam	jsaththasivam@hbku.edu.qa	Qatar Energy and Environment Research Institute, Hamad Bin Khalifa University (HBKU), Qatar Foundation (QF), Doha, Qatar.
Prof. Dr. Gordon Mckay	gmckay@hbku.edu.qa	Division of Sustainable Development, College of Science and Engineering, Hamad Bin Khalifa University (HBKU), Qatar Foundation (QF), Doha, Qatar.
Dr. Prakash Parthasarathy	pparthasarathy@hbku.edu.qa, prakrock@gmail.com	Division of Sustainable Development, College of Science and Engineering, Hamad Bin Khalifa University (HBKU), Qatar Foundation (QF), Doha, Qatar.

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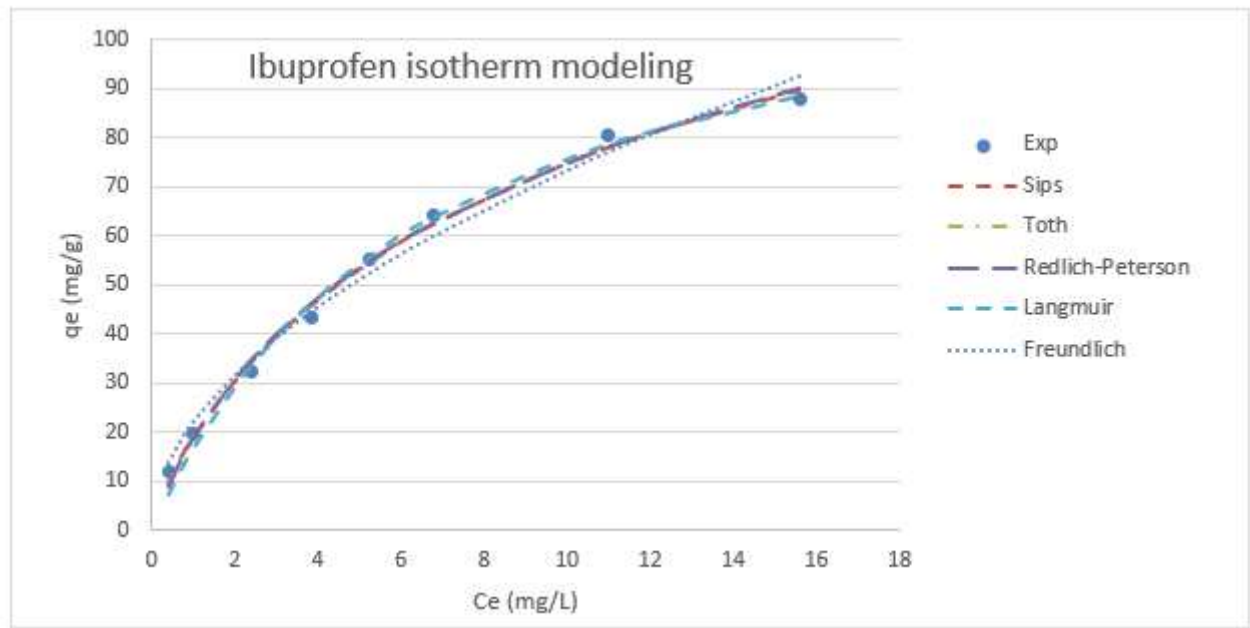
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Figures

Figure 1

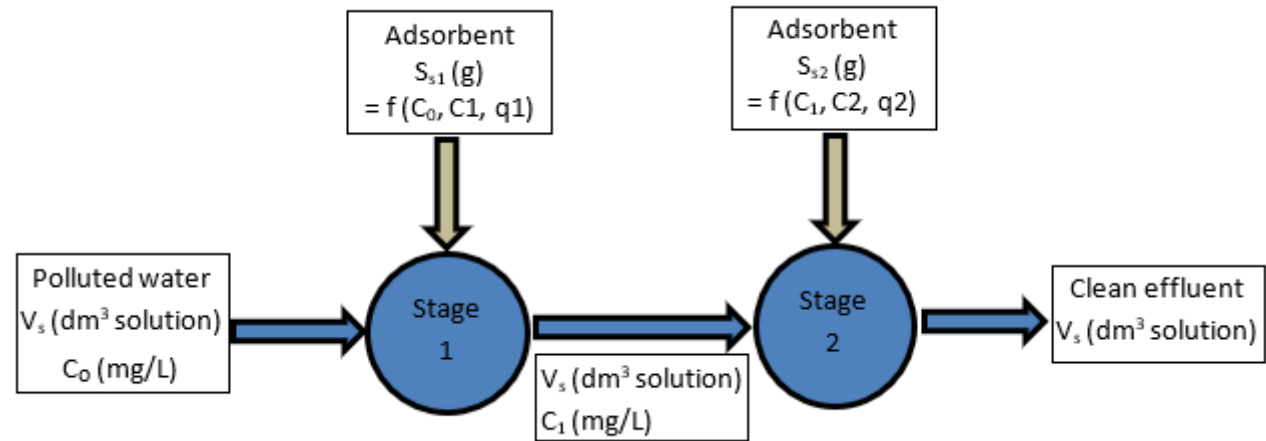Five isotherm models compared with the experimental IBU equilibrium data.
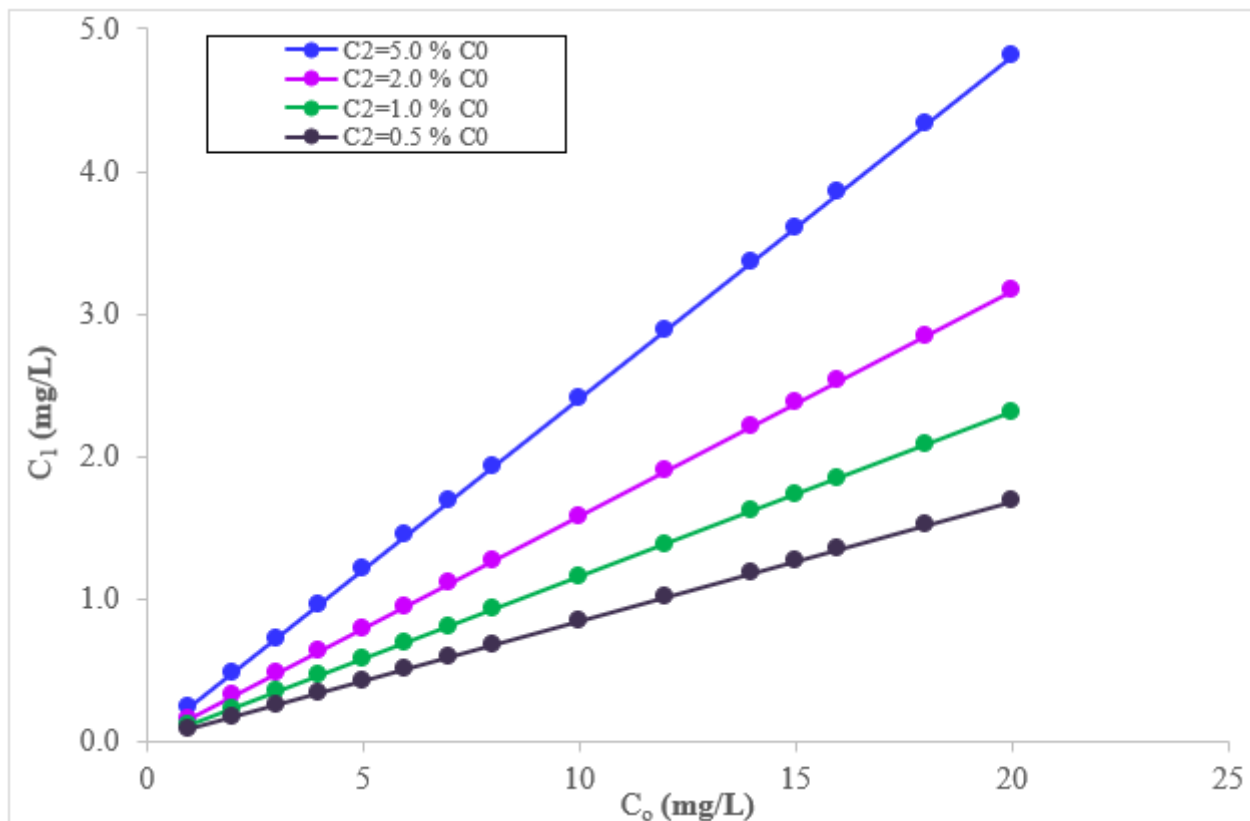

Figure 2

Schematic figure of a two-stage system

Figure 3

Interstage concentrations, C1, to remove different fixed % C0 IBU using the Langmuir-Freundlich model.
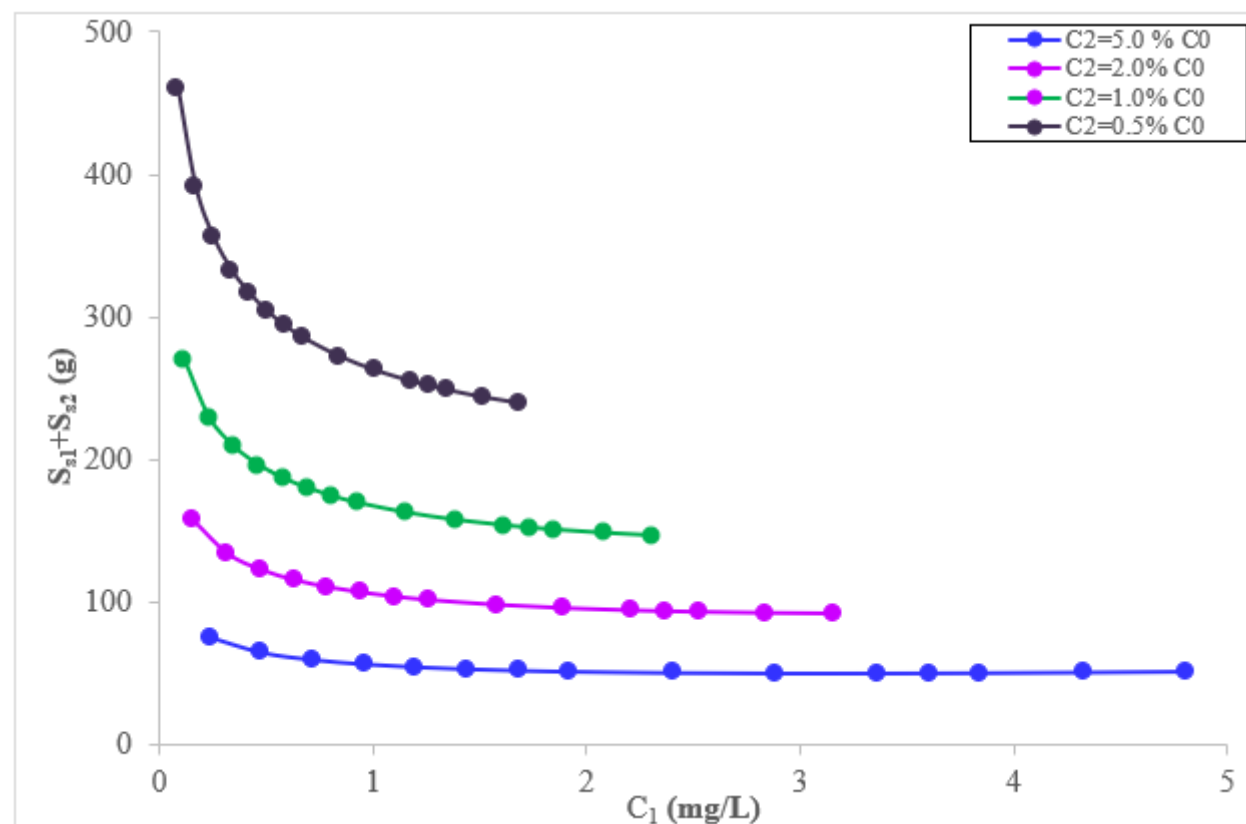

Figure 4

Minimum quantity of acid treated date stone activated carbon, S1+S2, against the interstage concentrations, C1, to remove IBU using the Langmuir-Freundlich model for different removal values, % C0.
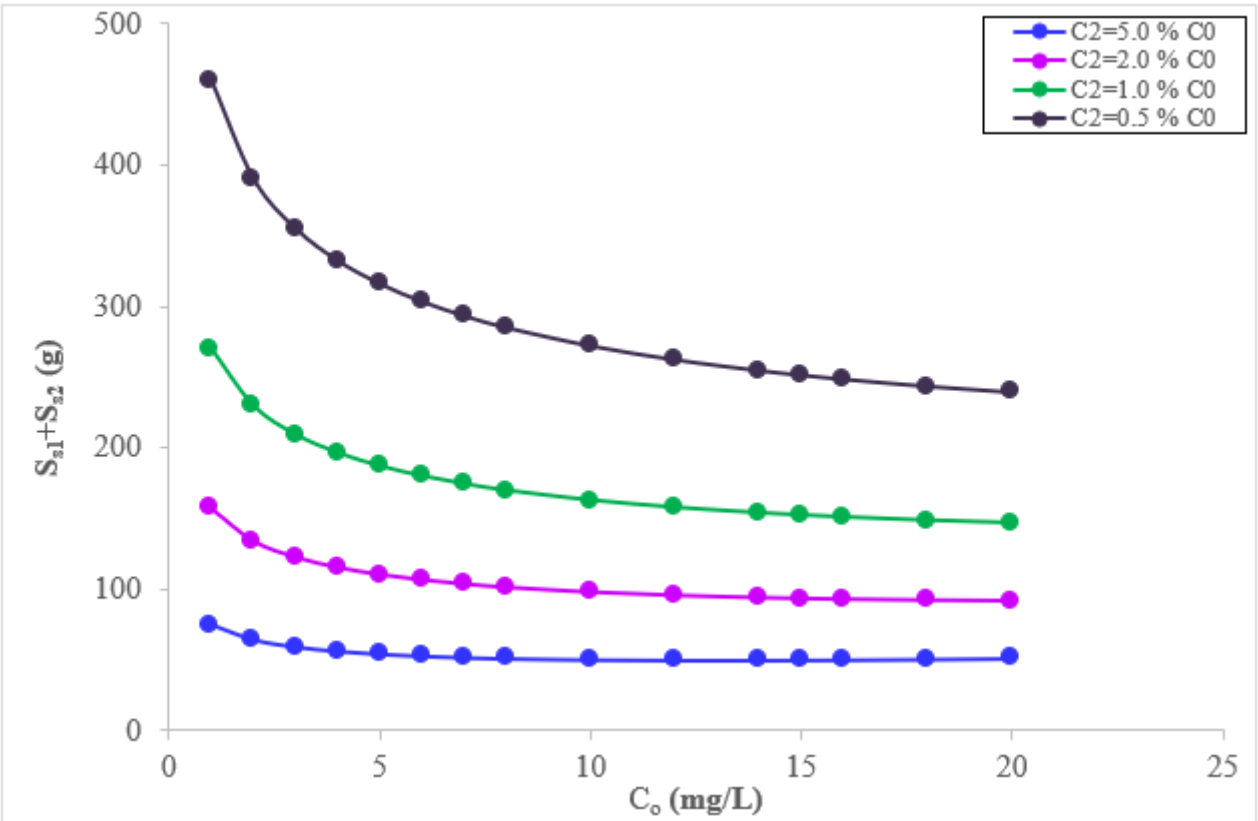

Figure 5

Minimum total quantity of acid treated date stone activated carbon, S1+S2, against the initial IBU concentration, C0, to remove a fixed % C0 IBU using the Langmuir-Freundlich model.
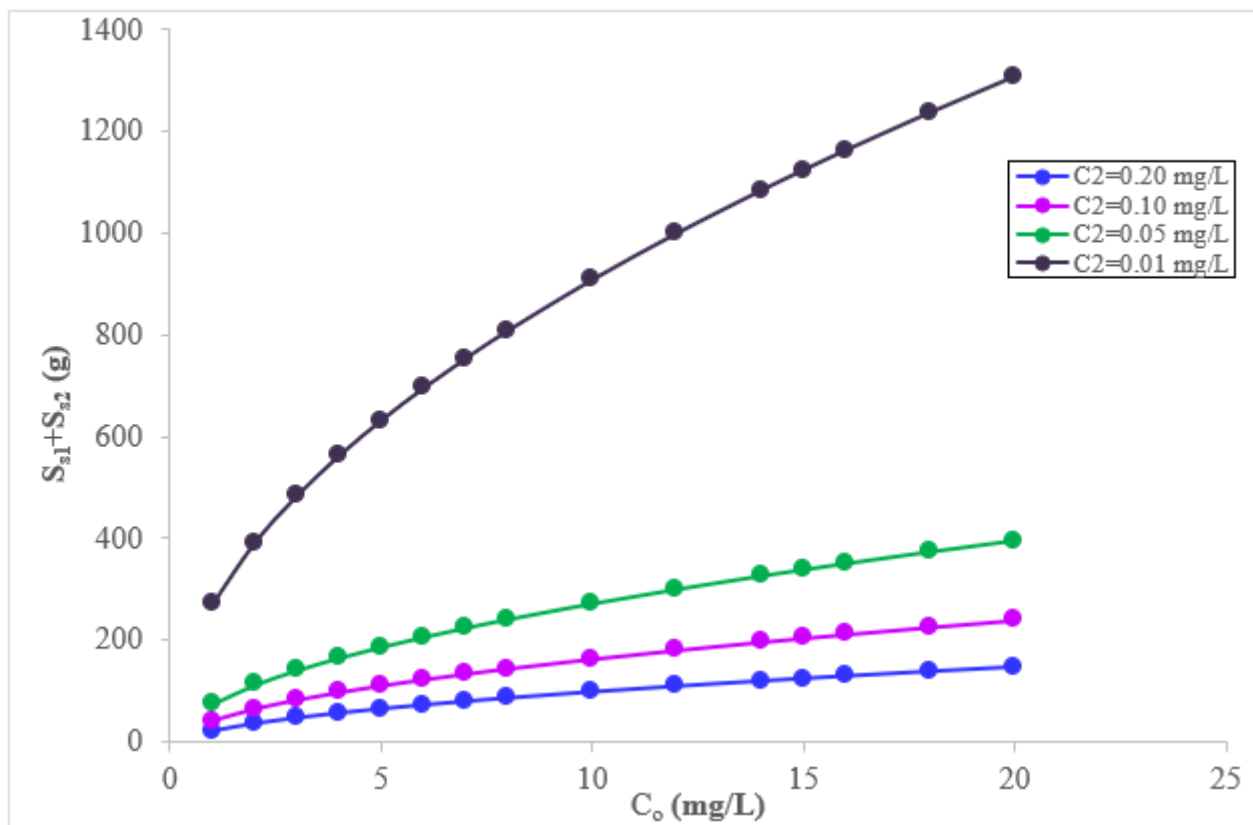
Figure 6

Minimum total quantuty of acid treated date stone carbon, S1+S2, to remove IBU applying the Langmuir-Freundlich model at different initial IBU concentrations, C0, for different set values of final IBU concentrations, C2, in the effluent
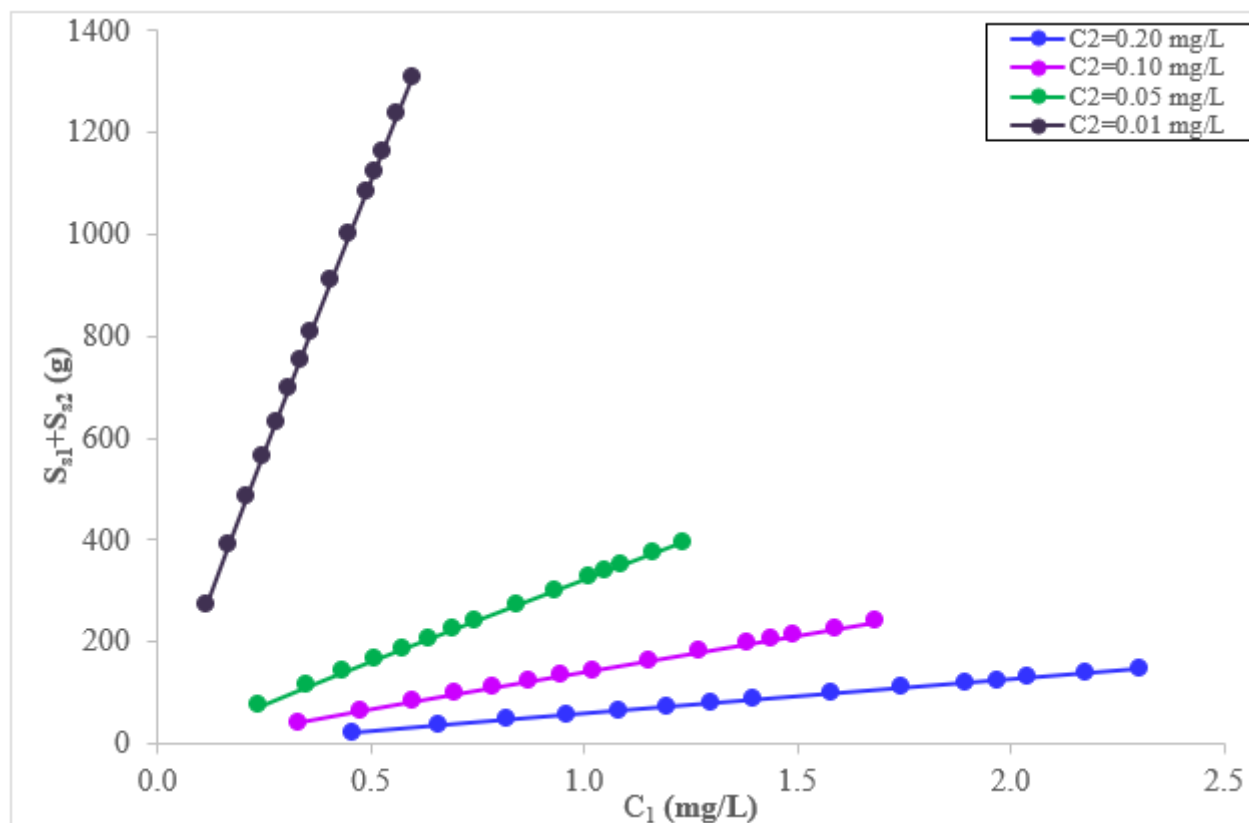
Figure 7

Minimum quantity of acid treated date stone carbon, S1+S2, to remove IBU against the interstage IBU concentration, C1, using the Langmuir-Freundlich model for the set values of final IBU concentrations in the effluent, C2.

Supplementary Files

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