Study of natural adsorbent chitosan and derivatives for the removal of caffeine from water
Serena Sanford, Kripa S. Singh, Sahil Chaini and Gaetan LeClair

**ABSTRACT**

The adsorption of caffeine was evaluated using natural adsorbent chitosan and three derivatives of the material. Raw, H$_2$O$_2$ pre-treated, and a chemically altered chitosan were compared to activated carbon. Activated carbon was found to have a high affinity for caffeine (98% removal) while raw chitosan performed poorly with an average adsorption of 15.9%. Batch tests in acidic and basic conditions as well as increasing dosage did not have an effect on the performance. Chemical modifications to chitosan included calcinated mesoporous materials and non-calcinated materials, both of which increased chitosan adsorption of caffeine to 29 and 40%, respectively. Hydrogen peroxide pre-treated chitosan performed best of chitosan-based adsorbents, and reached a 46% removal of caffeine in batch adsorption tests. The majority of the adsorbents had low correlation to the Langmuir, Freundlich, and Redlich–Peterson isotherm models. However, data were sufficient to compare adsorption capacity for caffeine among activated carbon, chitosan, and chitosan derivatives.

**Key words** | adsorption, caffeine, chitosan, mesoporous chitosan pharmaceuticals

**INTRODUCTION**

Activated carbon is currently the most effective adsorbent for removing pharmaceutical and personal care products (PPCP) and endocrine disrupting compounds (EDC) from water, and has been shown to remove up to 70 EDCs (Liu et al. 2009). Another study also showed that activated carbon was able to remove 90% of the 29 PPCP and EDC compounds studied in a bench scale system (Snyder et al. 2007). The disadvantage of using activated carbon is the high cost associated with the adsorbent (Monhan & Singh 2002). An adsorbent which is more economical and biodegradable would be ideal as a PPCP and EDC adsorbent.

Two materials which are widely available and naturally found are chitin and chitosan. Chitin is a naturally found mucopolysaccharide which is obtained from crustacean species (Ravi Kumar 2000). Chitosan is the N-deacetylated derivative of chitin and has been heavily applied in the adsorption of heavy metals and dyes from water (Modak et al. 2009). Numerous experiments have shown the effectiveness of chitosan or chemically modified derivatives in the adsorption of species such as lead, arsenic, copper and organic dyes (Kyzas & Lazaridis 2009).

Mesoporous materials are defined as inorganic solids containing pores, varying in size from 2 to 50 nm (Beck et al. 1992; Koodali & Zhao 2010). Some common applications of mesoporous materials are catalysts, ion adsorption, and separation (Beck et al. 1992; Innocenzi et al. 2008). Recently, mesoporous silica functionalized with phenyl groups was shown to have high adsorption affinity for bisphenol A (Kim et al. 2011). Chitosan has been shown to be an effective template for the synthesis of silica mesoporous beads with a large surface area (Chen et al. 2009, 2010). This study will determine whether a chitosan based silica mesoporous material will be effective for the removal of PPCPs and EDCs.

Pre-treatment with hydrogen peroxide was shown to greatly increase the adsorption capacity of chitosan for anionic dyes (Shen et al. 2011). Pre-treatment with hydrogen peroxide is a simple process, and allows for a material...
which is effective in pH regions below 6.5 (Shen et al. 2011). In this study, it is proposed that by pre-treating the raw chitosan with hydrogen peroxide, the material will have an increased response for PPCP and EDC compounds.

The purpose of the study is to evaluate the effectiveness of natural material chitosan, hydrogen peroxide pre-treated chitosan, and a mesoporous chitosan for the adsorption of PPCP and EDC compounds. Raw chitosan and the mesoporous chitosan were tested in all pH regions while pre-treated chitosan was only tested in acidic pH. Caffeine was chosen as the model pharmaceutical because it is typically labelled as a tracer species for pharmaceuticals (Comeau et al. 2008). By studying these natural materials for caffeine adsorption capacity, the feasibility of using these materials as PPCP and EDC adsorbents is evaluated.

MATERIALS AND METHODS

Materials and reagents

Minimum 85% deacetylated chitosan was obtained from Sigma Aldrich (Ontario, Canada), as well as caffeine (reagent grade), ethyl acetate (reagent grade), chitin (from shrimp shells), tetraethyl orthosilicate (TEOS) and 1,3-dimethyl-2-nitrobenzene. Sodium hydroxide solid pellets were obtained from Fischer Scientific (Ontario, Canada). Concentrated hydrochloric acid was obtained from Caledon (Ontario, Canada). Granular activated carbon was received from MCB Manufacturing Chemists, Canadian Lab Supplies (Quebec, Canada). Hydrogen peroxide (3%v/v) was obtained from Compliments (Ontario, Canada).

Synthesis of mesoporous chitosan

The procedure for synthesis of mesoporous chitosan was based on a similar synthesis by Chen et al. (2009). These highly ordered structures are synthesized using organic surfactants as templates, and adding a silica source to the template forming a liquid crystal template (Innocenzi et al. 2008). Deacetylated chitosan (0.8 g of 85%) was dissolved in 40 mL of a 3% acetic acid solution. The mixture was shaken vigorously for 5 min. Then, 48 mL of ethanol was added to solution, and the mixture was shaken for another 10 min. TEOS (13 mL) was added to solution, and the mixture was shaken to uniformity. The gel-like mixture was added drop-wise by syringe into a solution of 50% ammonium hydroxide. The small beads were allowed to dry over 3 days, or until the solvent had evaporated. The beads were then burned in a furnace (calcinated), using a temperature ramp of 5°C/min until they reached a temperature of 700°C. The temperature was held at 700°C for 1 h then the beads were cooled for use in adsorption tests. The surfactant or template is removed in the calcinations step, thus clearing the pores and generating a mesoporous material.

Synthesis of hydrogen peroxide pre-treated chitosan

The preparation of pre-treated chitosan was based on a similar procedure to that of Shen et al. (2011). Chitosan (0.5 g) was stirred at room temperature for 2 h in 0.2 M H2O2. The slurry was separated by centrifugation (Beckman Coulter Allegra, X-15R Centrifuge, Mississauga, Ontario), and the solid was washed with distilled water. The wet solid was then dried in a furnace (Barnstead Thermolyne 48000 Furnace, Asheville, NC, USA) at 80°C.

Batch adsorption test procedure

Batch adsorption tests were performed using an Orbital Shaker (Barnstead Lab-Line e-class Max Q 5000, Illinois, USA). Equilibrium adsorption tests performed for activated carbon determined 72 h of shaking was required to remove the bulk of the caffeine from solution, therefore all adsorbents were tested for 72 h. A 400 mL solution of 0.54 mg/L caffeine was placed into a vial along with varying doses of adsorbent (25 mg/L to 1 g/L). All tests were performed using distilled water spiked with caffeine. Neutral conditions were between pH 7.0 and 8.0 while acidic conditions, pH 2.9–3.3, were obtained by the addition of 2 M HCl. Basic conditions, pH 10.0–10.5, were obtained by the addition of 2.5 M NaOH. The pH was determined using a pH meter (Orion research model SA 250, Thermo Scientific, Ontario, Canada). The solutions were shaken at 150 rpm for 72 h with the temperature held constant at 20°C. The mixtures from the batch tests were filtered to remove adsorbent, and a 10 mL aliquot was taken for sample preparation and analysis.
Sample preparation and analysis

Solid phase extraction (SPE) reversed phase cartridges (Strata-X-polymeric, 3 mL, 30 mg, Phenomenex, California, USA) were used with an SPE chamber (Supelco Visiprep 24, Sigma Aldrich, Ontario, Canada) for sample preparation. The cartridges were pre-treated using 3 mL of methanol and 3 mL of distilled water. A 10 mL caffeine-water sample was added to the moist cartridges in increments of 3 mL. A flow rate of 12–15 mL/min was obtained using a vacuum line (Togola & Budzinski 2007). The cartridge was dried for 1 min. Next, the cartridge was soaked in 3 mL of methanol for 2 min. Finally, the methanol was collected from the cartridge, and an extra wash of 3 mL of methanol was performed to ensure all the analyte was collected (Togola & Budzinski 2007). The methanol-caffeine sample was then evaporated using a low vacuum rotary evaporator. A sample suitable for gas chromatography mass spectrometry (GC-MS) was made by adding 950 μL of ethyl acetate, and 50 μL of 66 mg/L 1,3-dimethyl-2-nitrobenzene was used as an internal standard.

The prepared samples were injected into a GC-MS (HP 5890 Series II gas chromatograph coupled to a HP 5971 series mass selective detector, Agilent, Ontario, Canada). The GC column used was 30 m long, 0.25 mm id, having a 0.25 μm film thickness (Zebron ZB-5 ms, Phenomenex, California, USA). The injection port temperature was set at 220 °C, the transfer line at 280 °C, and the ion source temperature at 173 °C. The GC oven temperature was as follows: 70 °C for the first minute, ramped up to 260 °C at a rate of 35 °C/min and held for 12 min. The GC-MS quantification was performed in single ion monitoring (SIM) mode using analyte fragments having a mass over charge ratio (m/z) of 134, 151, 193, 194, 202, and 236. Caffeine did not degrade when known concentrations were injected in the GC-MS, therefore, no chemical derivitizations were preformed prior to GC-MS injection.

Adsorption isotherms

The Langmuir, Freundlich, and Redlich–Peterson isotherm models were chosen to analyze the data. The Langmuir model is described by the following linear equation:

\[
\frac{C_e}{Q_e} = \frac{1}{Q_{\text{max}}} + \frac{1}{K_L Q_{\text{max}}} C_e
\]

where \(Q_e\) (mg/g) is the equilibrium caffeine concentration in the adsorbent, \(C_e\) (mg/L) is the equilibrium concentration of caffeine in the aqueous phase, \(Q_{\text{max}}\) (mg/g) is the maximum adsorption, and \(K_L\) (L/g) is the Langmuir equilibrium adsorption constant (Langmuir 1918; Tsai & Juang 2000; Kyzas & Lazaridis 2009). Data were modeled in linear form and the \(R^2\) value (correlation coefficient) was obtained. The Freundlich model (Equation (2)) can be described by the following linear equation:

\[
\log(Q_e) = \log(K_f) + \frac{1}{n} \log(C_e)
\]

where \(Q_e\) (mg/g) is the equilibrium caffeine concentration in the adsorbent, \(C_e\) (mg/L) is the equilibrium concentration of caffeine in the aqueous phase, \(K_f\) (L/g) is the Freundlich constant or relative sorption capacity, and \(n\) is a constant indicating adsorption intensity (Freundlich 1906; Tsai & Juang 2000; Kyzas & Lazaridis 2009). Data were modeled in linear form and the correlation coefficient was obtained.

The Redlich–Peterson model (Equation (3)) is a combination of the Langmuir and Freundlich models and combines three parameters into the equation:

\[
Q_e = \frac{K_R C_e}{1 + a_RC_e^n}
\]

where \(Q_e\) (mg/g) is the equilibrium caffeine concentration in the adsorbent, \(C_e\) (mg/L) is the equilibrium concentration of caffeine in the aqueous phase, \(K_R\) (L/g) and \(a_R\) (L/mg) are Redlich–Peterson isotherm constants, and \(\beta\) is the exponent (Redlich & Peterson 1958; Perez et al. 2007). When \(\beta\) is 1, the relationship becomes the Langmuir model (Equation (4)) and when \(\beta\) is 0, then the relationship can be described by Henry’s Law, as seen below in Equation (5) (Redlich & Peterson 1958; Perez et al. 2007):

\[
Q_e = \frac{K_R C_e}{1 + a_R C_e}
\]
\[ Q_e = \frac{K_RC_0}{1 + a_R} \]  

The Redlich–Peterson equation has three unknown parameters; \( \beta \), \( K_R \), and \( a_R \). Modelling the Redlich–Peterson equation in linear form involves optimizing a chosen value for \( K_R \) by obtaining the highest correlation coefficient (Redlich & Peterson 1958; Perez et al. 2007). Through this method, \( \beta \) and \( a_R \) can be obtained. When optimizing \( K_R \), the obtained value of \( \beta \) should not be above 1 or else the Redlich–Peterson theory does not apply (Redlich & Peterson 1958; Vasanth Kumar & Porkodi 2007). The linear form of the Redlich–Peterson model is shown in Equation (6):

\[ \ln \left( \frac{K_R C_e}{Q_e} - 1 \right) = \beta \ln (C_e) + \ln (a_R) \]  

**RESULTS**

**Brunauer Emmett Teller (BET) surface area**

All the materials were analyzed for BET surface area (Belsorp-Max, BEL, Japan). The samples were conditioned for 4 h at 100 °C. The results from the surface area analysis are presented in Table 1.

The surface area results found for activated carbon and chitosan are similar to literature values (Hu et al. 2000; Benguella & Benaissa 2002; Kamari et al. 2011). Chitosan had a surface area of 3.6 m²/g, which is close to the literature value of 1.2 m²/g (Benguella & Benaissa 2002). Activated carbon had a surface area of 618.9 m²/g, within the range of 800–1,500 m²/g which was found in the literature (Hu et al. 2000).

**Table 1 | Surface area results of adsorbents**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Surface area m²/g</th>
<th>Pore volume cm³/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon (granular)</td>
<td>618.9</td>
<td>0.7248</td>
</tr>
<tr>
<td>Chitosan</td>
<td>3.6</td>
<td>0.0111</td>
</tr>
<tr>
<td>Pre-treated chitosan</td>
<td>0.8</td>
<td>0.0032</td>
</tr>
<tr>
<td>Mesoporous chitosan</td>
<td>85.8</td>
<td>0.3315</td>
</tr>
<tr>
<td>Mesoporous chitosan (non calcinated)</td>
<td>143.0</td>
<td>0.3614</td>
</tr>
</tbody>
</table>

The surface area of the H₂O₂ pre-treated chitosan was significantly smaller than raw chitosan. The large difference between BET surface area of the raw and treated material is thought to be due to the increase in crystallinity when the material is pre-treated. In other studies, such as in the treatment of cellulose with 1% solution of H₂O₂, the reverse situation was seen (Lilitha & Sivaraj 2011). There was a decrease in crystallinity of the cellulose and an increase in surface area (Lilitha & Sivaraj 2011). Also, the study of ZSM-5 Zeolites showed increasing crystallinity caused a decrease in surface area (Aiello et al. 2005).

The surface areas of the mesoporous materials do not follow mesoporous theory. It is expected that a material which has clear pores would have a larger surface area than one with an organic compound contained in the intermolecular structure. However, the surface area results show that the material with chitosan (still encapsulated in pores) has a higher surface area. Upon analysis, it was determined that the heating temperature for the calcinated material was too high, thus causing fusing of the silica into spheres in some areas of the material. This theory was confirmed using transmission electron microscope (TEM) and energy dispersive X-ray (EDX), and could explain why a smaller surface area was obtained for the burned mesoporous material. The mesoporous material burned at a lower temperature could have a larger surface area than the material burned at a higher temperature due to excess carbon remaining in the pore structure which would increase the surface area of the material (Jagtap et al. 2011).

**Attenuated total reflection infrared spectroscopy**

Raw chitosan, pre-treated chitosan and mesoporous chitosan were analyzed using attenuated total reflection infrared spectroscopy (ATR-IR) fitted with an ATR-FTIR module and zinc-selenide crystal to observe the functional group differences between the adsorbents (Varian 640-IR, Ontario, Canada).

When analyzing the spectra of raw and pre-treated chitosan, seen in Figure 1, the two structures are chemically similar. The characteristic peaks of raw and pre-treated chitosan are shown at 1,628, 1,575 and 1,641, 1,570 cm⁻¹, respectively, corresponding to amide functionality (Kyzas & Lazaridis 2009; Mir et al. 2011), and located at 1,015, 524, 578, 484 cm⁻¹.
and 1,014 cm$^{-1}$ are the C-O stretches (Shen et al. 2011). There is also a broad O-H stretch around 3,280 cm$^{-1}$ for each of the compounds (Kyzas & Lazaridis 2009). Also, C-H stretches are found for each material at 2,850 cm$^{-1}$. There are no major differences in the IR spectra between the two forms of chitosan and this confirms that the pre-treatment of the raw material does not change any chemical functional groups on the adsorbent.

When examining the spectra of the mesoporous chitosan (Figure 2), both the uncalcinated and calcinated materials are quite similar. There is a characteristic silicon-oxygen stretch, at 1,048 cm$^{-1}$, but not many other functional group vibrations. The interesting point to note in the comparison between the calcinated and not calcinated spectra is the slight peaks pertaining to chitosan functional groups in the uncalcinated spectra. The faint O-H stretches at 3,268 cm$^{-1}$ and C-H stretches at 2,854 cm$^{-1}$ do indicate the presence of chitosan in the silica material. On the contrary, the calcinated material does not have any chitosan peaks. These results give confidence to the assumption that all the chitosan was burned off in the calcinated mesoporous materials.

### Transmission electron microscope analysis

Mesoporous chitosan was analyzed using a TEM (JEOL 2010 Scanning TEM, Tokyo, Japan). TEM images were recorded using a 4k×4k CCD camera and analyzed using Digital Micrograph software (Gatan Inc., California, USA).

Calcinated mesoporous chitosan showed a three-dimensional structure but lacked uniformity. Pore size was estimated to be 9 nm, but the material was not uniform in pore size, as seen in Figure 3. The material was determined to be mesoporous, due to presence of pores in the size region of 2–50 nm (Beck et al. 1992; Koodali & Zhao 2010).

The uncalcinated material had non-uniform pores between 8 and 9 nm in size. There were significantly fewer pores than the calcinated material. The uncalcinated mesoporous chitosan could be described as very flat. The uncalcinated material can be seen in Figure 4.
Scanning electron microscopy

A scanning electron microscopy (SEM) (JEOL JSM 6400 digital SEM, Tokyo, Japan), was used to analyze the surfaces of the pre-treated and raw chitosan materials. Images were analyzed and recorded using Gellar dPict digital image acquisition software (Gellar, MA, USA).

In SEM analysis, Shen et al. (2011) found that the pre-treated materials appeared to have a smoother surface, and postulated that the amorphous areas in chitosan were removed by the hydrogen peroxide pre-treatment. Chitosan has a chemical structure which is partially amorphous, and crystalline, and contained in these structures are hydrogen bonds. When chitosan is treated with hydrogen peroxide, the hydrogen bonds between the amorphous and crystalline structures are disrupted, and once reformed, the chemical structure in chitosan is more ordered, and smooth. It has been shown that the hydrogen peroxide pre-treatment of chitosan causes an increase in hydrophilicity and freeing of the functional groups (Shen et al. 2011). Reformation of the chitosan structure does not change the quantity or presence of functional groups but does facilitate access to these chemical groups (Shen et al. 2011). In the current study, it was quite evident during SEM analysis that the raw materials had rougher textures. In Figures 5 and 6, the difference between the raw and treated chitosan is shown.

Batch adsorption tests

Batch adsorption tests of the adsorbents were used to obtain data to develop the isotherms. The summary of the activated carbon isotherm models are shown in Figure 7, while a summary of the adsorption of caffeine by each adsorbent is shown in Figure 8, as well as the error accumulated in the sampling process. Accumulated error originates from duplicate experiments, and GC-MS injections.
Based on the constants and correlation coefficients obtained for the model, one can determine how well the data are modeled by an isotherm. Freundlich isotherm constants are indicative of adsorption. If the value of constant \( n \) is above 1, it indicates that the adsorption of caffeine onto the adsorbent increases the free energy for subsequent adsorption (Schwarzenbach et al. 2003). When \( n < 1 \), the adsorbate is bound with weak free energy (Schwarzenbach et al. 2003). Negative \( n \) values are attributed to poor caffeine adsorption and low correlation to the Freundlich model.

Langmuir constant, \( K_L \), measures the affinity of the adsorbent for the adsorbate (Klepetsanis et al. 2000). A large positive value, such as 55.41 L/mg for activated carbon tests, indicates high affinity and effective adsorption while the negative values obtained indicate no affinity (Reynolds 1982).

Activated carbon data were best described by the Langmuir model (\( R^2 = 0.96 \)) as presented in Table 2. Both the Freundlich and Redlich–Peterson models also yield high correlation coefficients. As seen in Figure 7, the activated carbon isotherm models show a favorable adsorption curve.

Chitosan in neutral pH was effectively described by both the Freundlich and Langmuir models with correlation coefficients of 0.98 and 0.90, respectively (Table 2). When chitosan (in all pH solutions) was modeled with the Redlich–Peterson equation, \( \beta \) was found to be above 1,

### Table 2 | Isotherm values for Langmuir and Freundlich models

<table>
<thead>
<tr>
<th>Constants</th>
<th>Freundlich</th>
<th>Langmuir</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( K_F ) (L/g)</td>
<td>( n )</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>19.5</td>
<td>1.82</td>
</tr>
<tr>
<td>Chitosan (neutral)</td>
<td>( 6.47 \times 10^{-11} )</td>
<td>0.0595</td>
</tr>
<tr>
<td>Chitosan (acidic)</td>
<td>( 8.96 \times 10^{-4} )</td>
<td>-0.268</td>
</tr>
<tr>
<td>Chitosan (basic)</td>
<td>0.00965</td>
<td>-0.835</td>
</tr>
<tr>
<td>Calcinated chitosan (neutral)</td>
<td>( 1.43 \times 10^{-5} )</td>
<td>-0.141</td>
</tr>
<tr>
<td>Calcinated chitosan (acidic)</td>
<td>0.0354</td>
<td>-1.22</td>
</tr>
<tr>
<td>Calcinated chitosan (basic)</td>
<td>( 2.58 \times 10^{17} )</td>
<td>0.0322</td>
</tr>
<tr>
<td>Non-calcinated chitosan (neutral)</td>
<td>6.28</td>
<td>0.413</td>
</tr>
<tr>
<td>Non-calcinated chitosan (acidic)</td>
<td>1.15 \times 10^{-4}</td>
<td>-0.182</td>
</tr>
<tr>
<td>Non-calcinated chitosan (basic)</td>
<td>1.69 \times 10^{-5}</td>
<td>-0.151</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}_2 ) pre-treated chitosan</td>
<td>0.044</td>
<td>-0.892</td>
</tr>
</tbody>
</table>

Figure 7 | Activated carbon isotherm.

Figure 8 | Summary of chitosan and activated carbon adsorption isotherms.
meaning the Redlich–Peterson theory behind the isotherm model did not apply. Redlich–Peterson theory requires \( \beta \) to be below 1. Mesoporous calcinated materials were poorly described by all models, and as seen in Table 3, \( \beta \) was found to be above 1 in all pH conditions. Non-calcinated mesoporous materials in basic pH had high correlation coefficients for both the Freundlich and Langmuir models (0.99, and 0.93 in Table 2). However, the negative isotherm constants obtained for both the Languir and Freundlich equations indicate poor fitting to the theoretical models. The pre-treated material was not described by the models, as seen by low correlation values in Tables 2 and 3.

**Discussion of the adsorbents**

Activated carbon was the most effective adsorbent for removing caffeine. As shown in Figure 8, at a concentration of only 250 mg/L, activated carbon adsorbed almost 100% of the caffeine in solution during the 72 h adsorption tests. Previous studies such as those by Liu et al. (2009) and Bundy et al. (2007) have already documented the effectiveness of activated carbon. Liu et al. (2009) showed that a surface treated activated carbon had a capacity for commonly found EDC, bisphenol A, of 432.34 mg/g. Also, Bundy et al. (2007) have found that up to 94% of caffeine present in natural water could be removed with a granular activated carbon step in water treatment. In the present study, the large surface area of activated carbon and the shared hydrophobic character of both the adsorbent and adsorbate allowed for almost complete adsorption of the analyte.

The mechanisms behind chitosan’s adsorption of dyes and heavy metals lie within the functional groups. Chitosan has hydroxyl groups and amino ligands present on the surface of the material, both of which can be considered active sites for adsorption (Copello et al. 2011). However, chitosan was not effective at adsorbing the trace caffeine during the batch tests. As seen in Figure 8, there was no effect on adsorption by increasing the adsorbent dose. The highest caffeine adsorption was 25% at a chitosan dose of 100 mg/L, in neutral conditions. The poor performance could be due to the surface properties of the adsorbent and adsorbate. Chitosan contains free amino groups (due to the deacetylation from chitin structure) and it has been found that when the pH of solution is 4.3, 99% of the free amino groups are protonated into \( \text{NH}_3^+ \) (Nomanbhay & Palanisamy 2005). Caffeine is a weakly basic compound that does not ionize except for extreme pH conditions, such as below 1 and above 12 (Young et al. 2008). In neutral water conditions, amine groups would not be protonated, and the caffeine analyte would still be weakly basic. These conditions would not enhance or promote an electrostatic interaction to occur. Also, chitosan, being a hydrophillic material (Copello et al. 2011) would not induce hydrophobic

### Table 3

<table>
<thead>
<tr>
<th>Isotherm values for Redlich–Peterson model</th>
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<tbody>
<tr>
<td><strong>Constants</strong></td>
</tr>
<tr>
<td>Activated carbon</td>
</tr>
<tr>
<td>Chitosan (neutral)</td>
</tr>
<tr>
<td>Chitosan (acidic)</td>
</tr>
<tr>
<td>Chitosan (basic)</td>
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<tr>
<td>Calcinated chitosan (neutral)</td>
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<tr>
<td>Calcinated chitosan (acidic)</td>
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<tr>
<td>Calcinated chitosan (basic)</td>
</tr>
<tr>
<td>Non-calcinated chitosan (neutral)</td>
</tr>
<tr>
<td>Non-calcinated chitosan (acidic)</td>
</tr>
<tr>
<td>Non-calcinated chitosan (basic)</td>
</tr>
<tr>
<td>H₂O₂ pre-treated chitosan</td>
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</table>
caffeine for adsorption in the same magnitude as hydrophobic activated carbon. The small surface area of chitosan in comparison to activated carbon could also explain why a greater response was not obtained. The condition where adsorption was expected to be most promising was in acidic pH. However, results indicate that the highest adsorption was 27% of caffeine at a chitosan dosage of 750 mg/L (Figure 8). The poor performance of chitosan suggests that the charged amine groups are not sufficient enough to promote adsorption.

As hoped, the pre-treated chitosan material did perform relatively well in comparison to raw chitosan. Figure 8 shows a comparison among the effectiveness of raw chitosan, activated carbon, and the pre-treated chitosan. A 45% adsorption was seen at the adsorbent dosage of 1 g/L with relatively small error in the results. The effectiveness of the material is thought to be primarily due to the freeing of the chemical functional groups. By pre-treating the chitosan with hydrogen peroxide, the surface is etched and functional groups are easier to protonate in acidic pH. Basic caffeine would have a greater electrostatic attraction to a more positively charged material.

Mesoporous chitosan had better results than raw chitosan, as seen in Figure 9. The results varied in adsorption capacities (20–27%), and did not follow a trend with concentration. The calcinated mesoporous chitosan consists of only a silica pore structure, a result of removing organic material by calcination. The surface characteristics of silica material are due to a variety of functional groups (≡Si-OH, ≡Si-O...H...O, ≡SiOH₂, and ≡Si-O⁻), mostly consisting of silanols (Bui & Choi 2009).

Bui & Choi (2009) found that a similar mesoporous silica, SBA-15, could adsorb some PPCP and EDC compounds. Surface charge of the silica material was found to have the most effect on the adsorption mechanism (Bui & Choi 2009). When the silica material is used at pH below 4, the silica surface has a net positive charge which can enhance adsorption of some pharmaceuticals (Bui & Choi 2009). Consequently, above this pH range, the silica framework would be negatively charged (Copello et al. 2011). The surface charges of the silica material would explain the poor performance of the material in neutral conditions; weakly basic caffeine would experience repulsion from the negatively charged silica surface. However, acidic conditions should have yielded a better caffeine adsorption through favorable interactions between the basic caffeine and protonated silicon functional groups. Poor performance in acidic conditions could be attributed to the large spherical formations of silicon in the material which were caused by high heating which blocked many of the available adsorption sites for caffeine.

Using non-calcinated mesoporous chitosan as an adsorbent resulted in one batch test trial with a large percent adsorption. A dosage of 750 mg/L of adsorbent in neutral pH conditions adsorbed 40% of the caffeine in solution, as seen in Figure 9. Like the other adsorbents, a trend in concentration is not evident from the results. The error in the results of both the mesoporous chitosan (calcinated and not calcinated) is primarily due to synthesis conditions. Mesoporous materials can be affected by humidity and temperature when being synthesized (Tate et al. 2005). Several batches were made of these materials; however, there was a limited ability to control humidity and temperature for synthesis. Despite having the same stoichiometric amounts, the different batches synthesized could have different morphologies. The different morphologies would result in different adsorption capacities and different surface areas.

The non-calcinated mesoporous materials consist of organic chitosan encapsulated inside a silica framework. This material not only has the capability of protonation of silica groups (below pH 4) but also protonation of the amine group side chains on chitosan. However, like the calcinated material, at higher pH, the silica functionality becomes
negatively charged. As seen in Figure 9, neutral conditions did not adsorb a significant amount of caffeine. This can be attributed to the negatively charged silica groups repelling caffeine. In acidic solution, both the chitosan and silica groups are protonated. This would be a very favorable electrostatic interaction with caffeine. Speculation as to why the material did not perform as was expected could be due to the same factors as mentioned for the calcinated material, but could also be due to the structure. Perhaps having chitosan contained in the silica structure lowers the available surface sites for adsorption. Therefore, the media could only adsorb as much caffeine as space would permit. Regardless, these materials show great promise, and an extensive study into their framework would be required to fully understand the reason behind the poor performance.

CONCLUSIONS

Raw, pre-treated, and chemically modified chitosan were not as effective as activated carbon for adsorbing PPCP tracer compound caffeine, which was shown through batch adsorption tests. Mesoporous chitosan (calcinated and non-calcinated) performed better than raw chitosan (25%) for the adsorption of caffeine with batch tests yielding 28, and 40% caffeine adsorption, respectively. However, the materials were still not nearly as effective as activated carbon where batch tests adsorbed 100% of caffeine in solution. Pre-treated chitosan performed best of all chitosan based materials (46% adsorption of caffeine) when batch studies were done in acidic water conditions. The pre-treatment of chitosan proves that simple procedures can be done to increase the adsorption capacity of chitosan, and gives insight into the potential possibility of other pre-treatment conditions that would further improve the performance of chitosan as a PPCP and EDC adsorbent.

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