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Preparation, characterization of chitosan/bamboo charcoal/poly(methacrylate) composite beads

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Abstract. Preparation and characterization of a low-cost, novel steam-activated bamboo charcoal (BC) and poly(methacrylate) (PMAA) bound with chitosan (CTS) to form chitosan/bamboo charcoal/poly(methacrylate) (CTS/BC/PMAA) composite beads is reported for the first time in this paper. The characteristics are revealed by techniques such as X-ray photoelectron spectroscopy (XPS), thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC), scanning electron microscopy (SEM), Brunauer Emmett Teller (BET), solution pH and pH at point of zero charge (pH_{pzc}). The composite beads possessed a dominant acidic surface group of 0.663 mmol g^{-1}, as revealed by Boehm titration method. This acidity was confirmed by its solution pH of 6.46; pH_{pzc} of 6.70 and increase in oxygen surface via XPS analysis. N_2 adsorption–desorption isotherms at 77 K of the beads revealed high BET surface area (SA) of 681.15 m^{2}g^{-1}. Langmuir model affords a SA of 773.34 m^{2}g^{-1}. SEM showed the microporous nature of the composite beads. The properties of CTS/BC/PMAA composite beads were compared to CTS/BC and neat BC. Thermal stability and successful coating of 5.1 wt% of PMAA and 6.8 wt% of CTS to CTS/BC/PMAA beads were shown by DSC and TGA analyses. The composite beads showed low carbon particle released at pH 7.4 and 6.8. Furthermore, dynamic adsorption revealed that CTS/BC/PMAA composite beads can be used to capture a polar substance, such as creatinine.

Keywords. Bamboo charcoal/chitosan/polymethacrylate; composite beads; characterization; pH point of zero charge; creatinine; column adsorbent.

1. Introduction

Bamboo plant has recently been considered as an important biomass resource material for the production of bamboo charcoal (BC) due to its low cost [1], eco-friendly attributes [2] and renewability [3]. BC has been used in various applications as adsorbent for the removal of organic [4] and inorganic [5] toxic contaminants from aqueous solutions [6], nanotechnology [3] and in biomedicine [7].

Chitosan (CTS) is a biodegradable, biocompatible and non-toxic polymer, which can be used as a coating material for BC to produce bamboo charcoal beads (BCBs) [8,9]. This composite has been published by our group as adsorbent for albumin and phenylalanine but there is no published work on the characterization of this composite [6,8].

Acrylates like poly(methacrylate) (PMAA) have also been used as coating to pharmaceuticals and activated charcoal (AC) to produce smooth coating with great mechanical strength but readily accessible to polar, dissolved substances [10]. Furthermore, poly(methylmethacrylate), a biocompatible polymer [11], has been used to coat ACs together with CTS as adsorbent for extracorporeal filter cartridges for the removal of doxorubicin, a chemotherapeutic drug [12].

The advent of technology which can probe the surface and other properties have led to the characterization of these materials [9]. Vital to the development of adsorbent materials for various applications is the understanding of their properties as this information feeds into the fabrication and design as well as performance evaluation (e.g., adsorption capacity of the material) [9]. Typical techniques used to characterize

composite material are based on the analysis of their surface area (SA), heat and mass difference of the material as it changed with temperature over time, morphology, etc. The properties and composition of BC can also be investigated using Boehm (acid/base) titration [13], elemental analysis, pH at point of zero charge (pH_{pzc}) [14], immersion calorimetry [15], spectroscopy and others.

In this study, as-prepared BC derived from moso bamboo (*phyllostachys pubescens*) was combined with PMAA and bound with CTS to produce the composite beads. BC particles displayed an alkaline property (pH 12), hence its composite with PMAA and acidic solution of CTS can neutralize its alkalinity. Furthermore, BC particles can pose clinical risk of emboli in the blood vessels if used directly for haemoperfusion [8]. Hence, its composite with CTS can address this problem if used as adsorbent material for blood dialysis. Moreover, BC particles and BC/CTS composite preferentially adsorb L-phenylalanine (35.5 mg g^{-1}) over bovine serum albumin (3.4 mg g^{-1}) suggesting that the surface of BC and its composite with CTS is non-polar [6,8]. Its composite with PMAA rendered it more accessible to polar substance. In this study, a model polar molecule (creatinine) was used to adsorb to the composite beads. This composite material therefore is a three in one adsorbent material to address three problems. First, the alkalinity of BC; second, the non-polar character of BC surface and third is the risk of emboli if used directly as adsorbent for blood dialysis. Hence, this study delves on the preparation and characterization of novel chitosan/bamboo charcoal-containing poly(methacrylate) composite beads (CTS/BC/PMAA). Its adsorption performance to creatinine was investigated using continuous dynamic adsorption for 4 h. Its physico-chemical characteristics were investigated using techniques such as X-ray photoelectron spectroscopy (XPS), thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC), scanning electron microscopy (SEM), SA and pore size distribution using Brunauer Emmett Teller (BET), solution pH and pH at pH_{pzc}. Furthermore, particle release experiment and equilibrium adsorption were also conducted.

2. Experimental

2.1 *Materials and characterization*

(please refer to supplementary information)

2.2 *Preparation of beads as adsorbent*

Briefly, three different beads were prepared; namely, CTS beads, CTS/BC, CTS/BC/PMAA beads.

2.2a *Chitosan beads*: Chitosan solution was prepared by mixing neat CTS powder in acetic acid (2% w/w). The mixture was stirred at 4°C for 8 h to produce a clear, viscous, homogeneous mixture of CTS, which was used in preparation of composite beads such as CTS/BC and CTS/BC/PMAA. The viscous solution was extruded via a syringe pump at a rate of 10 ml h^{-1}, using an 18-gauge needle into a coagulation solution bath (NaOH:methanol, 3:1 v/v) at room temperature (RT). The resulting beads were washed with hot followed by cold deionized water until neutral pH of 6.9–7.1 of the washed solution. The beads were dried overnight at 65°C in a thermostated oven. The dried bead was denoted as CTS bead.

2.2b *CTS/BC beads and CTS/BC/PMAA beads*: For CTS/BC beads: 1.5 g CTS (2% w/w) solution was mixed with 50 mg BC.

For the preparation of CTS/BC/PMAA beads: 1.5 g CTS solution was added to the premixed 50 mg BC and 15 mg PMAA as shown in figure 1. The two types of mixtures were further stirred separately for 8 h at 4°C. The resulting dispersions were also extruded through a syringe pump using the same procedure for CTS beads as described above.

3. Results and discussion

3.1 *Preparation*

3.1a *Synthesis of PMAA and preparation of CTS/BC/PMAA beads*: Poly(methacrylate)-co-ethylene glycol dimethacrylate was prepared using methacrylic acid (MAA) as the monomer and ethylene glycol dimethacrylate as the crosslinker. MAA has been shown to be a good monomer for creatinine adsorption. MAA is a versatile monomer of choice intended for various applications ranging from chromatographic packing to antibody mimics and molecular imprinting for creatinine [16–18]. This polymer was synthesized by bulk polymerization format via free radical using azo-bis-isobutyronitrile as the initiating species.

Vital to the preparation of the beads is the dynamic viscosity of the mixture including its stirring time. The viscosity of the freshly prepared 2% CTS solution was between 451 and 510 cP. This viscosity was maintained by stirring the mixture at 4–6°C upto 8 h. The total stirring should not exceed 24 h because viscosity of acidic solution of CTS is affected by factors such as temperature and storage time [19]. Acidic solution of CTS is known to decrease in viscosity upon storage at RT due to hydrolysis and polymer degradation in acetic acid medium [19,20]. As a result, freshly prepared CTS solution was used to prepare the beads. The viscosity of the mixtures (CTS/BC and CTS/BC/PMAA) were between 603–606 and 698–725 cP, respectively. The average diameter of CTS/BC and CTS/BC/PMAA beads are 1.55 and 1.49 mm ($n = 50$), respectively, using UPM digital caliper.

3.2 *Characterization*

3.2a *Surface morphology*: The SEM micrographs of the beads are shown in figures 2 and 3. Figure 2a shows the spherical bead and 2b is a higher magnification of the bead.
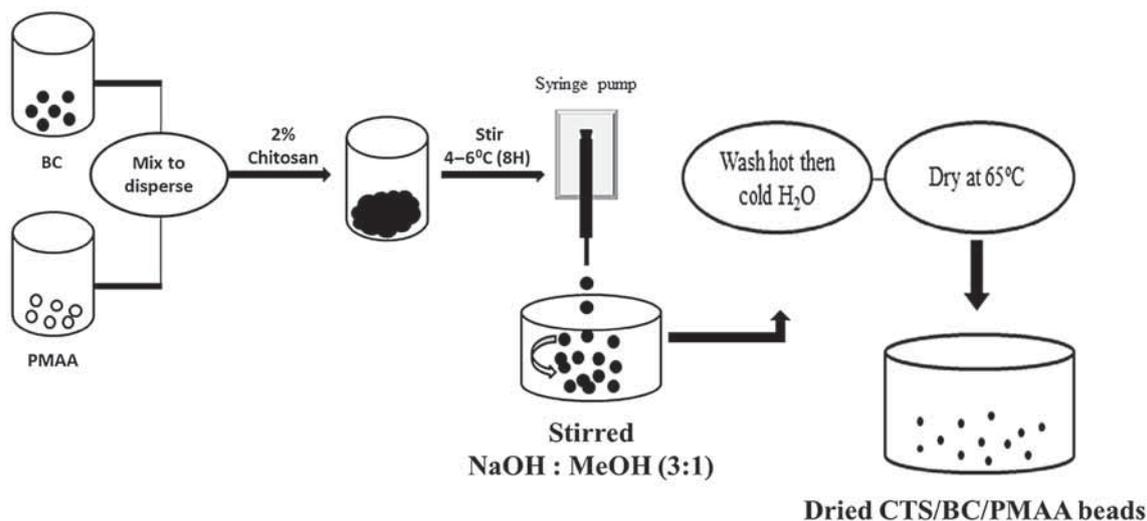
Figure 1. Schematic representation for the fabrication of the composite beads. PMAA and BC were mixed with chitosan and stirred at 4–6°C for 8 h followed by extrusion through a syringe pump. The resulting beads were washed with hot water followed by cold water and dried in an oven.
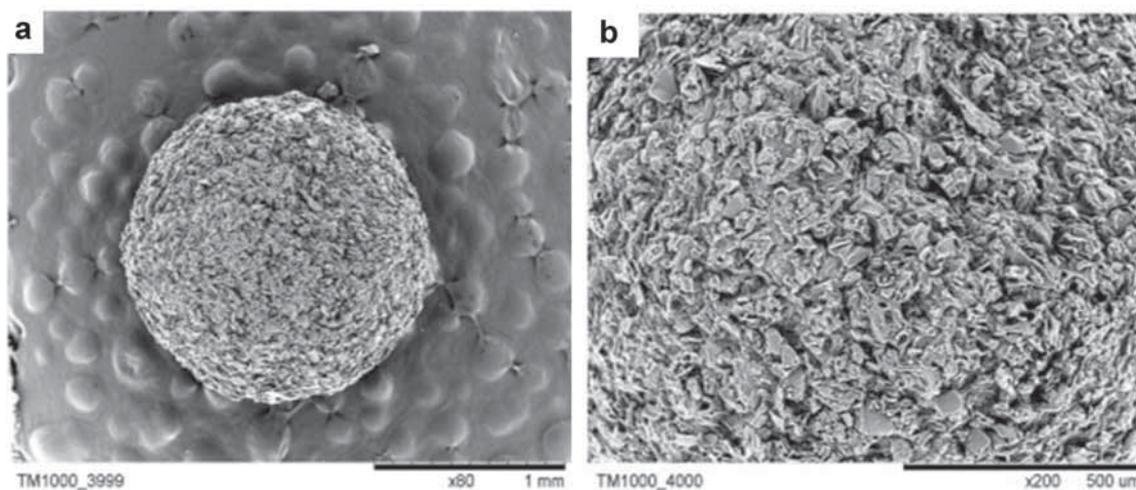

Figure 2. SEM images of the CTS/BC/PMAA spherical bead (**a**) at X80 and (**b**) X200 magnifications.

Surface morphology of BC (figure 3a) appeared heterogeneous with particles of different sizes and irregular shapes [21]. Macropores in BC are visible. PMAA (figure 3b) are more granulated and are regularly shaped. The CTS/BC and CTS/BC/PMAA beads do not have much difference with each other but textural change can be supported by the BET results in which mesoporous PMAA and CTS beads become microporous when combined with BC.

Surface and cross-section (figure 3c–f) appeared homogeneous and uniform distribution of CTS and PMAA in the beads is observed in which individual components are not anymore distinguishable except for the macropores found in BC. The presence of macropores in the image justifies the effect of high temperature and increased time for activation that would result in pore widening. Steam-activated BC used in this study

was prepared at high temperature (850°C) and activated for 90 min similar to the report somewhere [22]. Treatment in these conditions resulted in widened pores because steam water reacts either on the pore walls or on the carbon surface during the first stages of activation. In addition, some authors reported that high temperature activation results in higher microporosity development and higher SA (S_{BET}) until maximum is reached and it results in massive destruction of micropores and become mesopores [23–25]. These observations are supported by the BET results discussed in the next section.

3.2b *Surface area, porosity and textural characteristics*: N_2 adsorption–desorption isotherms at 77 K of CTS/BC and CTS/BC/PMAA beads exhibited a specific SA, BET of
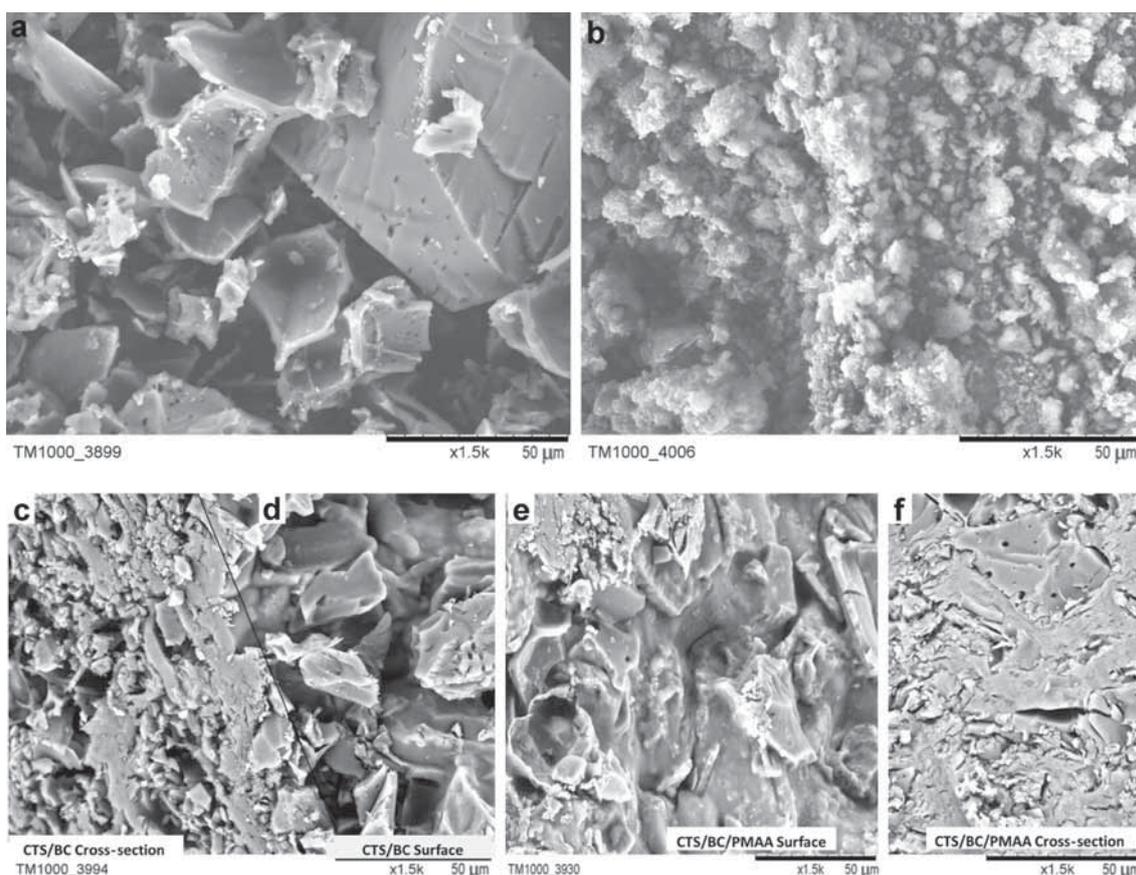
Figure 3. SEM images at higher magnifications: (**a**, **b**) BC and PMAA; (**c**, **d**) CTS/BC, (**e**, **f**) CTS/BC/PMAA surface and cross-section (X1.5 K). Image of cross-section was prepared by cutting liquid N_2-frozen bead [10].

658.83, 681.15 $m^2 g^{-1}$, respectively. Langmuir model affords a SA of 873.70, 773.34 $m^2 g^{-1}$ for the two composite beads, respectively. A decreased in SA when neat BC is combined with CTS and PMAA is observed. This reduction in SA is also reported somewhere [26]. Furthermore, pore size distribution of the two composite beads (CTS/BC and CTS/BC/PMAA) shown in figure 4a and c show higher occurrence of micropores with an average pore width of less than 2 nm. The two beads show monolayer adsorption–desorption isotherms of N_2 gas indicating Type I Langmuir isotherm as shown in figure 4b and d. This is a characteristic of materials with limiting uptake and narrow pore size distribution that are essentially microporous in nature [27]. There is a strong interaction between adsorbent and adsorbate where high adsorption at relatively low pressure can be observed. The plots also show finely divided surface with limited adsorption occurring as P/P_0 approach 1. In addition, the close loop hysteresis further indicates a high amount of micropores, which confirms the Langmuir adsorption–desorption isotherm using N_2 as adsorbed molecules.

3.2c *Acid/base character of adsorbents*:   The total surface acids associated with carboxylic, phenolic and lactonic reacted with NaOH [28]. Conversely, total surface basicity,

which are usually associated with pyrones, quinone, chomenes, ethers, carbonyl groups, pi-electron rich systems in the graphene sheets of the exposed graphene layers and other Lewis basic groups reacted with hydrochloric acid, determined by Boehm titration, which is shown in table 1 [29,30].

BC exhibited a total surface basicity of 0.924 mmol g^{-1} and total surface acidity of 0.804 mmol g^{-1}. The aqueous solution of BC confirmed the basic property as it possessed a pH of 10.25. This indicates presence of Lewis basic groups such as C–O, C = O, as well as the C = C pi-electron rich system as confirmed by XPS, discussed in the next section. Furthermore, the pH_{pzc} of BC is 8.37, this is the pH at which the surface charge of BC is zero. For CTS/BC and CTS/BC/PMAA, the pH_{pzc} was established at 6.81 and 6.70, respectively. The decrease of pH_{pzc} from 8.37 of neat BC to 6.81 and 6.70 for CTS/BC and CTS/BC/PMAA beads, respectively, implies the acidic property of the composite beads. Furthermore, neutralization of the basic functional groups found on BC with the protonated amino groups found in CTS and carboxyl groups (COOH) in PMAA took place when composite beads were prepared. This becomes an advantage because the pHs of the composite beads are very close to the physiologic pH (7.4), which indicates the potential of this material for use in biomedical applications.
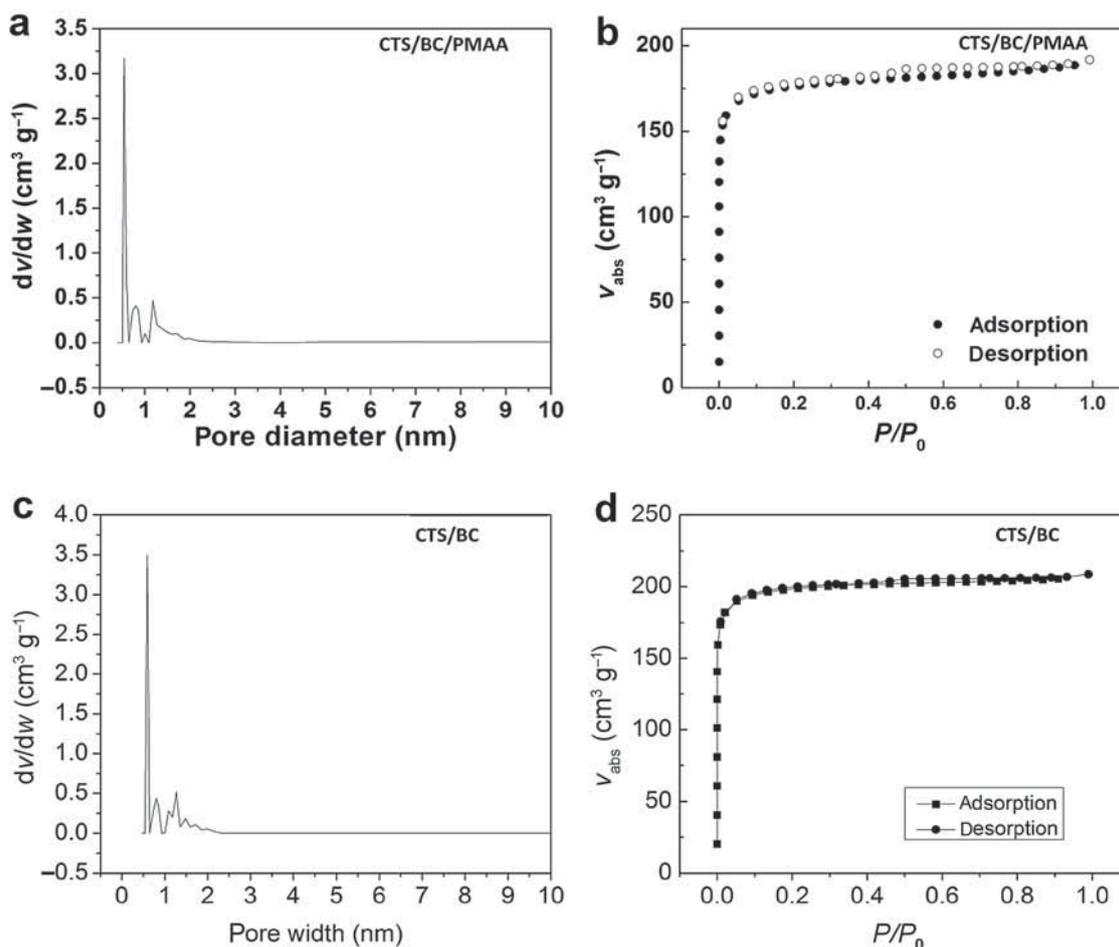
Figure 4. BET analysis of adsorbents (**a**) CTS/BC/PMAA pore size distribution, (**b**) CTS/BC/PMAA Langmuir N_2 adsorption–desorption, (**c**) CTS/BC bead pore size distribution, (**d**) CTS/BC bead Langmuir N_2 adsorption–desorption (IUPAC definition of micropores <2 nm, mesopores 2–50 nm and macropores >50 nm) [31].

Table 1. pH point of zero charge (pH_{pzc}) and total surface acidity and basicity of adsorbents containing steam-activated BC.

Sample ID	pH solution	Total surface basic groups (mmol g^{-1})	Total surface acidic groups (mmol g^{-1})	pH_{pzc}
BC	10.25 ± 0.007	0.924 ± 0.036	0.804 ± 0.161	8.37 ± 0.007
CTS/BC	6.46 ± 0.007	0.560 ± 0.152	0.594 ± 0.118	6.81 ± 0.003
CTS/BC/PMAA	6.46 ± 0.014	0.565 ± 0.288	0.663 ± 0.105	6.70 ± 0.007

Total surface acidity/basicity: determined by Boehm titration.

BC, steam-activated bamboo charcoal; CTS/BC, chitosan/bamboo charcoal beads; CTS/BC/PMAA, chitosan/bamboo charcoal/polymethacrylate beads.

Calculations: Total surface basicity = mmol reacted with HCl/gram adsorbent.

Total surface acidity = mmol reacted with NaOH/gram adsorbent.

3.2d *Functional groups*: XPS peaks of steam-activated BC, CTS/BC and CTS/BC/PMAA shown in figure 5 confirm the presence of COO, C–O and C = C groups detected by Boehm titration. The surface binding state of C1s of the three adsorbents shows the presence of graphitic carbons, COOH or ester groups between 285 and 289 eV.

Results of deconvoluted C1s peaks of BC, CTS/BC and CTS/BC/PMAA showed three different spectral features that fit the C1s envelope, as shown in figure 5c. One was the unmodified carbon C–C and/or the C = C at around 283.6–284.5 eV. Second, the two oxygen-containing carbons, C–O and COO at around 285.5–285.8 eV and 288.0–289.0 eV,
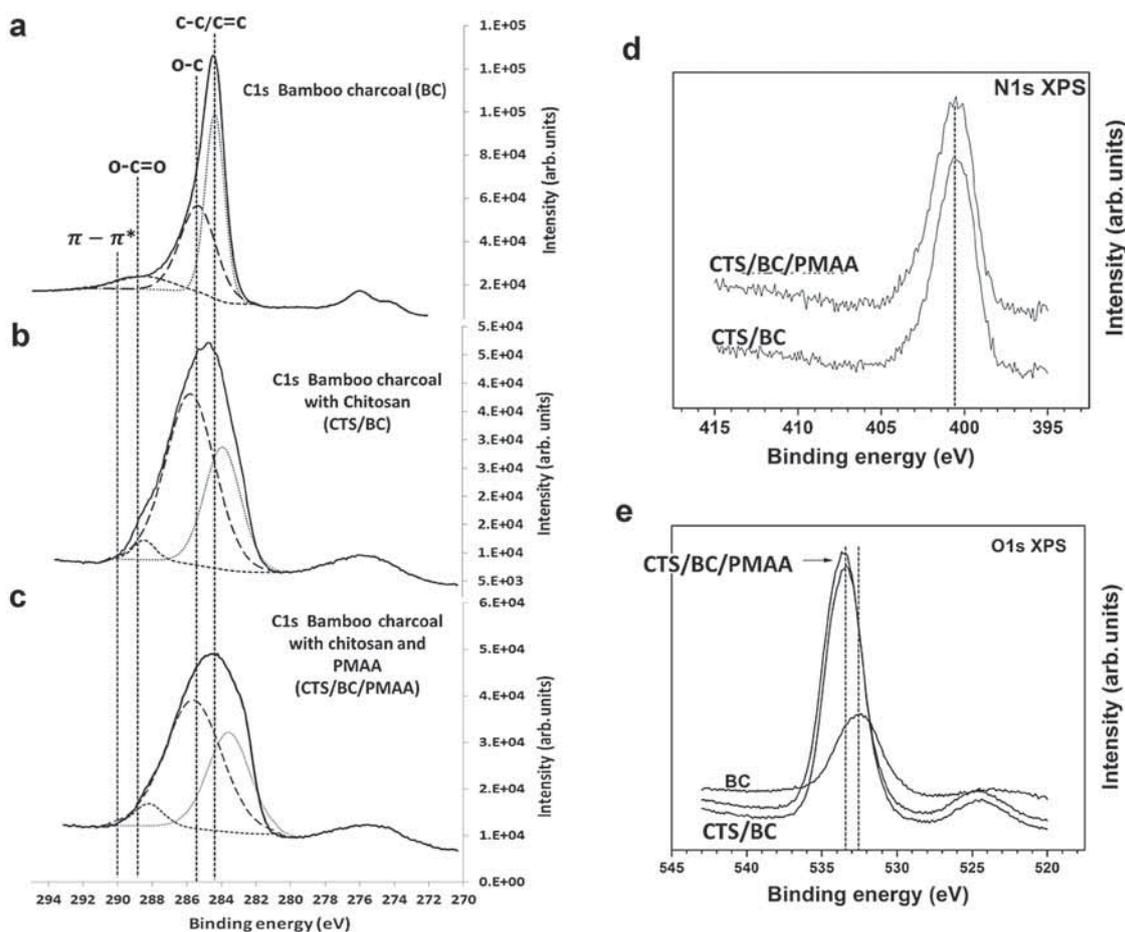
Figure 5. XPS peak fitting of deconvoluted C1s of (**a**) BC, (**b**) CTS/BC, (**c**) CTS/BC/PMAA and overlay XPS peaks of (**d**) N1s of CTS/BC and CTS/BC/PMAA and (**e**) O1s of BC, CTS/BC and CTS/BC/PMAA. No N1s peak was detected based on survey scan conducted on BC.

respectively [32]. The binding energy at 289.0 eV is assigned to $O - C = O$ was found broad in BC. This peak has shifted to lower binding energy and became more pronounced (or sharper) in CTS/BC (288.5 eV) and CTS/BC/PMAA (288.0 eV) composite beads. These shifts to lower binding energy are indicative of the interactions between COO of BC and/or PMAA and NH of CTS. The peak at 285.5 eV is assigned to C–O in BC, this peak has shifted slightly higher binding energy in CTS/BC (285.6 eV) and CTS/BC/PMAA (285.8 eV). These shifts to higher binding energy indicate increased C–O in CTS/BC and CTS/BC/PMAA composite beads.

XPS for N1s and O1s showed typical features for microporous materials as shown in figure 5d and e, respectively. O1s peaks revealed at 532.5–533.5 eV. The peak at 532.5 eV found in BC has been slightly shifted to higher binding energy (533.5 eV) for CTS/BC and CTS/BC/PMAA. This indicates increase in O content in the composite beads. Increase in oxygen content such as presence of C–O and $O–C = O$ has been suggested to be COOH responsible for the acidic nature of carbon as reported by some researchers [33,34]. The N1s peak

at around 398–403 eV found in the samples was found to be an sp^2 or sp^3 nitrogen.

3.2e *Homogeneity and thermal stability*: Figure 6a displayed a sharp endothermic melting temperature, T_m peak at 74.6°C of neat PMAA indicating a relatively uniform molecular weight, MW within the sample [35].

Conversely, CTS beads showed no endothermic peak for loss of water near 79°C indicating that the sample was anhydrous [36]. While an exothermic peak appeared at 303°C, which corresponds to the degradation temperature of CTS (T_{CTS}). This has been previously reported somewhere [36–38].

In CTS/BC composite, an endothermic peak was apparent at 70.1°C, indicating the loss of water in the sample. In CTS/BC/PMAA composite bead, the T_{CTS} of CTS was observed at a reduced peak area (2350 mJ of CTS to 1981.14 mJ of CTS/BC/PMAA). The decrease in T_m (66.77°C) for CTS/BC/PMAA beads as compared to T_m (71.6°C) of
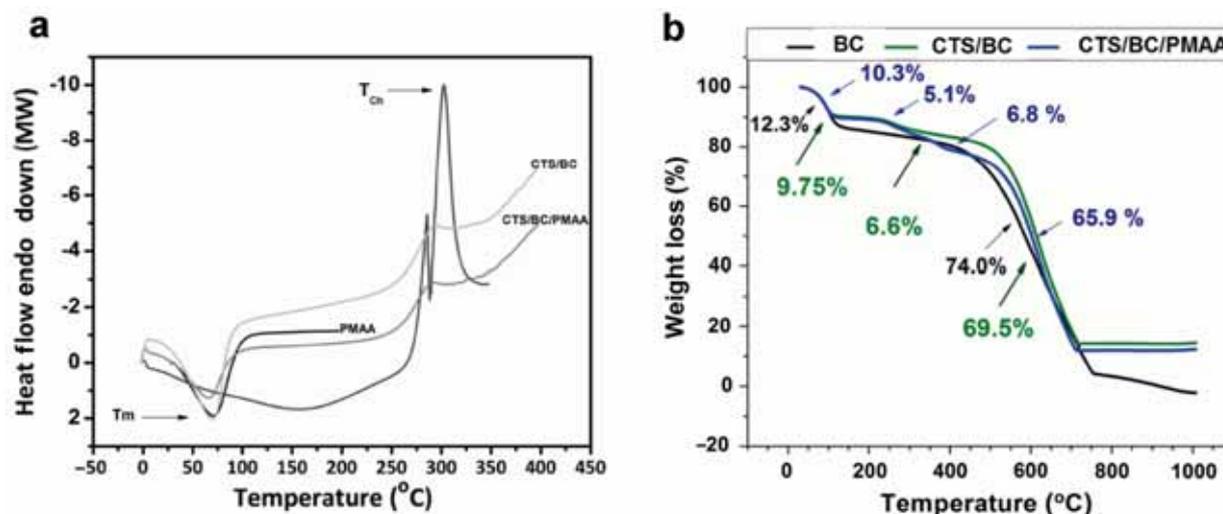
Figure 6. (**a**) DSC thermogram of neat PMAA, CTS beads, CTS/BC and CTS/BC/PMAA composites, as obtained by heating from −50 to 450°C at a rate of 2°C min⁻¹. (**b**) TGA of BC (black curve), CTS/BC (green curve) and CTS/BC/PMAA (blue curve).

neat PMAA could be due to CTS and PMAA polymer–polymer interaction and morphological effects as previously reported somewhere [39,40]. Furthermore, this polymer–polymer interaction directly influences the miscibility of the two polymers, which was successfully described by the binary interaction model where the presence of hydrogen bonding, electrostatic and dipole–dipole as the most common intermolecular interactions occurring between two different polymer chains [39,40]. In this case, electrostatic interaction between the protonated amino (NH_3^+) groups in CTS and negatively charged COO^- of PMAA. H-bonding as well as hydrophobic interactions between non-polar moiety of CTS and PMAA could also be possible in the composite beads. These interactions are demonstrated by the depression of T_m from 71.6 of PMAA to 66.77 of CTS/BC/PMAA [41].

Figure 6b shows the thermal degradation and stability of BC-containing adsorbents using TGA under air atmosphere. All three adsorbents revealed weight loss of adsorbed and bound water at around 29°C of 12.3, 9.75 and 10.3% for BC, CTS/BC and CTS/BC/PMAA, respectively. BC exhibited the highest loss (12.3%) of adsorbed and/or bound water. This may be due to its powdery structure and microporous nature, which was highly adsorbent compared to the bead format. CTS/BC/PMAA displayed a higher water loss of 10.3% compared to CTS/BC of 9.75%. The addition of PMAA to form CTS/BC/PMAA, resulted in its ability to adsorb more water as it exhibited higher water loss. This is due to the addition of COOH, which can H-bond with water. CTS in CTS/BC and CTS/BC/PMAA beads exhibited two main decomposition stages [39].

In CTS/BC beads, CTS started to decompose at temperature between 100 and 382°C and completely burnt at 724°C while that in CTS/BC/PMAA, it started to decompose at 306−465°C and completely burnt at 746°C. The decomposition temperature of CTS/BC/PMAA is higher than CTS/BC.

Table 2. Carbon particle release data.

			Absorbance unit	
pH	CTS/BC	CTS/BC/PMAA	Morley and Chang*	Chandy**
7.4	0.0197	0.0052	0.006	0.0055
6.8	0.001	0.001	—	—

*Using collodion-coated petroleum pitch [42]; **using chitosan-coated AC [43].

This means that CTS/BC/PMAA composite beads possessed higher degree of thermal stability compared to CTS/BC. Furthermore, results indicated that 5.1 wt% of PMAA has been coated to CTS/BC/PMAA and 6.6 and 6.8 wt% of CTS has been coated to CTS/BC and CTS/BC/PMAA, respectively. This means that a successful coating of CTS and PMAA has been done to BC.

3.2f *Carbon particle release*: The carbon particle release at pH 7.4 and 6.8 for CTS/BC/PMAA composite beads afford an absorbance reading of 0.00525 and 0.001 absorbance units, respectively. The values are lower than the particle release reported by Morley and Chang (0.006 absorbance units) and Chandy (0.0055 absorbance units), both at pH 7.4 as shown in table 2 [42,43]. This indicated that the presence of PMAA in CTS/BC/PMAA rendered the material to be mechanically sturdy with lesser carbon particle release.

Since CTS/BC/PMAA beads showed low carbon particle release, the composite beads were used as column packing for a flow-through experiment for 4 h of simulating dialysis time. Results (figure 7) show that the amount of creatinine adsorbed (mg g⁻¹ and %), decreased as time lapsed upto 4 h.

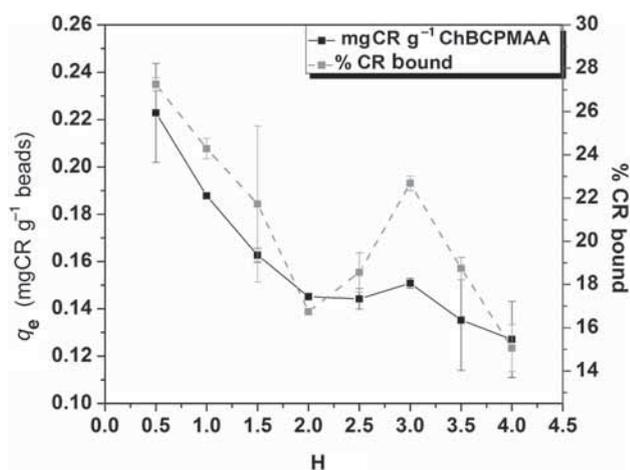After 30 min the amount of creatinine adsorbed was 0.22 mg g⁻¹ equivalent to 27.3% of the total creatinine, after 4 h

Figure 7. Dynamic adsorption of creatinine (CR) to CTS/BC/PMAA for 4 h continuous flow through of $100 \, \text{mg l}^{-1}$ creatinine (at pH 7 in phosphate buffer) using a peristaltic pump at a flow rate of $5 \, \text{ml min}^{-1}$.

of dialysis, amount of creatinine adsorbed decreased to 0.13 mg creatinine per gram beads equivalent to 15.1% of the total creatinine. A decrease of about 12% from 0.5 to 4 h of dialysis using only 40 mg beads. This indicates that the saturation point of the adsorbent has not yet been achieved after 4 h of dialysis. This shows that the composite beads can be used as column adsorbent for haemoperfusion application to remove toxic creatinine from the aqueous medium.

4. Conclusion

The preparation and characterization of the adsorbent composed of BC, CTS and PMAA to form CTS/BC/PMAA beads was ellucidated in this research. BET and Langmuir analyses revealed high SA of 681.15 and $773.34 \, \text{m}^2 \, \text{g}^{-1}$, respectively. The beads showed high occurrence of micropores with pore diameter of less than 2 nm. The Boehm titration showed acidic surface of $0.663 \pm 0.105 \, \text{mmol g}^{-1}$ of CTS/BC/PMAA beads and pH_{pzc} of 6.70. The aqueous solution showed acidic character having a pH of 6.46. The solution pH and pH_{pzc} are close to the physiological pH 7.4, which becomes an advantage to further explore the material for biomedical applications. The uniform distribution of CTS and PMAA in the composite beads was revealed by SEM. Successful coating of PMAA and CTS to neat BC was revealed by TGA, 5.1 wt% of PMAA has been coated to CTS/BC/PMAA and 6.8 wt% of CTS has been coated to CTS/BC/PMAA. The coating of the BC with PMAA and CTS rendered the composite beads with mechanical strength as indicated by low carbon particles released in the solution.

Dynamic adsorption showed a decrease of only 12% from 0.5 to 4 h of dialysis. This showed that the saturation point

of the beads have not yet been achieved after 4 h of dialysis. Hence, the potential of CTS/BC/PMAA composite beads is essential for the capture of an aqueous substance such as creatinine.

The use of biomass-derived activated charcoal obtained from plant source such as bamboo offers a number of advantages because it is renewable, ease of access and low price, hence this composite material composed of BC and PMAA bound with CTS is a potential column adsorbent for various applications.

Acknowledgements

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