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Evaluation of the adsorption capacities of activated carbon, titanium dioxide and alumina in reducing proteins and glycoproteins in model wine solutions

Niyi Rufai Samuel

Ahmadu Bello University, School of Basic and Remedial Studies, P. M. B. 6007, Funtua - Nigeria.

Abstract

The study investigated the adsorption capacities of bovine serum albumin (BSA), ovalbumin (OVA) and mucin (MUC) onto titanium dioxide, alumina and activated carbon, for the purpose of investigating the optimum conditions of pH and cations concentration of white wine required for the haze removal process. The results showed that the amounts of adsorbed OVA and BSA onto the three adsorbents were 1.32 ± 0.73 and 1.20 ± 0.46 times higher than the amount of MUC adsorbed onto the three adsorbents respectively. The amount of the proteins adsorbed from white wine model solution onto the various adsorbents increased by 6.25 ± 0.04 times as protein concentration is increased from 1.0 to 5.0 mg/mL. The percentage of adsorbed proteins increased between 12 to 16% following suspension of 50 mg adsorbent treated with calcium or magnesium ions in the proteins solutions. Amount of the proteins adsorbed to untreated TiO_2 at pH 3.0 and 7.0 were not different, however, at pH 7.0 pre-treatment of TiO_2 with calcium ion increased the adsorption significantly ($p < 0.05$). The optimization of the amounts of inherent proteins of wine solution adsorbed is an indicator of the efficient design of the sorption treatment plant for the haze removal process.

Keywords: White wine, haze, protein, adsorbent, adsorption capacity, optimization, indicator.

INTRODUCTION

Wine is one of the most popular drinks with low alcohol content. A wine's taste, aroma, sparkle and even its haze are qualities that are the doings of the proteins inherent to the grapes, rice or other products used to make it, and also to proteins that belong to yeast strains added for fermentation and hence the production of alcohol (Brown et al., 2006).

Protein fractions with low molecular weights (12 to 30 kDa), protein fractions with low isoelectric point, pI (4.1 to 5.8) and glycoproteins contribute to protein instability in white wines (Hsu et al., 1987).

Study to reduce proteins in white wine models was carried out using three proteins – bovine serum albumin (BSA), ovalbumin (OVA) and lysozyme (LSZ) – adsorbed onto zirconium oxide surface, although the protein adsorption capacity is lower than sodium bentonite. Zirconium oxide showed adsorption selectivity and a preference for removing the unstable proteins, thus stabilising white wine (Pachova et al., 2001). Achaerandio et al. (2001) studied the effect of the ethanol concentration and protein molecular weight on the capacity of bentonite to adsorb the proteins (BSA, OVA and LSZ) in a model solution. The adsorption capacity of bentonite to BSA and LSZ tend to increase with increase in ethanol concentration, but no effect on OVA.

The adsorption of blood proteins and body fluids onto metals and ceramics for body implantation purposes dictates their biocompatibility (Hench, 1991). The adsorption increases with decreasing pH, although the effect is less marked at lower protein concentrations (Ellingsen, 1991). Pretreatment of Ti powder of surgical grade with calcium or magnesium alone, or combined resulted in increased adsorption of mucin to Ti (Lori and Nok, 2003).

This study aims to evaluate the adsorption capacities of activated carbon, titanium dioxide and alumina in reducing proteins and glycoproteins in model wine solutions. The adsorptive properties were investigated as a function of residence time, adsorbate concentration, pH and ionic composition of the wine model. An investigation of the effects of pH and cations concentrations of wine solution on the haze removal process is highly essential for the attainment of optimum economic derivation from the industrial brewing of wine.

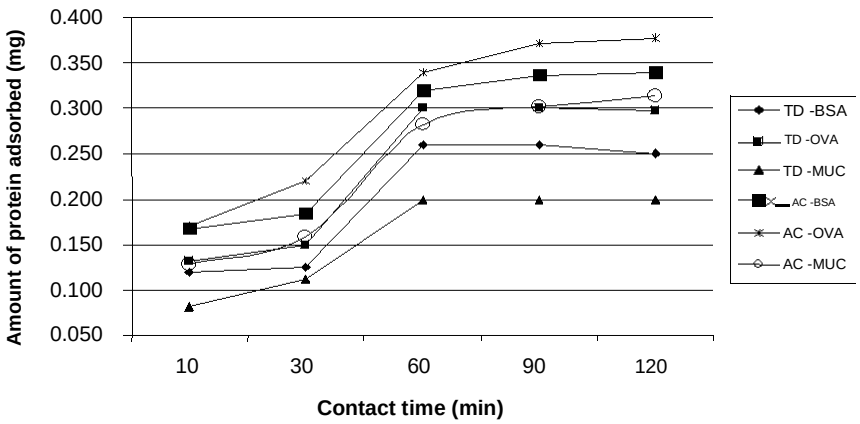

Figure 1. Time profile for the adsorption of adsorbate (1.0 mg/mL) onto 15 mg massTiO2 and activated carbon

MATERIALS AND METHODS

Materials

Preparation of activated carbon

Coconut shells were obtained from Zaria market in Kaduna State – Nigeria. They were sun-dried and then oven-dried at 100 – 105°C for 6 h. The shells were then pulverised by a wiley pulveriser to 150 µm mesh size. The samples were carbonised in a furnace at 500°C for a residence time of 5 min. Two grams of the carbonised particles were activated with 2 mL of 0.10 M H_3PO_4 solution at 800°C for a period of 5 min. The activated samples were then washed with 0.5 M acetic acid and thoroughly rinsed with deionised water and dried (Gimba and Bahago, 2004).

The other adsorbents used for the study are: Commercially pure titanium (Ti) powder of particle size 200 µm (BDH Chemical Ltd., Poole, England), with a purity of 99.7% ± 0.01 by analysis with atomic absorption spectrophotometry (Buck Scientific 200A). Ti powder surface consist mainly of titanium dioxide (TiO_2) as shown by X-ray photo-electron spectroscopy (XPS) data (Sutherland et al., 1993).

Alumina (BDH Chemical Ltd., Poole, England) having particle size ranging from 10 - 15 µm in particle size.

The three proteins used for the study are: Bovine serum albumin, BSA (Sigma – Aldrich Co. USA) an acidic protein, with molecular weight 67.0 kDa and isoelectric point, pI 4.7; ovalbumin, OVA (Sigma – Aldrich Co. USA) an acidic protein with molecular weight 43.0 kDa with pI 4.5 and mucin, MUC (Nacatai, Tesque Inc., Kyoto, Japan) an acidic glycoprotein with molecular weight 400.0 kDa.

Protein adsorption study

Aliquots (1.0 mL) of 1.0 mg/mL protein solution (BSA, OVA and MUC) were used as the white wine model system. Each of these was added to samples of TiO_2 (15 or 50 mg) in a polypropylene (PP) centrifuge tube. The mixture of each experimental group was continuously shaken in a shaker at 298 K, for residence times of 10, 30, 60, 90 and 120 min. The samples were microcentrifuged in an auto-bench centrifuge (Baird and Tatlock Ltd., England) at 1500 g for 2 min and 0.5 mL of the supernatant assayed for protein using Bradford method (Bradford, 1976).

The amount of adsorbed protein was calculated by subtracting the amount of unadsorbed (free) protein remaining in the supernatant from the amount of protein in the control (protein solution not suspended in TiO_2 powder sample) . The procedures were repeated for samples of activated carbon, AC and alumina, ALM as adsorbents (in triplicate).

The effect of adsorbate concentration was investigated by using protein solutions of concentration 5.0 mg/mL and adsorbents mass of 50 mg.

Effect of cations and pH on the adsorption of the proteins of white wine model solution

The adsorbents (TiO_2, Al_2O_3 and AC) were pretreated by suspending 100 mg sample for 24 h at 298 K in 5.0 mL of 0.1 M $CaCl_2$, 0.1 M $MgCl_2$ or 0.1 M KCl. The samples suspended in doubly distilled water served as control. The powders were then washed thrice with doubly distilled water and air-dried for 24 h. Fifty milligram of the untreated, calcium- treated; magnesium- treated or potassium-treated samples were suspended in 1.0 mL of a solution containing 1.0 mg/mL BSA, OVA or MUC, adjusted to pH 3.0 or 7.0 with citric acid – disodium phosphate buffer. The suspensions were shaken for 90 min, and the adsorbed proteins determined as described above.

RESULTS AND DISCUSSION

The results were compared using Student-Newman-Keul's test by one-way analysis of variance (ANOVA) with statistical significance taken at $P < 0.05$. Results presented in the Figures 1 to 6 are expressed as mean of triplicate values ± standard deviation.

As displayed in Figures 1 to 4 more binding sites were provided by increasing the adsorbent mass and a resulting increase in the amount of adsorbed proteins with increase in contact time. A statistically significant increase in the amount of the three proteins adsorbed was recorded as the contact time increased from 30 to 60 min. Another finding from the study is that the saturation

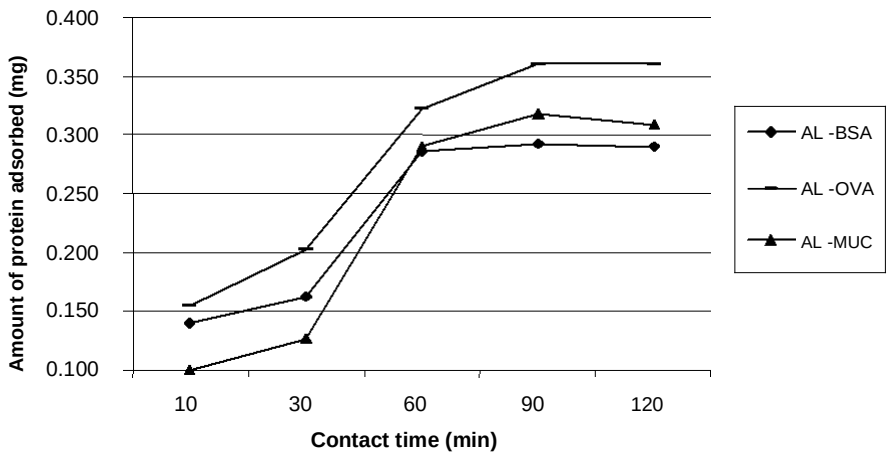

Figure 2. Time profile for the adsorption of adsorbate (1.0 mg/mL) onto 15 mg massalumina.

of the adsorption process took place at 60 min for TiO_2, 90 min for Al_2O_3 and 120 min for activated carbon. The amounts of adsorbed mucin (mg) onto TiO_2 increased steadily from 0.082 to 0.200 in the 15 mg group; and from 0.260 to 0.344 in the 50 mg group as the incubation time extended, using 1.0 mg/mL BSA solution. The results showed that the amounts of adsorbed OVA and BSA onto the three adsorbents were 1.32 ± 0.73 and 1.20 ± 0.46 times higher than the amount of MUC adsorbed onto the three adsorbents respectively. This can be traced to the low molecular weights of OVA and BSA, and their low structural stability. Conformational changes in the 'soft proteins' can lead to some unfolding, which results in an increased number of protein sites contacting the surface. Some protein molecules may become detached in favour of the spreading of other adsorbed molecules (Sotherquist and Walton, 1980). The glycoprotein, MUC has the least diffusion rate due to its high molecular weight and the least adsorbed amount onto the three adsorbents.

For the removal of the proteins from the model white wine solution investigated, the results showed that the total amount of adsorbed proteins onto activated carbon (AC) and Al_2O_3 were 1.39 ± 0.48 and 1.22 ± 0.56 times higher than the amount onto TiO_2 respectively. Maximum adsorption/ 1 mg adsorbent were attained at 60 min contact time for the three adsorbents. With values 0.0252 ± 0.003/ mg TiO_2, 0.0356 ± 0.002/ mg Al_2O_3 and 0.0400 ± 0.001/ mg AC by the use of OVA as adsorbate.

Bovine serum albumin (BSA) molecules was reported to strongly adsorb onto Calcium hydroxyapatite, CaHap mainly through a specific electrostatic attractive force between negative charges on BSA and localised positive ones on CaHap surfaces (Kazuhiko and Tatsuo, 2000). Binding of mucin molecules onto titanium surfaces is speculated as being that the surface-exposed carboxyl group may be attracted to the oxide covered surface of titanium by electrostatic interaction. Hydrophilicity of the titanium – linked O^- surface makes it to attract water and could be another suggested factor for its lower adsorptive capacity than do AC and Al_2O_3. A number of factors are important in determining the amount of protein on surfaces, including the magnitude and sign of charge of both the protein and the surface and the degree of hydration of the protein (Diana and Graham, 1996).

Increasing the adsorbate concentration to 5.0 mg/mL increased the amount of the proteins adsorbed significantly. The amount of the proteins adsorbed from white wine model solution onto the various adsorbents increased by 6.25 ± 0.04 times as protein concentration is increased from 1.0 to 5.0 mg/mL. At high concen-tration, the surface is covered by a thicker boundary layer due to very little time for the molecules to change confor-mation before the surface is covered (Omoniyi et al., 2007).

The surface of coconut shell contains abundant oxygen and hydrogen groups which can decompose to CO_2 and water on carbonation. The abundance of surface complexes causes AC to be a good absorber of many gases and aqueous chemicals (Pradhan and Sandle, 1999). The highest saturation time for the adsorption study was recorded as 120 min using AC; this can be attributed to the numerous macro pores on its surface, and makes the adsorbent standout in the haze removal process.

Effect of cations on proteins adsorption onto TiO_2

The percentage of adsorbed proteins increased between 12 to 16% following suspension of 50 mg adsorbent treated with calcium or magnesium ions. A significant difference was recorded in the amount of proteins adsorbed onto the calcium and magnesium treated adsorbents compared to the potassium treated one (Figure 5). As presented in Figure 6 the amount of the

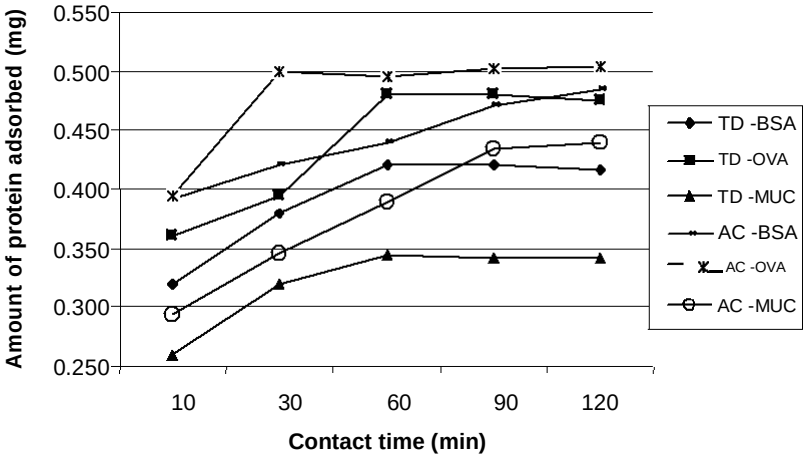

Figure 3. Time profile for the adsorption of adsorbate (1.0 mg/mL) onto 50 mgmass TiO_2 and activated carbon.

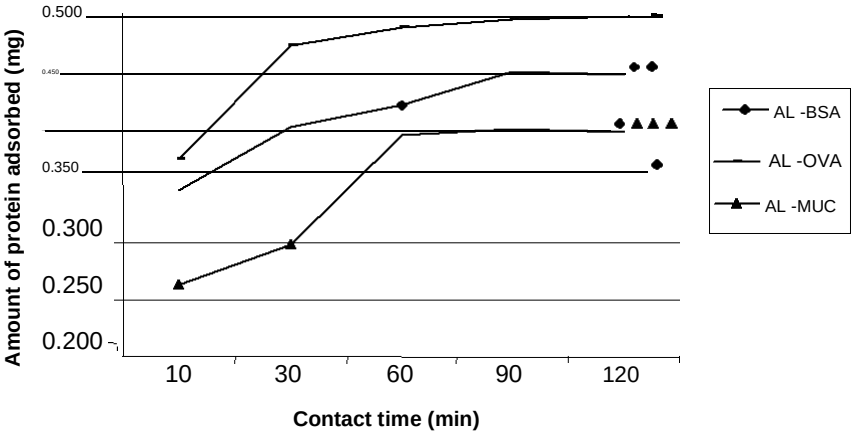

Figure 4. Time profile for the adsorption of adsorbate (1.0 mg/mL) onto 50 mg massalumina.TD = TiO_2; AC = activated carbon; AL = Al_2O_3.

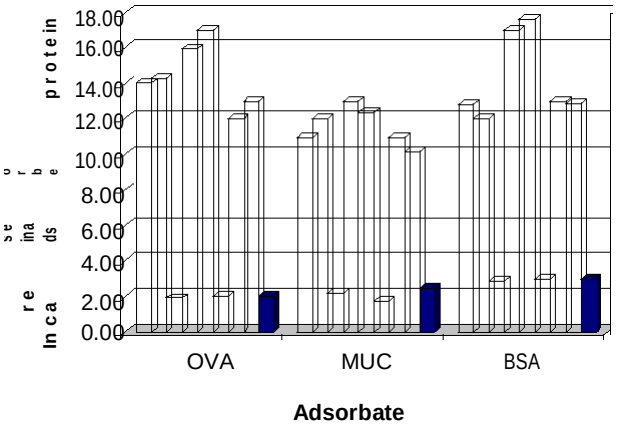

Figure 5. Effect of cations on the adsorption of proteins ontoadsorbents.Ca = calcium; TD = TiO_2; K = potassium; Mg = magnesium; AC = activated carbon; AL = Al_2O_3.

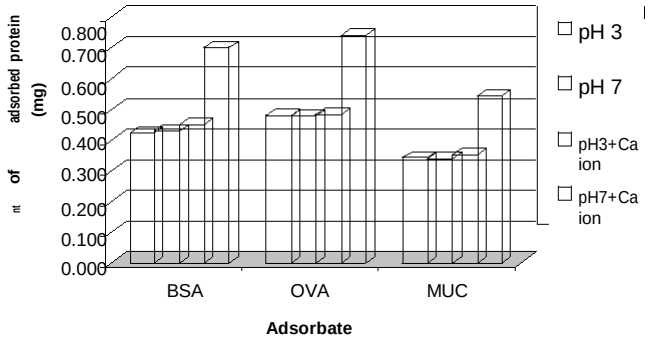

Figure 6. Effect of pH and cation on adsorption onto TiO_2.

proteins adsorbed to untreated TiO_2 at pH 3.0 and 7.0 were not different. However, at pH 7.0 pre-treatment of TiO_2 with calcium ion increased the adsorption significantly.

Conclusion

Finally, the result showed AC as an efficient adsorbent for the removal of haze in white wine, having demonstra-ted a positive correlation in the amount of the proteins and glycoproteins adsorbed onto it compared to Al_2O_3. The data lead to the inevitable conclusion that divalent cations like Ca^{2+} or Mg^{2+} can serve as bridging agents in the adsorption process that result to increased adsorp-tion.

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