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Population balance model development and experimental validation for the heteroaggregation of oppositely charged micro- and nano-particles

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ABSTRACT

The properties of heteroaggregates (aggregates of particles that are different in various aspects such as size, surface charge) depend on the properties of the particles along with the initial relative concentration of the particles. In this article, the heteroaggregation of two different types of oppositely charged hydrogel particles, alginate microparticles and chitosan nanoparticles were studied. A population balance model (PBM), popularly used to model particulate processes was developed based on the inter-particle interactions such as van der Waals, electrostatic and hydration in order to study the effect of initial relative concentration of alginate and chitosan on the final heteroaggregate size distribution. The presence of three different regimes (namely, 'dispersed, uncoated', 'agglomerated' and 'dispersed, coated') based on the initial concentration of alginate and chitosan was observed both from the model calculations and the experiments. In addition, to better understand these interactions, the effect of various process parameters on the aggregation kinetics were studied.

1. Introduction, background and objectives

Colloidal particles suspended in liquid medium have a tendency to aggregate due to attractive van der Waals force. When these particles are charged they are also subject to electrostatic double layer attraction or repulsion force depending on the electrostatic surface charge of the particles. For hydrophilic particles in water, the water molecules that are attached to the particles, as a result of their hydrophilicity, gives rise to an additional hydration force. Another important factor controlling the aggregation of these particles is the hydrodynamic force which arises from the particles having to move the water molecules that are in between each other, out of the way to aggregate. A combination of these forces produces aggregates which are loosely divided into two categories: homoaggregates and heteroaggregates. Homoaggregates are aggregates of one kind of particles and heteroaggregates are aggregates of particles that differ in various attributes such as size, electrical surface charge, etc. In colloidal science, heteroaggregates are gaining popularity due to their versatile applicability. Traditionally, core–shell particles, produced by heteroaggregation have been used for xerography, printing ink where micron sized polymer core is coated with nano-sized carbon black pigments (Zubitur et al., 2009). Heteroaggregates have also been used for drug delivery applications (Sarmento et al., 2007; Sezer, 1999). A new method to stabilize colloidal solutions of negligibly charged microspheres by introducing highly charged nanoparticles in the solution and forming nanoparticle 'halos' (i.e., a layer of nanoparticles on microspheres) has been developed recently (Tohver et al., 2001). Due to the layer of highly charged nanoparticles on the microspheres, these aggregates attain a

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similar surface charge and repel each other instead of agglomerating. Customized heteroaggregates for instance can also be used for water purification applications (Yu et al., 2013). This is based on the idea that oppositely charged components of the heteroaggregates will adsorb toxic anions and cations which include charged heavy metal compounds such as cadmium, mercury, lead, chromium and arsenic from waste-water.

The properties of the heteroaggregates depend not only on the material properties of the components but also the size, composition and surface charge. Hence, it is very crucial to understand the mechanism of heteroaggregation and to be able to control aggregation and form heteroaggregates of desired size and composition.

Chitosan and alginate have been suggested by researchers as good water purifying agents. Chitosan which is derived from chitin found in crustacean cells and alginate which is produced from algae and certain bacteria, are abundant, biocompatible and environment-friendly. Moreover, in the gel particle form, both alginate and chitosan show comparable metal ion adsorption capability to that of more popularly used ion exchange resins (Bailey et al., 1999; Gotoh et al., 2004; Kyzas and Deliyanni, 2013; Ng et al., 2002, 2003; Ngah et al., 2002; Williams et al., 1998).

Traditionally, the formation of colloidal aggregates has been studied in the literature as kinetic processes with a kernel for purely diffusive systems. Fuchs (1934) introduced the Fuchs stability ratio to account for the effect of various interaction forces such as van der Waals, electrostatic, hydration forces on aggregation rate. Derjaguin (1934), and subsequently Derjaguin and Landau (1993) and Verwey and Overbeek (1948) formulated the effect of van der Waals and electrostatic forces on aggregation.

There has also been work reported on the model development of colloidal system. Axford (1997) studied the reaction-limited aggregation of colloidal silica by using a population balance model (PBM). Furusawa and Velev (1999) investigated the effects of various important parameters such as the particle size ratio, the particle zeta potential and the electrolyte concentrations on the interaction of amphoteric latex particles and silica, and succeeded in controlling the size and composition. Schaer et al. (2001) studied the aggregation kinetics of silica particle precipitation in a batch reactor and proposed a mechanism for the aggregation process. They also used a PBM to model the aggregation process. Lattuada et al. (2003) performed experiments and used a PBM for studying the reaction-limited aggregation of polymer colloids. Peukert et al. (2005) used a PBM to study the production of nanoparticles of controlled size for nanoparticle precipitation and nanomilling applications. López-López et al. (2005) modeled the binary diffusion-limited cluster–cluster aggregation of similarly sized oppositely charged particles and found out that at a relative concentration of the minority particles higher than a critical value, all initial particles formed one large cluster however with relative concentration below that value, stable aggregates were formed. Soos et al. (2006) compared their PBM results with experiments on colloidal aggregation, breakage and restructuring in turbulent flows. Sefcik et al. (2006) used a PBM to study the effect of mixing on aggregation and gelation of nanoparticles and competition between aggregation and gelation for a homogeneous system. Lattuada et al. (2006) used a PBM for modeling the aggregation between clusters. Tourbin and Frances (2007) compared several analytical technique to measure the size distribution of colloidal silica particles in suspension which were detailed in a previous work. Mao and McClements (2011) studied the heteroaggregation of oppositely charged lipid droplets and found that the aggregate properties depend on the ratio of positive to negative droplets and pH. Raikar et al. (2010) used population balance model to predict emulsion drop size distribution for a oil-in-water simulation improving upon a previously developed model by accounting for multiple drop breakage instead of a breakage distribution function exhibiting maximum probability for the formation of two equal sized droplets. In a subsequent work, by increasing number of daughter drops formed in an event of breakage and by introducing a maximum stable diameter, the model was further improved for a wide range of homogenization pressures (Raikar et al., 2011). To predict the drop size distribution at industrially acceptable high oil-to-surfactant ratio, Maindarkar et al. (2012) developed a population balance breakage-coalescence model in place of established breakage-only model. This model was advanced to predict drop size distribution for different surfactant types and concentration (Maindarkar et al., 2013). PBM also has been used to model the viscosity of suspension of highly anisotropic nanoparticles during aggregation (Puisto et al., 2012), to model the aggregation of solid lipid nanoparticles (Yang and Henson, 2012), to study the aggregation kinetics and effect of cluster size and structure on aggregation kinetics for aggregation of rigid colloidal particles (Babler et al., 2010). Atmuri et al. (2013) performed experiments with latex particles at different salt and particle concentration and compared the experimental results with PBM results.

Previous research (both modeling and experimental) has mainly focused on the aggregation of one kind of rigid colloidal particles. Since alginate and chitosan are oppositely charged, very different in terms of size (alginate microparticles are about 130 times bigger than the chitosan nanoparticles) and are not rigid particles, the system studied in this work is very different from commonly studied aggregating colloidal system where van der Waals interaction dominates over the electrostatic interaction. In this case however, the electrostatic interaction dominates in most cases.

The interactions between different kind of particles in the system is shown in Fig. 1. For alginate-alginate interaction, since both the particles are negatively charged there is a strong repulsive electrostatic force which dominates over the weak van der Waals attraction. For chitosan–chitosan, similarly there is a strong electrostatic repulsion which dominates over the van der Waals attraction. In the case of alginate–chitosan particles, the opposing charges result in a strong electrostatic attraction along with the weak van der Waals attraction. For neutral monoaggregates where the charge of the chitosan particles attached to the alginate particle is just enough to neutralize the negative surface charge of the alginate particle and any other type of particle, the only force present is the weak attractive van der Waals force. For negatively charged monoaggregates (where the positive charge of the all chitosan particles attached to the negatively charged alginate is less than the surface charge of the alginate particle) and any other kind of particle the forces in play are strong or weak (depending on the negative charge of the monoaggregate) electrostatic attraction or repulsion (depending on whether the other particle is charged and positively or negatively) and attractive van der Waals force. For positively charged monoaggregates (where the positive charge of the chitosan particles attached to the negatively charged alginate is more than the surface charge of the alginate particle) similarly the forces are van