

Stability of alumina, ceria, and silica nanoparticles in municipal wastewater

Lila Otero-González, Isabel Barbero, Jim A. Field, Farhang Shadman and Reyes Sierra-Alvarez

ABSTRACT

Inorganic oxide nanoparticles (NPs) are used in semiconductor manufacturing operations such as wafer chemical–mechanical planarization (CMP). Understanding the stability of NPs in municipal wastewater is essential for the evaluation of the fate of NPs released to municipal wastewater treatment plants (WWTPs). This study aimed to evaluate the stability of Al_2O_3 , CeO_2 , and SiO_2 NPs and CMP waste effluents containing these NPs in municipal wastewater. Al_2O_3 and CeO_2 NPs were destabilized by wastewater constituents, as indicated by the formation of large agglomerates. However, the same NPs in the CMP waste slurries showed high stability in wastewater, probably due to additives present in the slurry that modify the surface chemistry of the particles. Likewise, both the commercial SiO_2 NPs and the CMP waste slurry containing SiO_2 NPs showed substantial stability in wastewater since this NP has a very low point of zero charge, which suggests that this NP could be the hardest one to remove in conventional WWTPs by aggregation–sedimentation. In summary, the results indicate that wastewater may destabilize NPs suspensions, which would facilitate NP removal in WWTPs. However, some chemicals present in real CMP slurries may counterbalance this effect. More research is needed to completely understand the surface chemistry involved.

Key words | Al_2O_3 , CeO_2 , CMP slurry, nanoparticle aggregation, SiO_2 , wastewater treatment

Lila Otero-González (corresponding author)
Isabel Barbero
Jim A. Field
Farhang Shadman
Reyes Sierra-Alvarez
Department of Chemical and Environmental
Engineering,
University of Arizona,
P.O. Box 210011,
Tucson,
Arizona 85721,
USA
E-mail: lilaoter@email.arizona.edu

INTRODUCTION

Different technological sectors have pursued the development of engineered nanomaterials during the last decades. Materials with sizes of less than 100 nm have been designed, produced and used in multiple applications. Semiconductor manufacturing is among the industries that use the unique properties of nanoparticles (NPs) in their operations. For example, abrasive NP-based slurries are used during wafer chemical–mechanical planarization (CMP) operations to enhance polishing performance. Inorganic oxides such as alumina (Al_2O_3), ceria (CeO_2), and silica (SiO_2) are the most commonly used NPs in CMP slurry formulations (Singh *et al.* 2002). NP slurries are diluted with large amounts of ultra-pure water during the CMP operation. It has been estimated that a large semiconductor manufacturing plant can consume more than 10,000 m^3 of ultra-pure water per day and that CMP processes can account for 30–40% of that water consumption (Corlett 2000; Klusewitz & McVeigh 2002). Consequently, significant amounts of CMP wastewater are generated and discharged.

Several wastewater treatment technologies such as coagulation–flocculation, electrocoagulation or membrane filtration are considered for the treatment of CMP effluents (Golden *et al.* 2000; Yang 2002). However, there is still a large amount of wastewater that is discharged into municipal sewage systems. Wastewater from CMP operations contains high concentrations of suspended solids in the form of NPs, mainly Al_2O_3 , CeO_2 and SiO_2 (Yang 2002). For example, in China and Taiwan, CMP effluents have been reported to contain very high concentrations of silica NPs ranging from 1.3 to 8.5 g L^{-1} (Liu *et al.* 2014). Al_2O_3 , CeO_2 and SiO_2 NPs have been shown to display cytotoxicity in numerous studies (Karlsson *et al.* 2014) and these three NPs are included in the Organisation for Economic Cooperation and Development (OECD) list of representative engineered nanomaterials that need urgent human health and environmental risk evaluation (OECD 2010). Therefore, understanding the fate of the discharged NPs in wastewater treatment plants (WWTPs)

will help the further risk assessment of these nanomaterials.

In conventional WWTPs, NPs can potentially be removed by two main mechanisms: settling and adsorption onto the biomass (Westerhoff *et al.* 2011). These two processes are highly dependent on the stability and surface charge of the NPs. For example, a study of removal of four different NPs by activated sludge showed that citric-acid-coated Ag NPs were the most stable and the hardest NP to remove. Moreover, the addition of extracellular polymeric substances destabilized the four NPs tested and increased their removal (Park *et al.* 2013). Some studies have provided valuable information about the stability of CeO₂ and SiO₂ NPs in different water matrices (Limbach *et al.* 2008; Keller *et al.* 2010; Tso *et al.* 2010) but very few included real domestic wastewater (Gomez-Rivera *et al.* 2012) and none of them tested real CMP waste effluent, whose chemistry can alter the results.

The aim of this work was to perform a preliminary assessment of the stability of three inorganic oxide NPs, Al₂O₃, CeO₂, and SiO₂, in municipal wastewater. The three NPs were obtained from two types of sources, either as commercial nano-powders or dispersed in CMP waste effluents. The final goal is to use the information obtained in this study for better predictions on the fate of CMP NPs during conventional municipal wastewater treatment.

MATERIALS AND METHODS

NPs and nanoparticle dispersions

Al₂O₃ (50 nm, 99% purity), CeO₂ (50 nm, 99.95%) and SiO₂ (10–20 nm, 99.5%) NPs were purchased from Sigma-Aldrich (St Louis, MO, USA). All materials were obtained as dry powders. NP dispersions (2 g L⁻¹) were prepared in 1 mM HCl (Al₂O₃ and CeO₂) or in deionized (DI) water (SiO₂) and sonicated using a 130-W ultrasonic processor (Cole-Parmer Instruments, Vernon Hills, IL, USA) at 70% amplitude for 15 min. The dispersions were allowed to rest for 2 days and the remaining suspended NPs were used as stocks for further experimentation. Al, Ce, and Si in the stock dispersions were analyzed by inductively coupled plasma–optical emission spectroscopy (ICP-OES Optima 2,100 DV; Perkin Elmer, Waltham, MA, USA) as previously described (Otero-Gonzalez *et al.* 2012).

CMP slurries and CMP waste effluents

CMP slurries were obtained from major suppliers. Al₂O₃ slurry (iCue 600Y75, 160 nm, 30% Al₂O₃ content, pH = 4.6)

was obtained from Cabot Microelectronics (Aurora, IL, USA), CeO₂ slurry (HS-8005, 110 nm, 5% CeO₂, pH = 4.2) from Hitachi Chemical (Cupertino, CA, USA), and fumed SiO₂ slurry (Planerlite PL-4217, 30 nm, 25% SiO₂, pH = 8.5) from Fujimi (Tualatin, OR, USA).

CMP wastewater samples were prepared using an on-site pilot-scale wafer polisher (Philipossian & Olsen 2003). The Al₂O₃ slurry was supplemented with 30% hydrogen peroxide (slurry:H₂O₂, 10:1, v/v), and the CeO₂ and SiO₂ slurries were diluted with DI water (1:9 and 1:1, v/v, respectively) prior to polishing. The final NP concentrations were approximately 27%, 0.5%, and 12.5% in the Al₂O₃, CeO₂, and SiO₂ slurries, respectively. The Al₂O₃ slurry was used to polish a 100-nm copper disc, and the CeO₂ and SiO₂ slurries were applied in the polishing of 100-nm blanket silicon oxide wafers. Samples of waste slurry were collected during polishing and used as stock dispersions for stability analysis.

Stability of NPs and CMP waste slurries in primary-treated municipal wastewater

The stability of commercial NPs and CMP waste slurries in primary-treated wastewater was evaluated by measuring the particle size distribution (PSD) and zeta potential (ζ -potential). NP stocks and CMP waste slurries were diluted in a ratio of 1:1 with membrane-filtered (25 nm) primary-treated municipal wastewater or DI water. The PSD and ζ -potential were determined in duplicate in a pH range of 4–10 using an automatic autotitrator (MPT-2; Malvern Instruments, Westborough, MA, USA) connected to a Zeta-sizer Nano ZS instrument (Malvern Instruments). The solutions used for pH adjustment were 0.5 M HCl, 0.5 M NaOH, and 0.25 M NaOH. PSD was determined by dynamic light scattering. The unit employs a 4 mW He-Ne laser with a wavelength of 633 nm, and a measurement angle of 173°. The refractive indices used for Al₂O₃, CeO₂, and SiO₂ were 1.765, 1.828, and 1.470, respectively. The ζ -potential of NP dispersions was measured with the same instrument using laser Doppler velocimetry and the Smoluchowski equation to correlate particle electrophoretic mobility to ζ -potential. Measurements were performed at 25 °C.

Primary-treated municipal wastewater was obtained from a local sewage treatment plant (Ina Road, Tucson, AZ, USA) and stored at 4 °C until use. The wastewater was characterized (Table 1) by measuring the pH, total and soluble chemical oxygen demand (COD), and the concentration of volatile fatty acids (VFAs; sum of acetic, propionic, and butyric acids).

Table 1 | Characterization of the primary-treated wastewater used in this study. Values show the average \pm standard deviation of duplicate samples

	Experimental value
pH	7.8
Total COD (mg L^{-1})	265.1 ± 0.1
Soluble COD (mg L^{-1})	117.6 ± 0.1
Total VFAs (mg L^{-1})	12.8 ± 1.5

VFAs were measured by gas chromatography (7890A GC System, Agilent Technologies, Santa Clara, CA, USA) as previously described (Otero-Gonzalez *et al.* 2014). Measurements of COD and pH were conducted according to *Standard Methods* (APHA 2005).

RESULTS AND DISCUSSION

PSD in aqueous suspensions

Figure 1 shows the hydrodynamic PSD of the NPs investigated. The original pH value of the Al_2O_3 , CeO_2 , and SiO_2 CMP slurries was 4.6, 4.2, and 8.5, respectively. For comparison, the pH of the suspensions of commercial NPs in DI water was adjusted to the same value (± 0.1) as in the corresponding CMP slurry. In general, the three CMP slurries presented a monodispersed PSD with a single peak of intensity around 100–200 nm. The average hydrodynamic particle sizes measured were 204, 163, and 153 nm for the Al_2O_3 , CeO_2 , and SiO_2 slurries, respectively, based on intensity. The dispersion of commercial Al_2O_3 NPs showed a PSD similar to that of the homologous CMP slurry and an average particle size of 171 nm (Figure 1a). Although the average size was slightly larger for the CMP slurry than for the commercial NPs suspended in DI water, the latter actually aggregated to a greater extent compared to the primary particle size reported (50 nm for the NP and 160 nm for the slurry). On the other hand, the DI water dispersions of commercial CeO_2 and SiO_2 NPs displayed an asymmetrical PSD (Figures 1b and 1c), which indicates the presence of a diverse population of particles with different aggregate sizes. For example, the PSD of SiO_2 NPs shows a clear peak of intensity at 460 nm and another smaller peak at 150 nm that overlaps with the larger one (Figure 1c). The average hydrodynamic sizes for CeO_2 and SiO_2 NPs were 334 and 534 nm, respectively. As was observed for Al_2O_3 NPs, the CeO_2 and SiO_2 commercial NPs dispersed in DI water also aggregated more than their homologous CMP slurry NPs. For example,

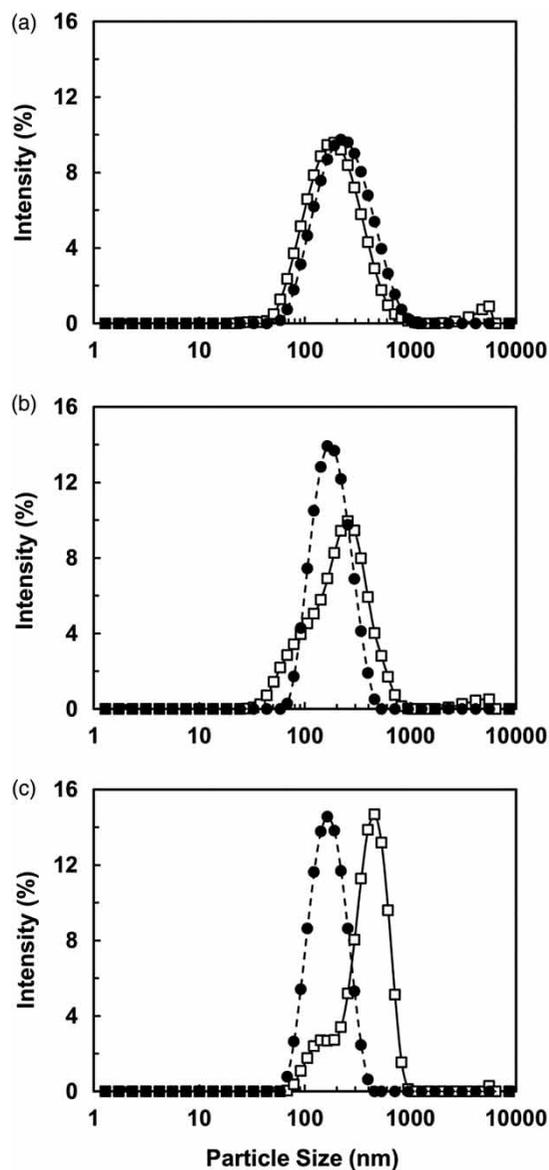


Figure 1 | Hydrodynamic PSD of Al_2O_3 (a), CeO_2 (b), and SiO_2 (c) NPs obtained as nanopowders and suspended in DI water (\square) and obtained as commercial CMP slurries (\bullet). The pH of the CMP slurries was 4.6, 4.2, and 8.5 for the Al_2O_3 , CeO_2 , and SiO_2 slurry, respectively. For comparison, the pH of the suspensions of commercial NPs was adjusted to the same value (± 0.1) as in the corresponding CMP slurry. The concentrations of Al_2O_3 , CeO_2 , and SiO_2 NPs after dilution were 258, 293 and 635 mg L^{-1} , respectively. The concentration of the CMP slurries was 0.01% (w/v). The results shown are from a single replicate of duplicate samples. Data variability was generally less than 5%.

the aggregate size of SiO_2 NPs in DI water was 36-fold larger than the primary particle size reported (10–20 nm).

Stability of commercial NPs in wastewater

The stability of the NPs in DI water and primary-treated wastewater was evaluated by measuring the average particle

size and ζ -potential over a range of pH values (4–10). In general, commercial NPs were more unstable in wastewater than in DI water, except SiO₂ NPs that had similar sizes in both matrices (Figure 2). The size of Al₂O₃ and CeO₂ NPs in DI water greatly increased at high pH values (pH >6) and the average aggregate particle sizes measured were in the order of a few μm (Figures 2(a) and 2(c)). Moreover, the size of Al₂O₃ NPs decreased again to values below 1 μm at approximately pH 10 (Figure 2(a)). Additionally, wastewater had a destabilizing effect on these two nanomaterials and the average size of the Al₂O₃ and CeO₂ particles was about 8 and 6 μm , respectively, over the entire range of pH values. On the other hand, the hydrodynamic size of SiO₂ NPs was not affected either by the medium or the pH value, and the average size ranged between 440 and

640 nm in both DI water and wastewater at any pH value (Figure 2(e)).

The ζ -potential measurements agree with the aggregation behavior observed. The point of zero charge (PZC) in DI water for Al₂O₃ and CeO₂ was observed to coincide with circumneutral pH values (8.5 and 7.0, respectively) (Figures 2(b) and 2(d)). In both cases, the NP surface charge at pH below 6 was markedly positive, which increases the repulsive forces between the particles and prevented excessive aggregation. At higher pH values, the surface charge becomes neutralized and aggregation takes place. Moreover, in the case of Al₂O₃ NPs the increase in the negative surface charge at pH 10 was enough to cause repulsion between particles and the average particle size decreased again to values below 1 μm (Figures 2(a) and 2(b)).

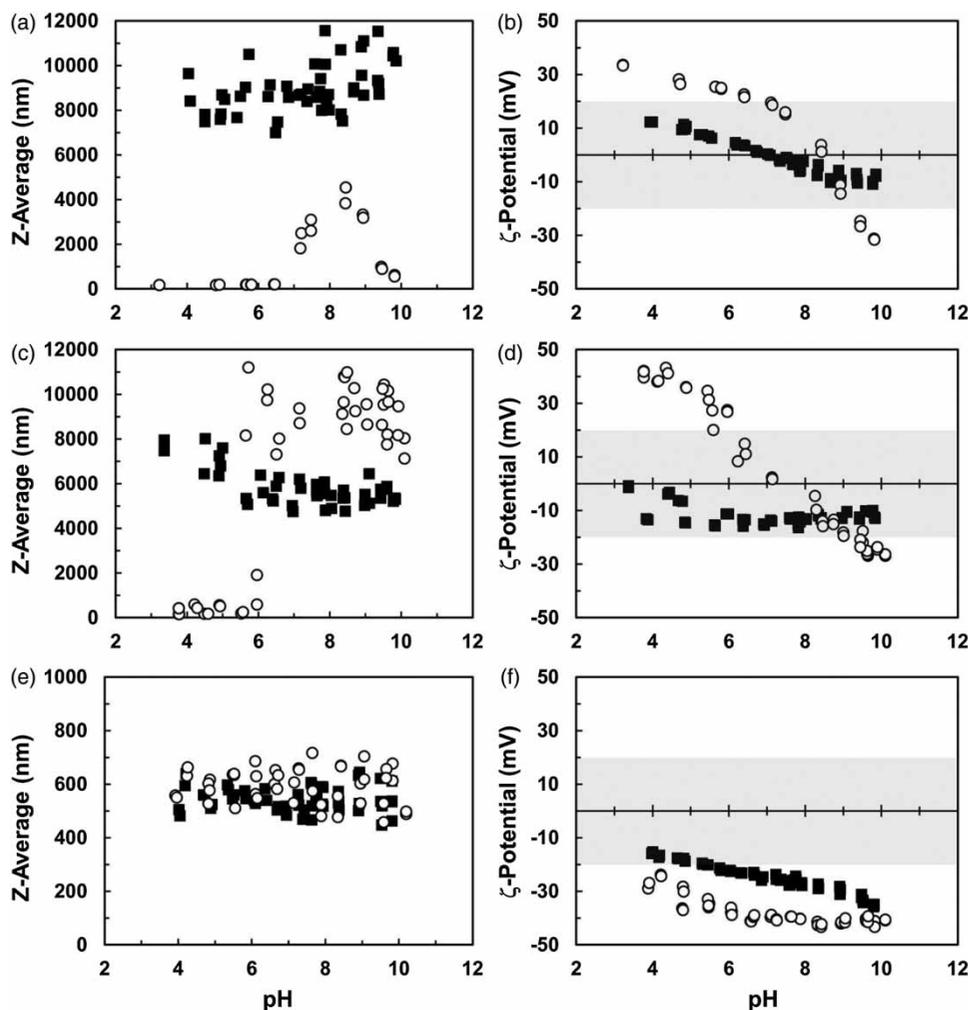


Figure 2 | Variation of average hydrodynamic particle size (Z-average) and particle surface charge (ζ -potential) with pH of the three commercial NPs tested: Al₂O₃ ((a), (b)), CeO₂ ((c), (d)), and SiO₂ ((e), (f)), when dispersed in DI water (○) and in membrane-filtered (25 nm) primary-treated municipal wastewater (■). The concentrations of Al₂O₃, CeO₂, and SiO₂ after dilution were 258, 293 and 635 mg NP L⁻¹, respectively. The gray area indicates the range of ζ -potential values (–20 to 20 mV) at which colloidal dispersions are not stable and aggregation can be expected. Figures show data for duplicate samples.

In the case of Al_2O_3 and CeO_2 NPs suspended in wastewater, the ζ -potential values were permanently in the range of -20 to 20 mV, which are the typical threshold values of unstable colloidal suspensions. These ζ -potential values agree with the large agglomerate sizes measured over the whole range of pH in the wastewater matrix (Figures 2(a) and 2(c)). Finally, the PZC of SiO_2 could not be determined over the range of pH tested and the surface charge was always significantly negative, either in DI water or wastewater, which precluded excessive aggregation of the particles (Figure 2(f)).

The results indicate a clear change in the surface chemistry of Al_2O_3 and CeO_2 NPs that promotes aggregation when these are transferred from DI water to wastewater. It is well known that ionic strength (IS) plays an important role in the stability of NPs. Several studies reported enhanced aggregation of Al_2O_3 and CeO_2 NPs with increasing IS (Van Hoecke *et al.* 2011; Rahman *et al.* 2013). Another study found a clear correlation between the IS and the ζ -potential of a CeO_2 NPs dispersion and showed a decrease in the absolute value of ζ -potential with increasing IS due to the compression of the electrical double layer (Li *et al.* 2011). The organics present in municipal wastewater may also affect the aggregation of NPs. However, their impact is more difficult to evaluate due to the high variability of the organic compounds in wastewater, which can range from short-chain fatty acids to large amphiphilic molecules. For instance, humic acids increased the aggregation of Al_2O_3 NPs at low pH, but promoted their stability at pH values close to the PZC (Ghosh *et al.* 2008). Another study reported increased stability of several inorganic oxide NPs, including CeO_2 , in the presence of natural organic matter from environmental water samples (Keller *et al.* 2010). The tendency of Al_2O_3 and CeO_2 NPs to aggregate in wastewater could facilitate their removal by sedimentation in WWTPs. In the case of SiO_2 , neither the IS nor the organic compounds had an important destabilizing impact, which suggests that this NP may be more persistent to this kind of treatment.

Stability of CMP waste slurries in wastewater

In contrast with the commercial NPs, the CMP waste slurry NPs displayed a high stability after slurry dilution with DI water and wastewater (Figure 3). Only Al_2O_3 NPs were aggregated when the CMP waste slurry was diluted with DI water and, surprisingly, wastewater had a stabilizing effect on these NPs (Figure 3(a)). On the other hand, wastewater did not have any stabilizing or destabilizing impact on CeO_2 and SiO_2 CMP NPs, and the average particle sizes

were around 200 and 150 nm, respectively, in both media (Figures 3(c) and 3(e)).

Although the effect of wastewater on the particle size was not very evident (except for the Al_2O_3 slurry), the influence on the particle surface charge was still obvious. The ζ -potential in DI water diluted suspensions of the three CMP waste slurries was extremely negative (approximately -50 mV) which is well outside the instability region. What is similar to the commercial NPs is the fact that the wastewater modified the ζ -potential, and the values measured were closer to the instability region (Figure 3), which may indicate the initiation of a destabilizing impact by the wastewater components.

Except for SiO_2 , the results differed for the commercial NPs and the CMP waste slurries. Most likely, the difference can be attributed to the presence of additives such as surfactants, complexing agents or oxidizers that are usually included in the CMP slurry formulations to improve their performance (Singh *et al.* 2002). It is reasonable that, at the ratio of dilution waste slurry:wastewater used in this study (1:1), the chemistry of the additives dominate over the chemistry of the wastewater components. It is expected that the behavior will change under a realistic situation where the CMP waste effluents are diluted to lower concentrations more probable to be found in WWTPs. On the one hand, an increased dilution factor would minimize the effect of the slurry additives on the NP stability, and the impact of the wastewater constituents would dominate. Under this scenario, the behavior could be similar to that described for the commercial NPs. On the other hand, a decrease in the NP concentration would also implicate less probability of particle collisions and could result in fewer and smaller NP aggregates. For example, it was observed that TiO_2 NPs suspended in seawater aggregated less and at a slower pace at 10 mg L^{-1} than at 50 and 100 mg L^{-1} , which led to a slower sedimentation rate at lower concentrations (Keller *et al.* 2010). More research is needed to fully understand the behavior of complex CMP effluents in municipal wastewater and to elucidate the capability of conventional WWTPs to effectively remove NPs before discharge into the environment.

CONCLUSIONS

In summary, Al_2O_3 and CeO_2 commercial NPs were largely destabilized in primary-treated wastewater, which promoted their aggregation. In contrast, SiO_2 NPs were

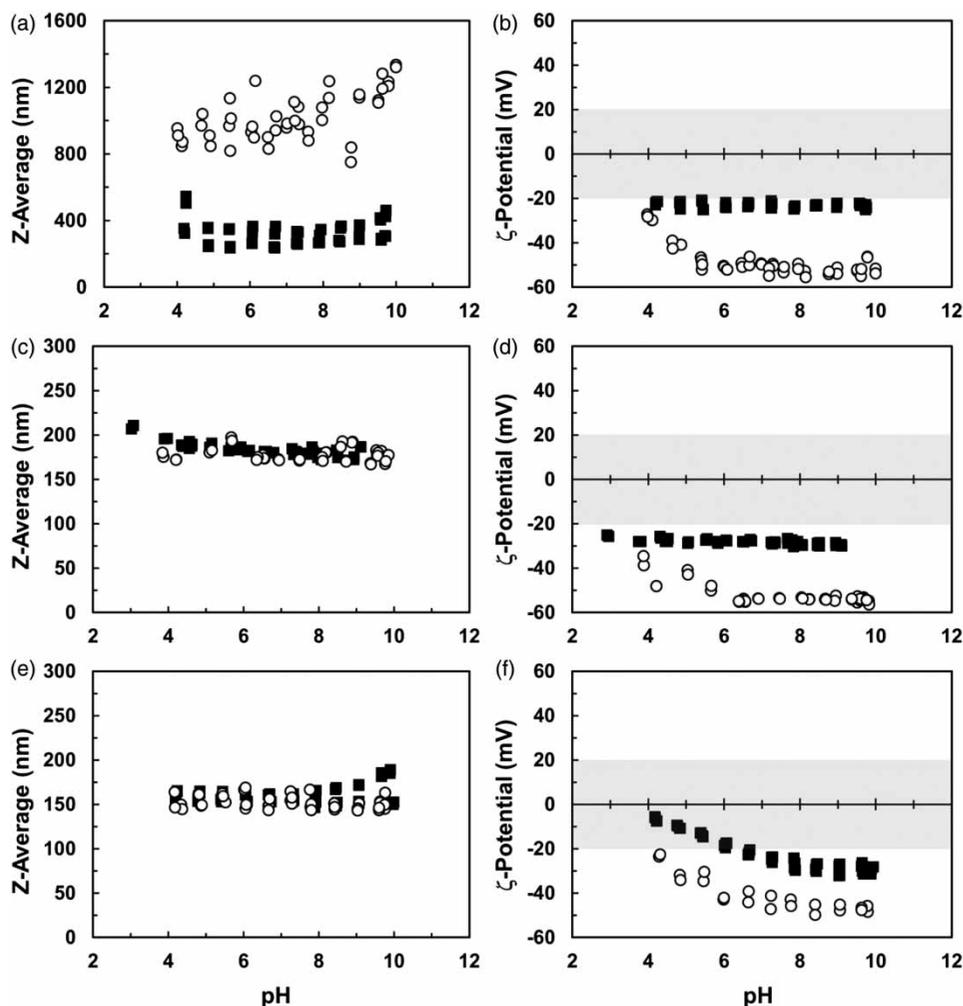


Figure 3 | Variation of average hydrodynamic particle size (Z-average) and particle surface charge (ζ -potential) with pH for the three CMP waste slurry NPs: Al_2O_3 ((a), (b)), CeO_2 ((c), (d)), and SiO_2 ((e), (f)), when diluted to a final concentration of 1 g/L with DI water (○) or with membrane-filtered (25 nm) primary-treated municipal wastewater (■). The gray area indicates the range of ζ -potential values (–20 to 20 mV) at which colloidal dispersions are not stable and aggregation can be expected. Figures show data for duplicate samples.

found to be considerably stable in wastewater and did not aggregate to a higher extent in wastewater than in DI water. These results suggest that Al_2O_3 and CeO_2 NPs may be removed by agglomeration–sedimentation in WWTPs, while SiO_2 NPs may be more persistent to this type of treatment.

On the other hand, the NPs in the three CMP waste slurries showed high stability when diluted 1:1 in both DI water and wastewater. This finding is most likely due to dispersant additives included in the commercial formulations of the slurries. In conclusion, although commercial NPs can serve as an approximation to the study of NP fate during wastewater treatment, there is a need for a better understanding of the physical chemistry of CMP effluents since these are expected to be important sources of NP discharge into wastewater systems.

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