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Dispersion and aggregation of single-walled carbon nanotubes in aqueous solutions of anionic surfactants

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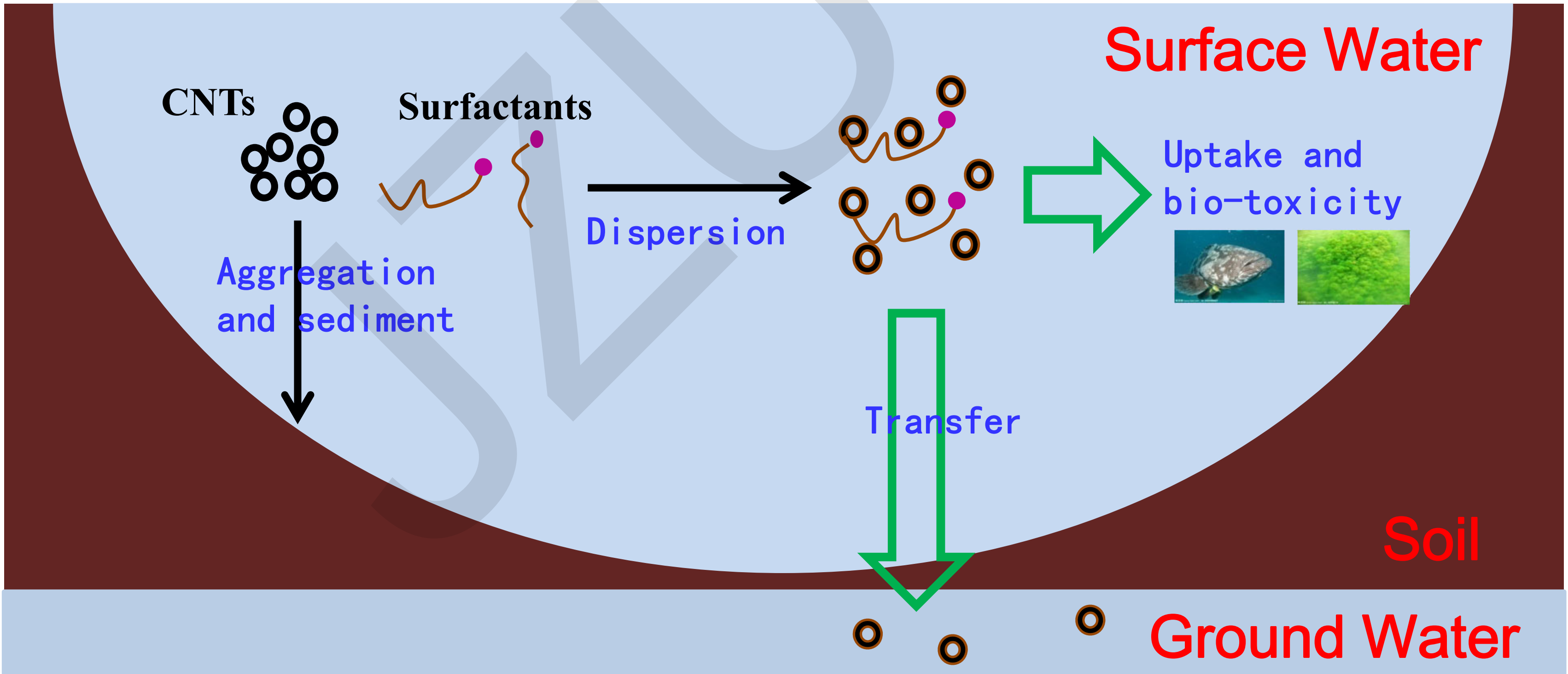
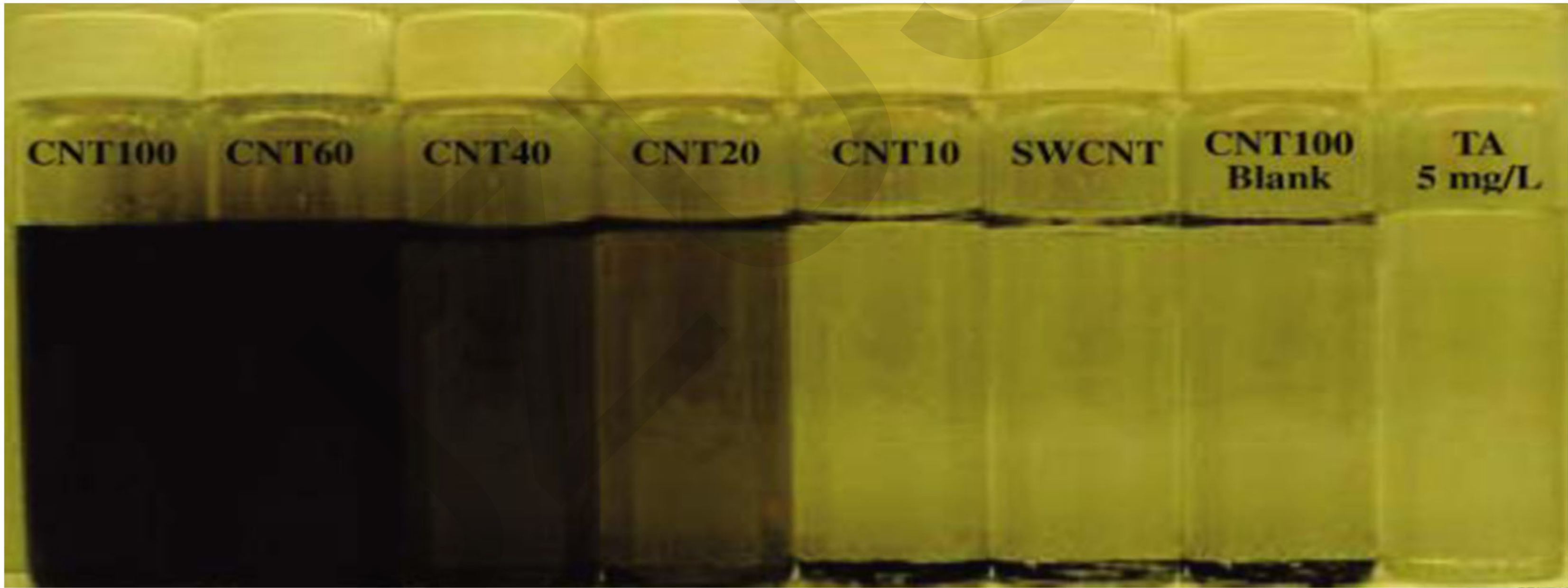
Background

- Carbon nanotubes (CNTs) can potentially cause damage to aquatic organisms, mammals, and human cells
- CNTs will inevitably enter the environment during their production, transport, handling, use, and disposal
- The dispersion and aggregation of CNTs in the aqueous environment are critical behaviors affecting their fate, bioavailability, and potential environmental and health risks



Background

- It has been widely reported that bulk CNTs can be dispersed and stably suspended in aqueous solutions of surfactants and natural organic matter (NOM) using sonication
- more stably suspended CNTs exhibit higher mobility and could thus be transported longer distances in the environment, thus posing greater ecological and environmental risks



Hyung and Kim, *Environ.Sci.Technol.* 2008
Bouchard *et al.*, *Environ.Sci.Technol.* 2012
Lin and Xing, *Environ. Sci. Technol*. 2008

Background

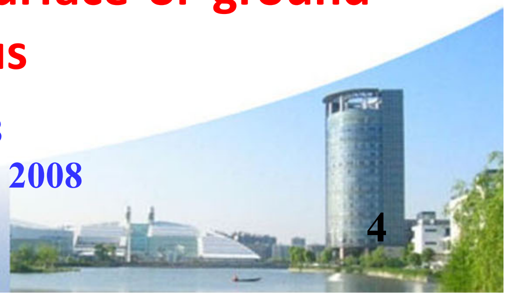
- Sonication is a method of vigorously agitating water and is an important process for dispersing or debundling CNT aggregates and bundles. However, sonication induces more extreme agitation than is encountered in the natural aqueous environment

  Therefore, milder methods, such as shaking, should be employed in experiments on the dispersion and suspension of bulk

- These current findings, i.e., stably suspended CNTs can remain stable in the prensence of environmental cations including Na^{+}, K^{+}, Mg^{2+}, and Ca^{2+}, were mostly obtained from experiments that employed higher concentrations of CNTs as well as dispersion typical of industrial applications rather those found in the environment

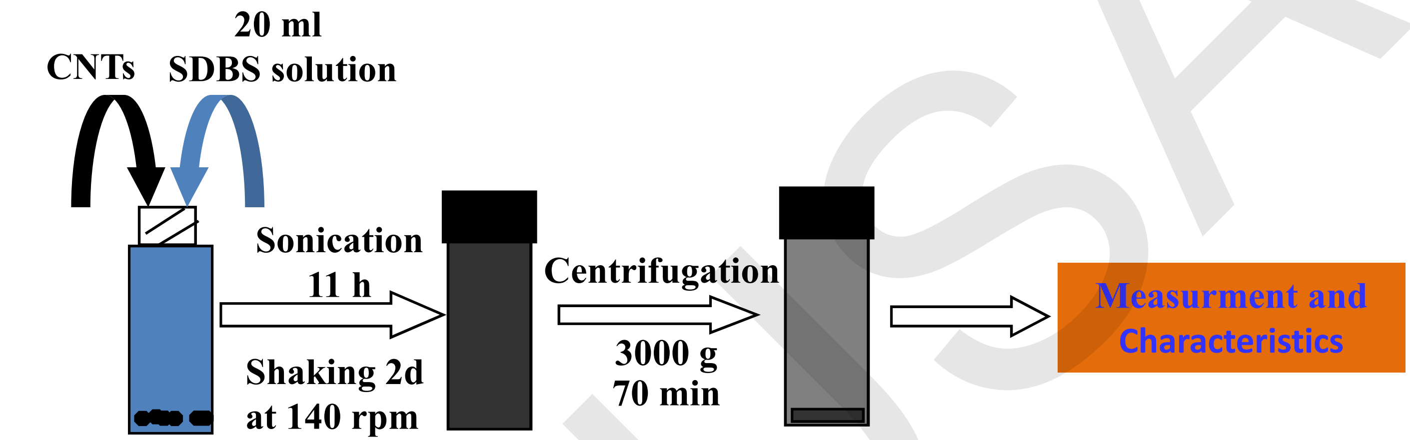
  The dilution of a stable suspension of CNTs to lower concentrations occurs as soon as the suspension is released into the surface or ground waters, as was not previously been considered in previous

Islam *et al., Nano Lett.* 2003
Bouchard *et al., Environ.Sci.Technol.* 2012
Saleh *et al., Environ.Sci.Technol.* 2008
Lin and Xing, *Environ. Sci. Technol.* 2008

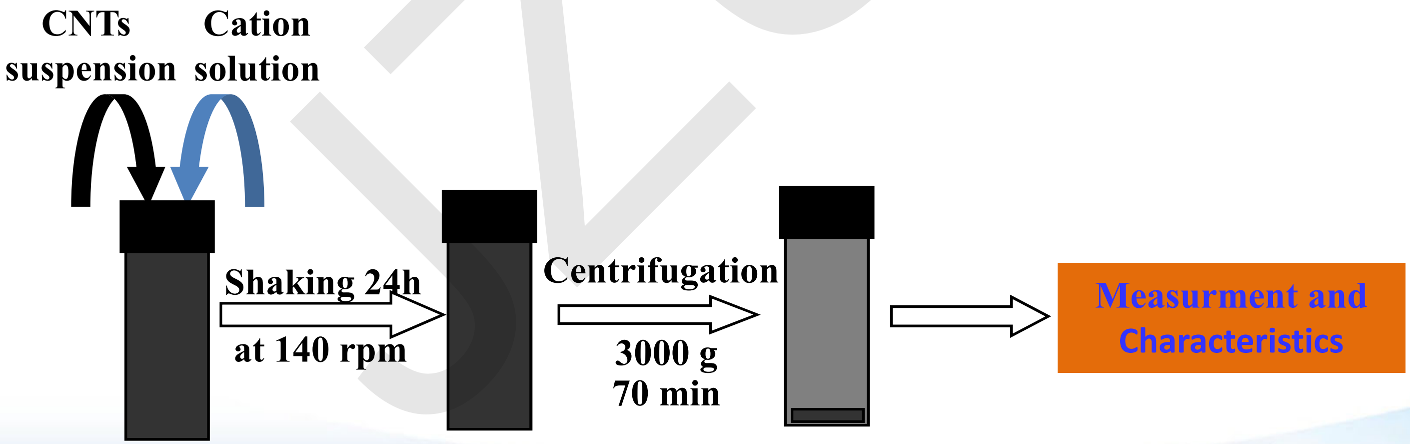


Experiments

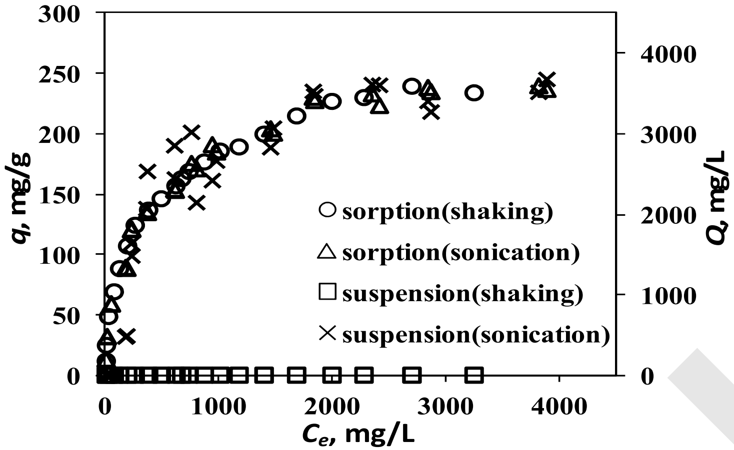
□ Dispersion experiments



□ Aggregation experiments



Results and Discussion



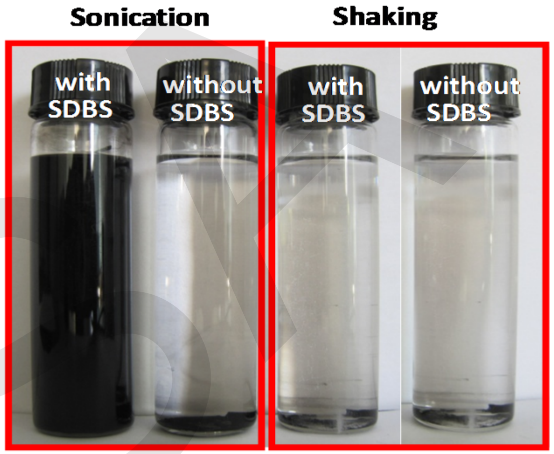


Fig. 1 - Amounts of stably suspended SWCNTs (*Q*, mg/L) and adsorbed SDBS on SWCNTs (*q*, mg/g) versus the equilibrium SDBS concentration (C_e, mg/L) after the SWCNTs (with an initial dose of 7 500 mg/L in solution) were sonicated for 11 h or shaken for 2 d (top). Images of the dispersion of SWCNTs in 0 and 5 000 mg/L SDBS solutions after sonication and shaking (bottom).

- With only shaking at 140 rpm, SWCNTs cannot be stably suspended in water and SDBS solution
- With the assist of sonication, SWCNTs can be dispersed and stably suspended in the SDBS solution, but not in water
- Both of sonication and SDBS play important roles in the dispersion of SWCNTs in water, bulk SWCNTs cannot be dispersed, stably suspended, or transported long distances at significant concentrations in the environment

Results and Discussion

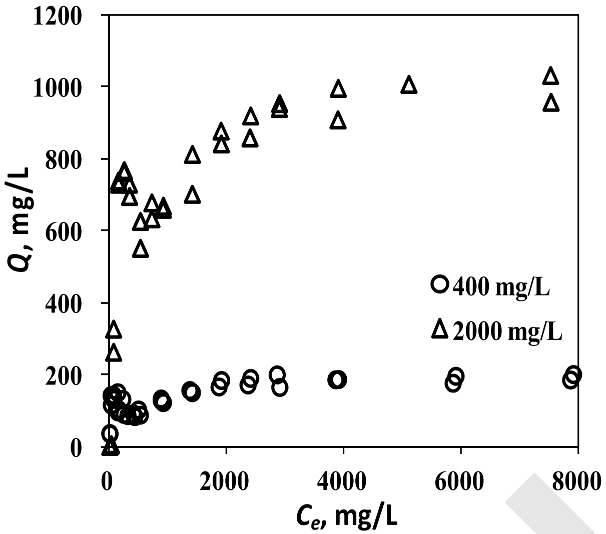


Fig. 2 - Amounts of stably suspended SWCNTs (*Q*, mg/L) at the SWCNT doses of 400 mg/L and 2 000 mg/L versus the equilibrium SDBS concentration (*C_e*, mg/L) after sonication for 11 h.

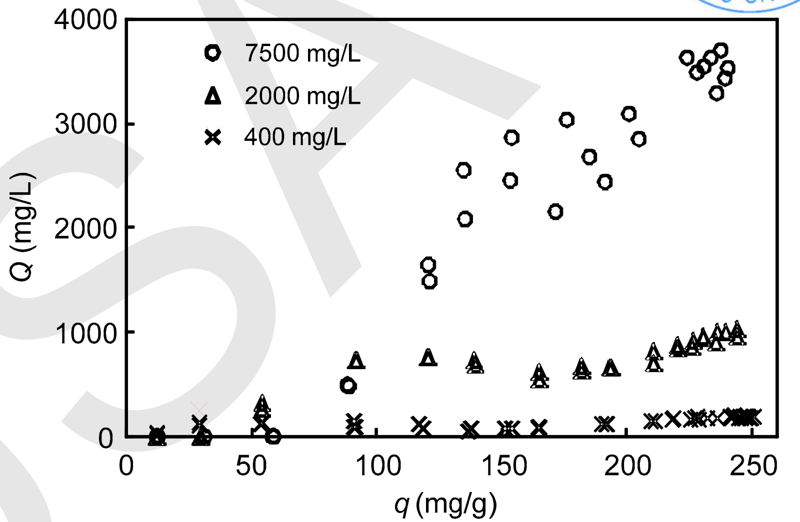


Fig. 3 Amounts of stably suspended SWCNTs at three doses of SWCNTs (i.e., 400, 2000, and 7500 mg/L) versus the amount of SDBS adsorbed on the SWCNTs

- The addition of more SWCNTs resulted in more SWCNTs being dispersed and stably suspended
- The amount of stably suspended SWCNTs (Q) increased with the amount of SDBS adsorbed on the SWCNTs (q), indicating that the adsorption of SDBS plays an important role in the dispersion of SWCNTs

Results and Discussion

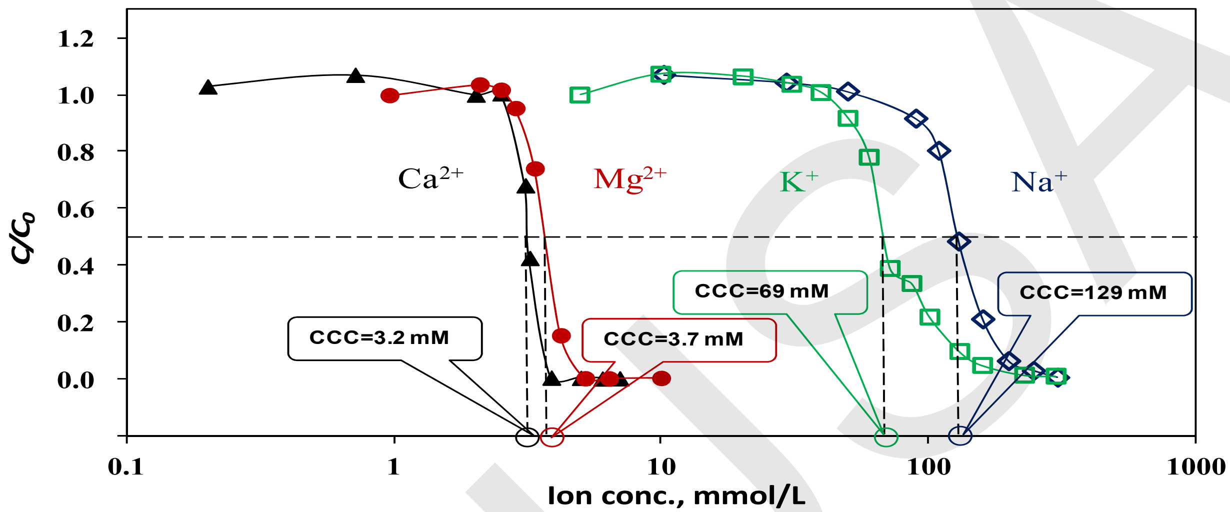


Fig. 6 - SWCNT stabilization in 2500 mg/L SDBS solution as a function of ionic strength.

- The SDBS-suspended SWCNTs largely retain their stability at low ion concentrations, and re-aggregated and deposited at high ion concentrations,
- Divalent ions are more effective to aggregate suspended SWCNTs
- The concentrations of Na^{+}, K^{+}, Ca^{2+}, and Mg^{2+} to aggregate suspended SWCNTs were much higher than their average concentrations in fresh river water (ie, 0.22, 0.034, 0.16, and 0.36 mmol/kg, respectively) but lower than those in surface seawater (ie, 470, 10.2, 53, and 10.3 mmol/kg, respectively)

Results and Discussion

- After the stable SWCNT suspension was diluted, the ion concentrations for re-aggregation of SWCNTs decreased significantly
- This decrease indicates that stably suspended SWCNTs do not retain environmental stability that would allow them to be transported long distances, because, as soon as they are released into the environment, dilution will occur and environmentally relevant cations will coagulate the diluted suspension of SWCNTs

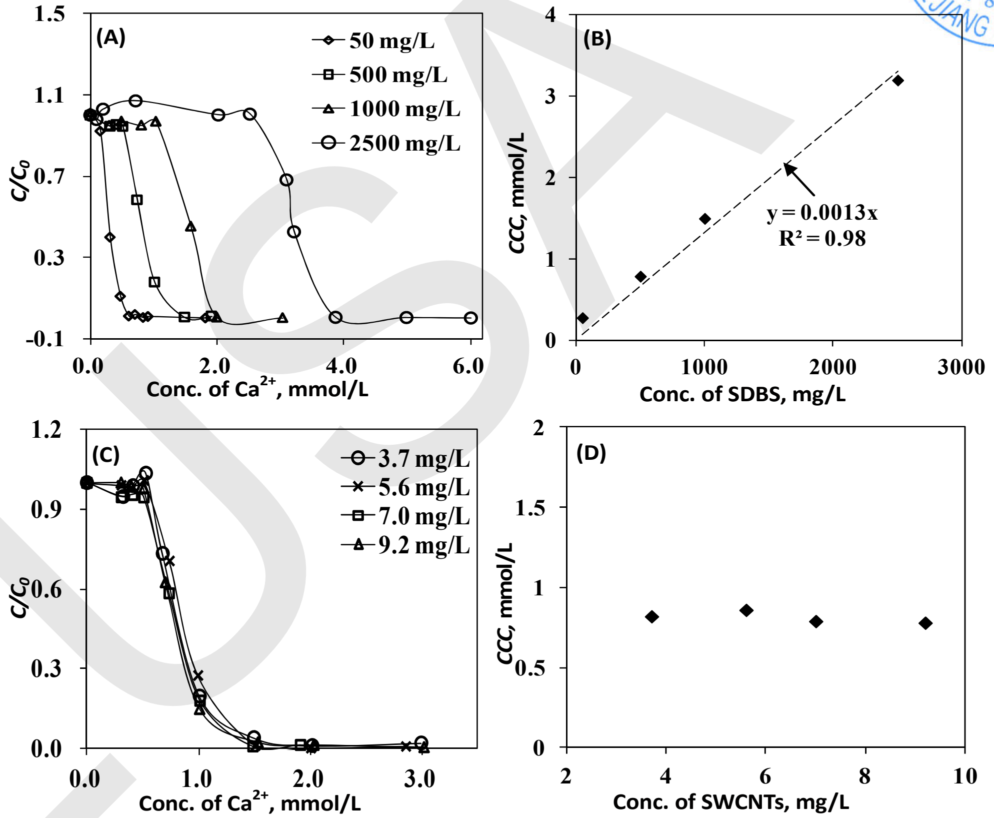


Fig. 8 - The stability of SDBS suspended SWCNTs (A) at four SDBS concentrations and (C) at four SWCNT concentrations as a function of ionic strength (Ca^{2+}), and the CCC values of Ca^{2+} for the aggregation of suspended SWCNTs as a function of (B) SDBS and (D) SWCNT concentrations.

Conclusions

- Bulk SWCNTs could not be dispersed and stably suspended in water and SDBS solution by shaking at 140 rpm, although they can be stably suspended in SDBS solution by sonication
- Even through sonication, SWCNTs suspended in SDBS do not remain stable at the presence of environmentally relevant cations after dilution.
- Both SDBS and sonication play important roles in the dispersion of SWCNTs, with sonication breaking down large aggregates of SWCNTs, while SDBS adsorbed on the SWCNTs inhibits the coagulation and aggregation to maintain the stability of the suspension in water
- The re-aggregation of suspended SWCNTs in the presence of cations was dependent on the SDBS concentration rather than the SWCNT concentration in the suspension
- These observations suggest that SWCNTs will not travel long distances in significant concentrations in the natural environment