

Understanding the stability of nanoplastics in aqueous environment: Effect of ionic strength, temperature, dissolved organic matter, clay, and heavy metals

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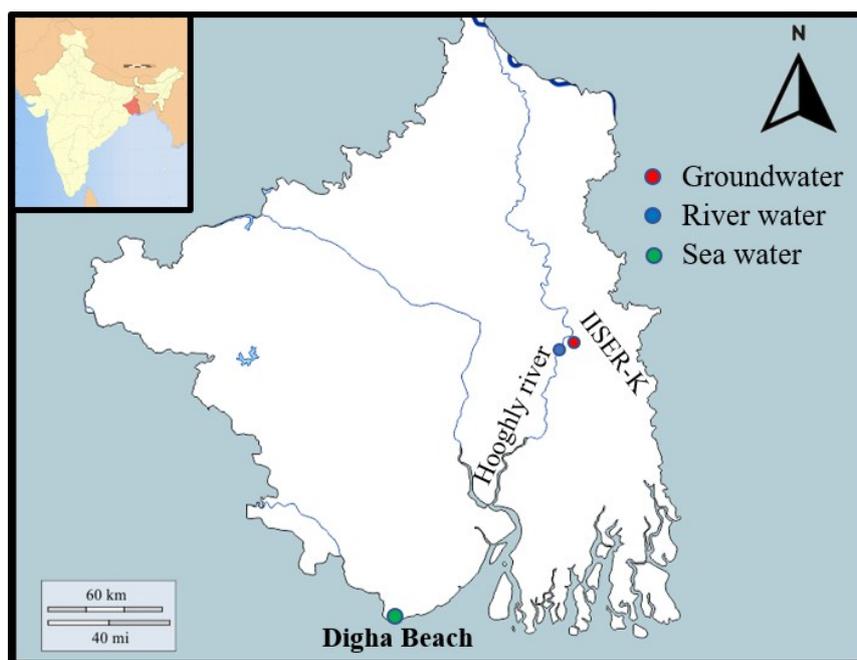


Figure S1: Map of sampling site for river-water, groundwater and seawater from Hooghly River, Indian Institute of Science Education and Research- Kolkata campus and Digha beach, West Bengal, India, respectively.

Table S1: Characteristics of water samples from Hooghly River, groundwater from Indian Institute of Science Education and Research- Kolkata and seawater from Digha, India.

Water parameter	River-water	Groundwater	Seawater
Location	22.9316 ⁰ N	22.9614 ⁰ N	21.3736 ⁰ N
	88.4092 ⁰ E	88.5180 ⁰ E	87.3159 ⁰ E
pH	8.4	7.3	8.3
Dissolved oxygen (mg/L)	7.4	--	10.1
TDS (mg/L)	255	538	36,000
Conductivity (μS)	430	890	--
TOC (mg/L)	1.90	3.33	4.89
Salinity (ppt)	--	--	20
Na⁺ (mg/L)	12.21	29.44	7777.31
NH₄⁺ (mg/L)	0.02	0.19	--
K⁺ (mg/L)	2.45	0.91	263.13
Mg²⁺ (mg/L)	5.33	22.58	673.36
Ca²⁺ (mg/L)	18.49	111.64	310.64
SO₄²⁻ (mg/L)	21	13	1,700
NO₃⁻ (mg/L)	2	3	--
Cl⁻ (mg/L)	25	32.5	14,500
HCO₃⁻ (mg/L CaCO₃)	75	275	250
Ionic Strength (M)	0.3 X 10 ⁻²	0.11 X 10 ⁻¹	0.48

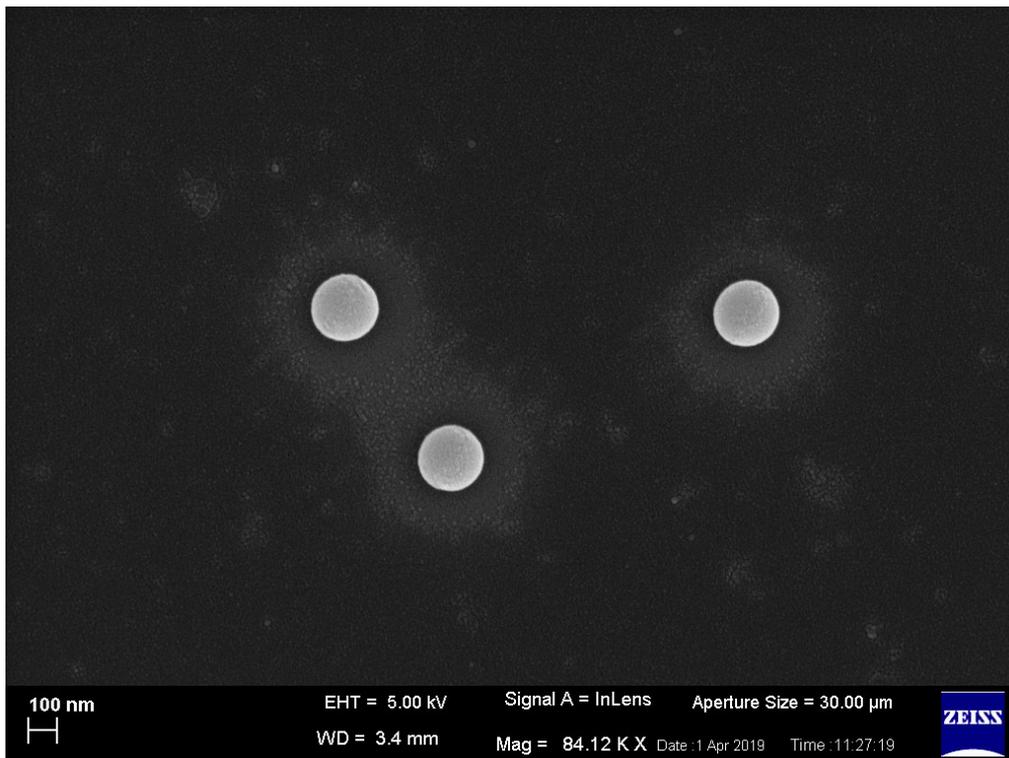


Figure S2: SEM images of polystyrene nanoplastics (PS NPs) representative.

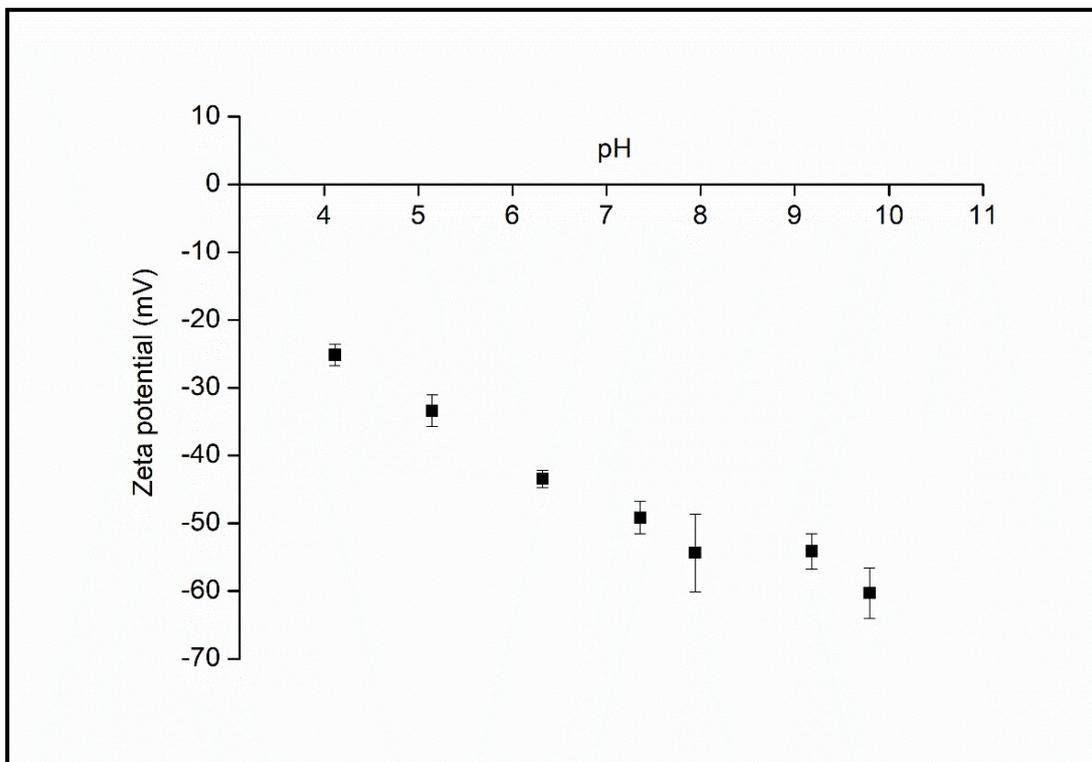


Figure S3: Zeta potential vs pH titration of PS NPs.

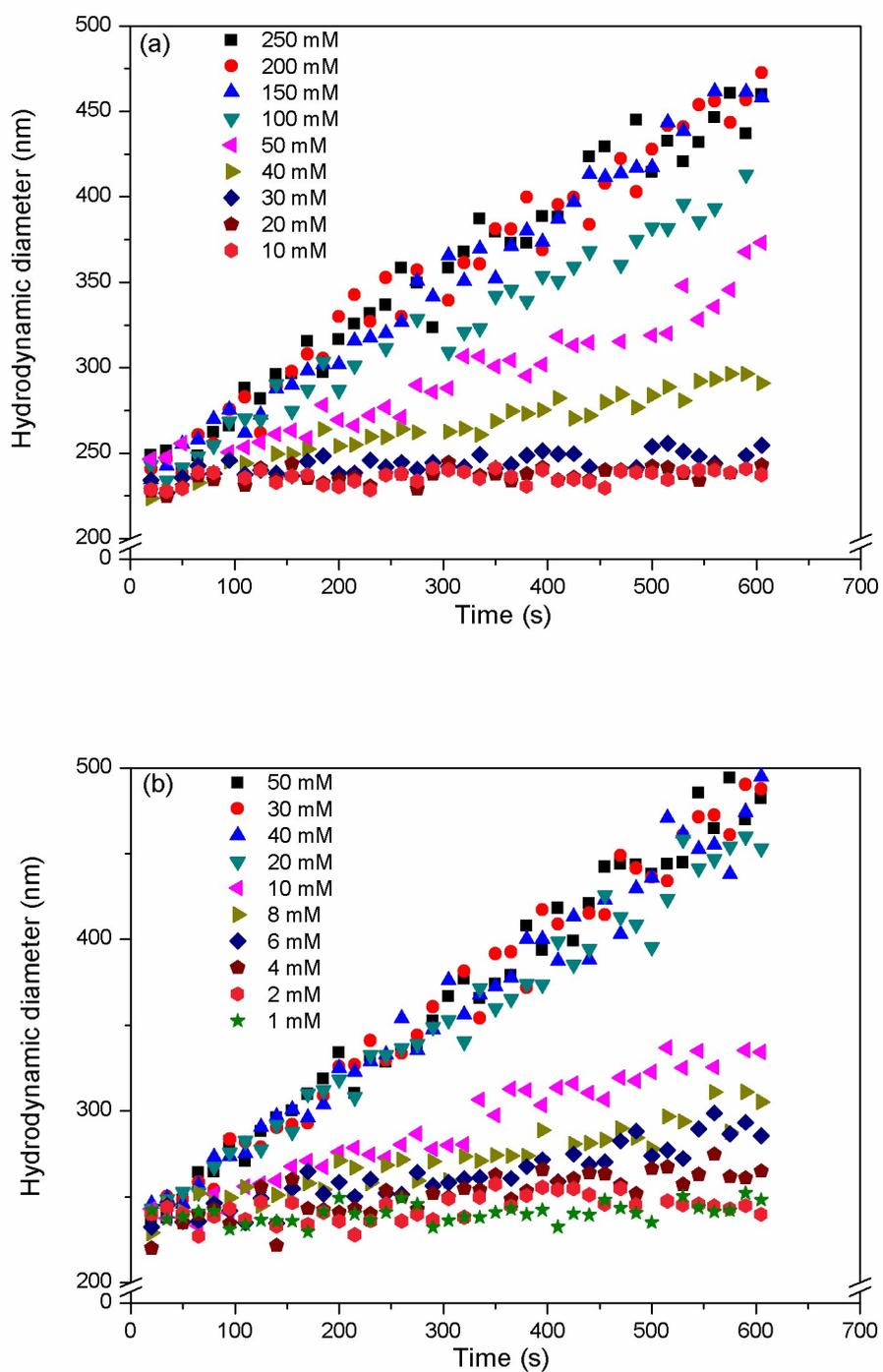


Figure. S4: PS NPs (10 mg/L) aggregation with varying salt concentration (a) NaCl and (b) CaCl₂ at pH 6 (T= 25°C).

DLVO interaction energy:

According to Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, the stability of the particles is governed by the sum of potential energy caused by the Vander Waals attraction and electrostatic repulsion experienced by the particles as a function of separation distance^{1, 2}. Therefore, PS NPs aggregation was evaluated theoretically by calculating DLVO interaction energy as a function of distance (h) which is given as the sum of electrostatic repulsion (V_D) and Van der Waals attraction (V_H)³.

$$V_T = V_D + V_H$$

$$V_H = \frac{-Ar}{12hk_B T}$$

where A is Hamaker constant (for PS NPs calculation it was taken as 0.8×10^{20} J)⁴, r is the radius of the particle, k_B is the Boltzmann constant and T is the absolute temperature.

$$V_D = \frac{2\pi\epsilon_0\epsilon r\phi^2 \ln\left(1 + e^{-h/\kappa^{-1}}\right)}{k_B T}$$

where ϵ_0 is the permittivity of vacuum, ϵ the dielectric constant of water, ϕ is surface charge densities, and κ^{-1} is Debye length which is given as:

$$\kappa^{-1} = \sqrt{\frac{\epsilon_0\epsilon k_B T}{2N_A q^2 I}}$$

q is the elementary charge; N_A is the Avogadro's number, and I is the ionic strength.

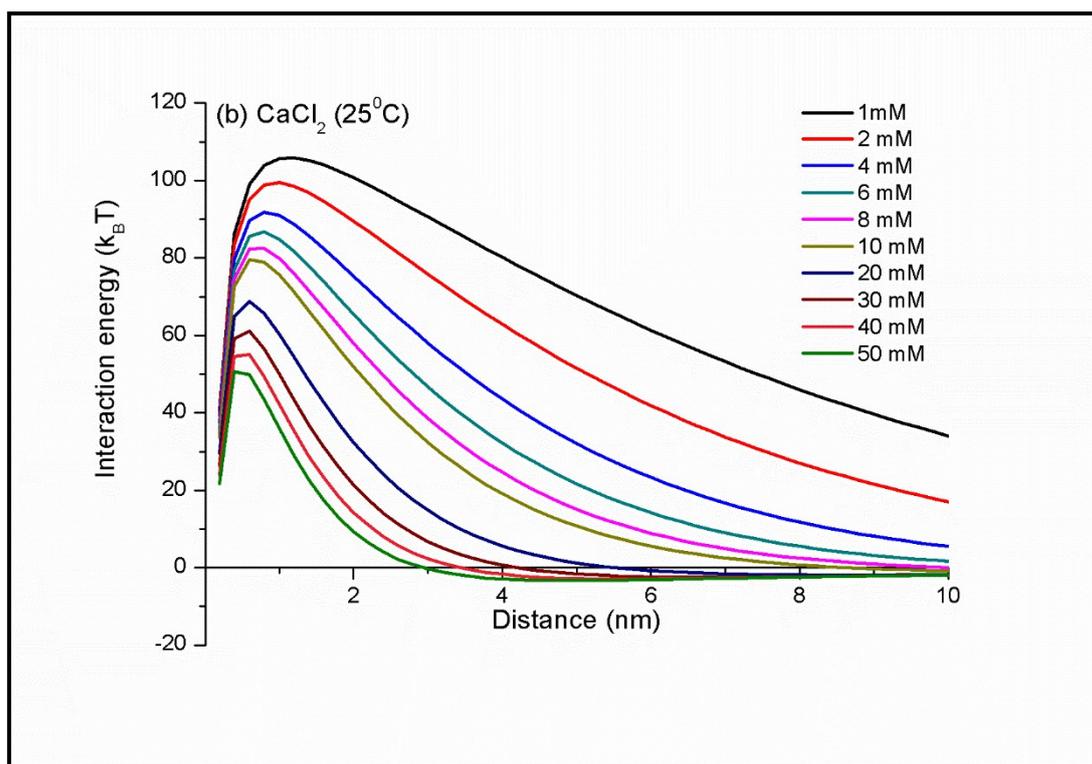
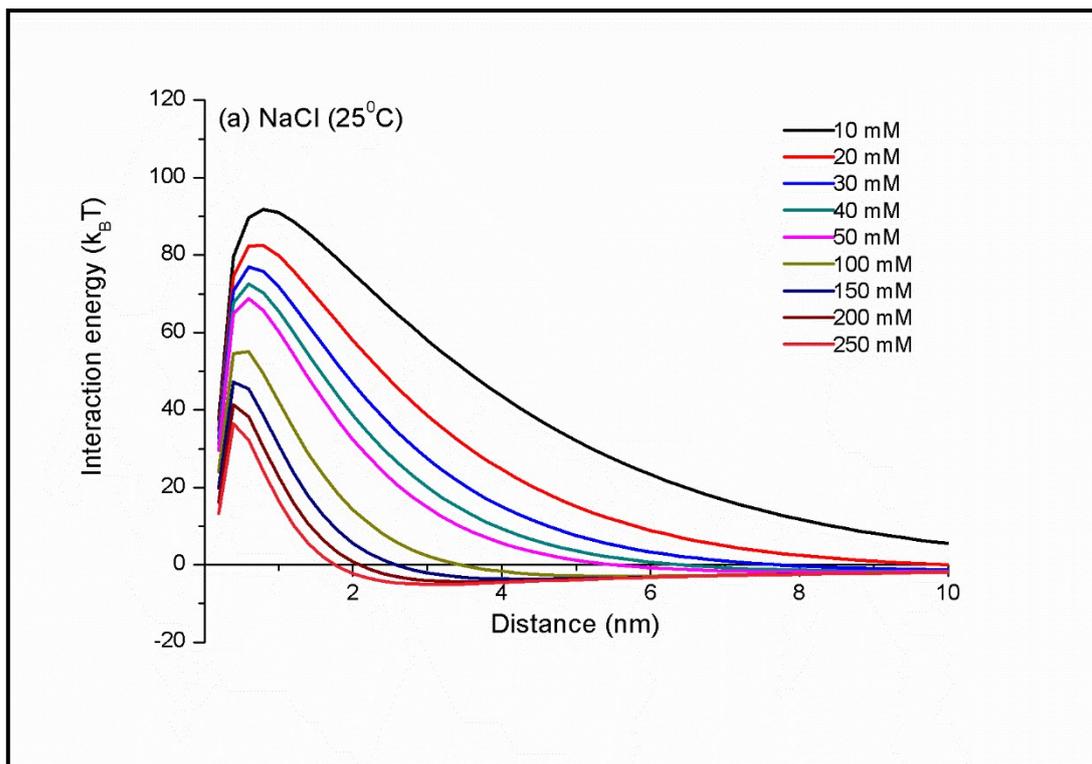


Figure S5: DLVO interaction energy profile as function of separation distance for PS NPs in presence of (a) NaCl and (b) CaCl₂ (T = 25°C).

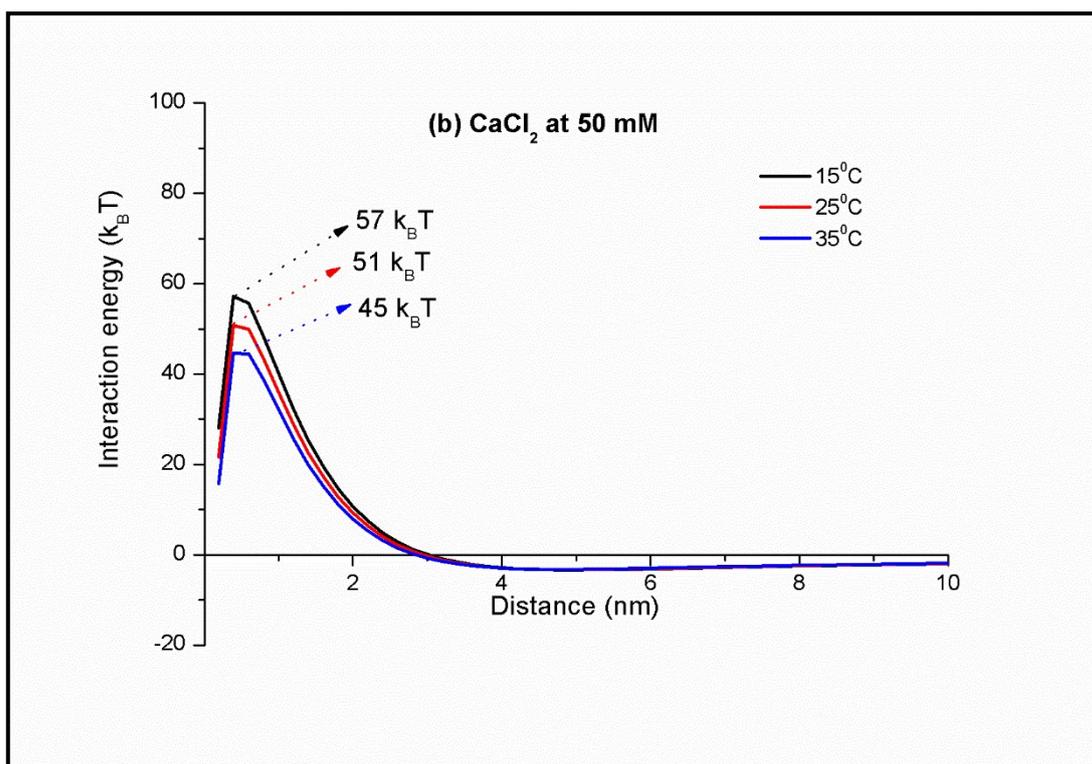
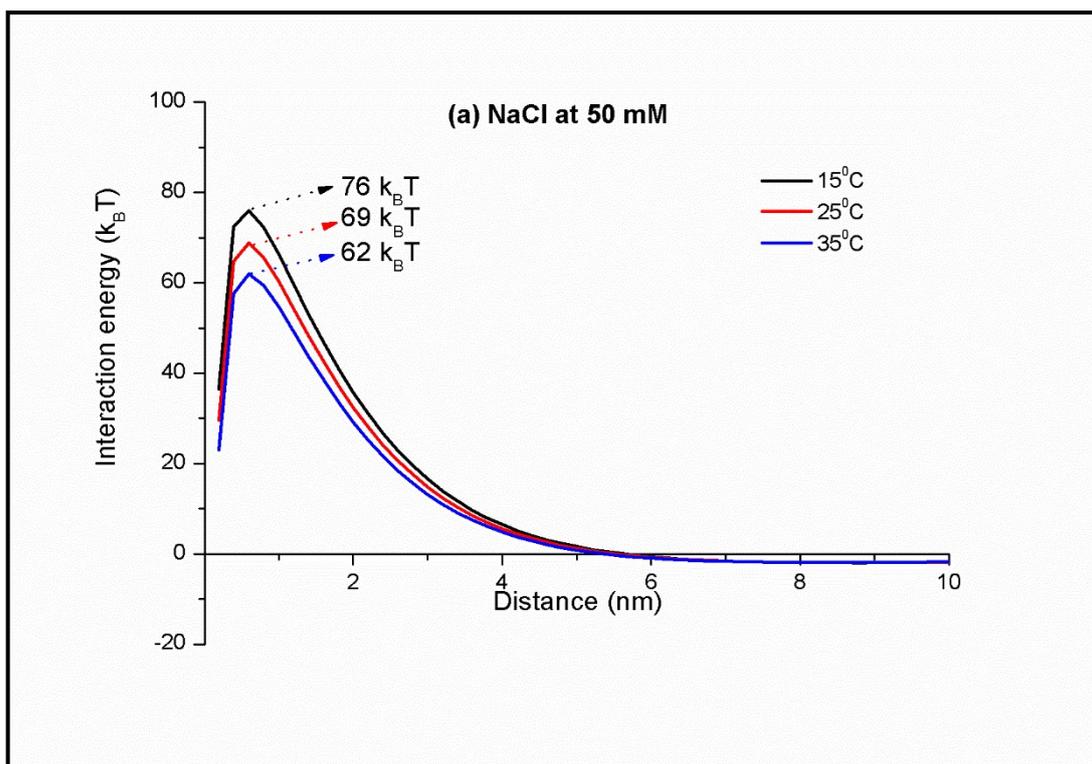


Figure S6: DLVO interaction energy profile as function of separation distance for PS NPs in presence of 50 mM (a) NaCl and (b) $CaCl_2$ at varying temperature ($T = 15^\circ C, 25^\circ C$ and $35^\circ C$).

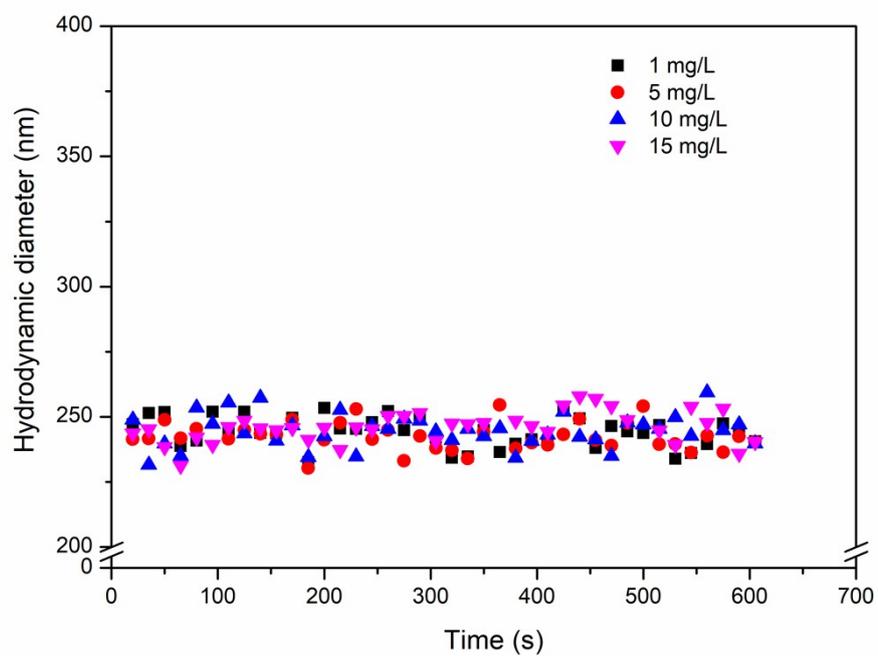


Figure. S7: PS NPs (10 mg/L) with humic acid (concentration 1, 5, 10, 15 mg/L) at pH 6 (T= 25°C).

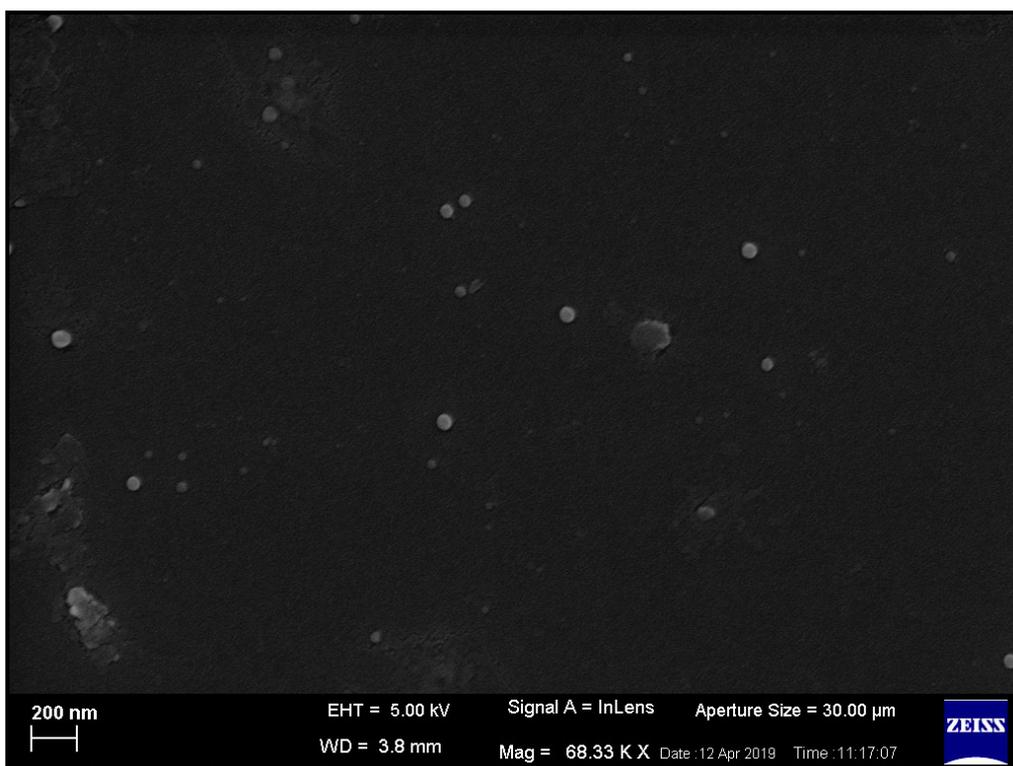


Figure S8: SEM image of bentonite clay colloids.

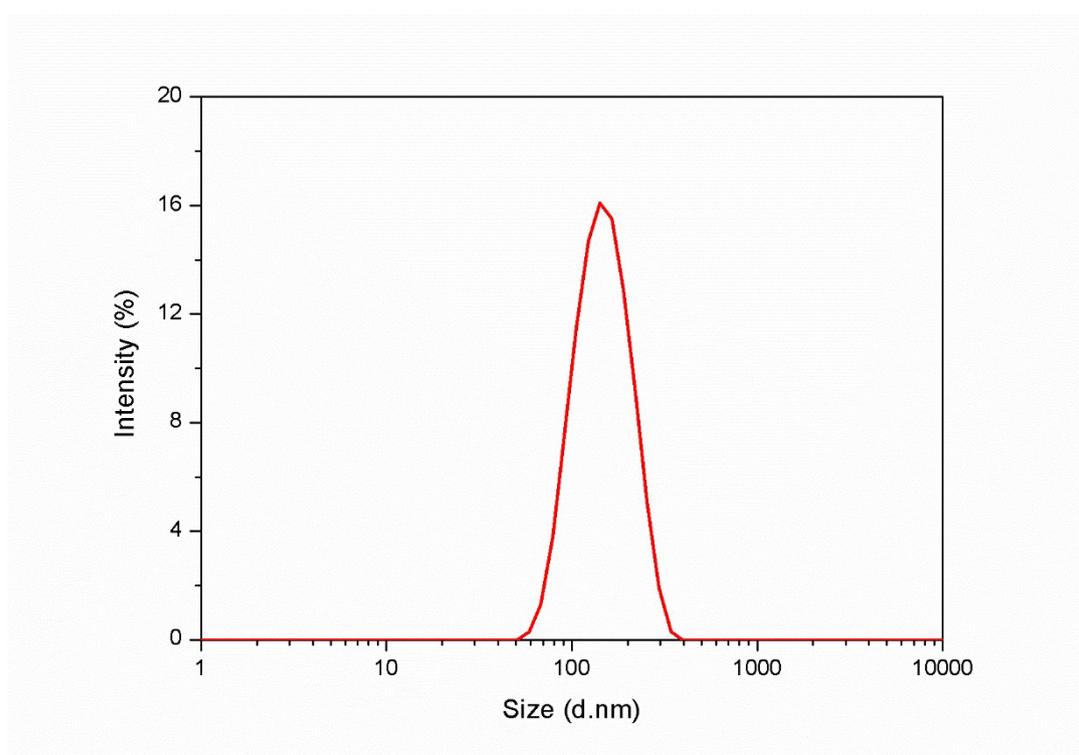


Figure S9: Bentonite clay colloids size distribution (by intensity) using DLS technique.

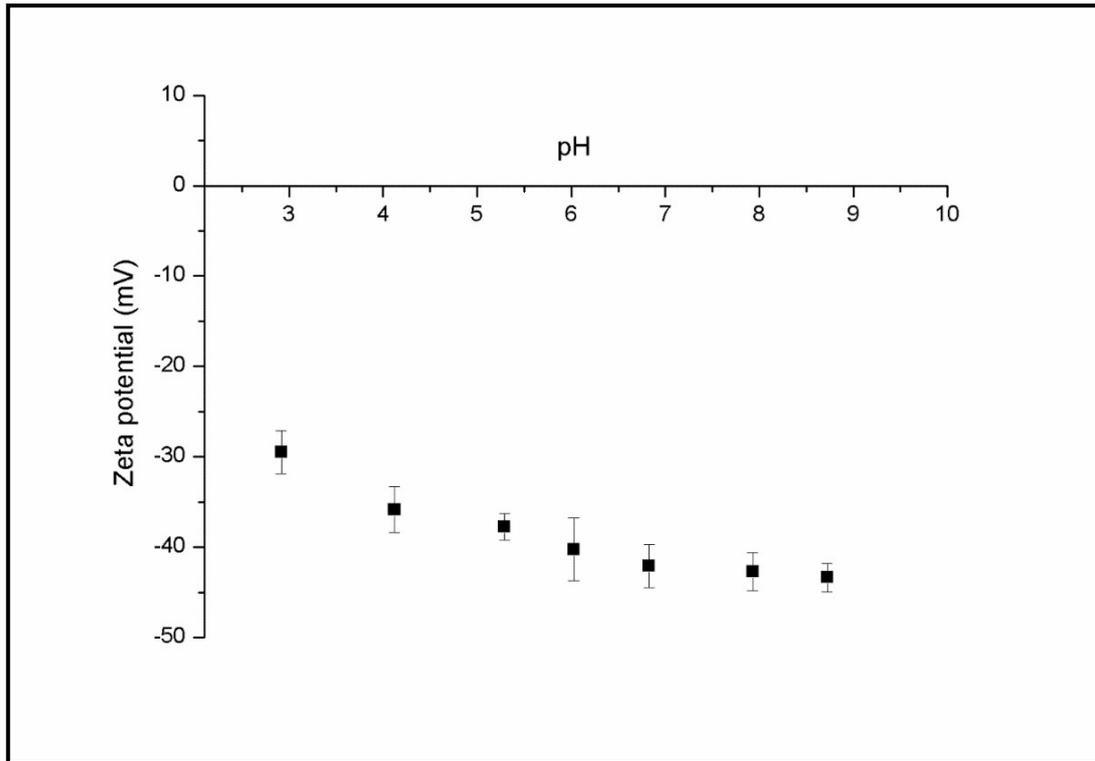


Figure S10: Zeta potential vs pH titration of bentonite clay colloids.

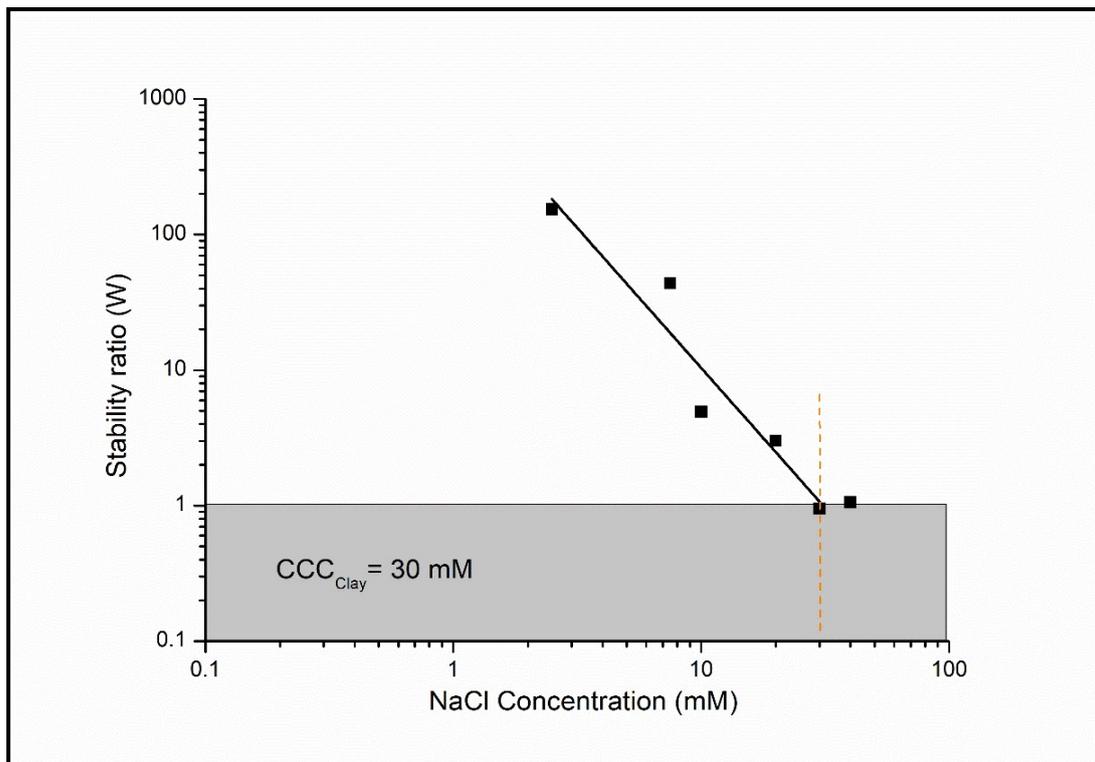


Figure S11: Bentonite clay colloids stability as factor of ionic strength.

Sample preparation for cryo-TEM

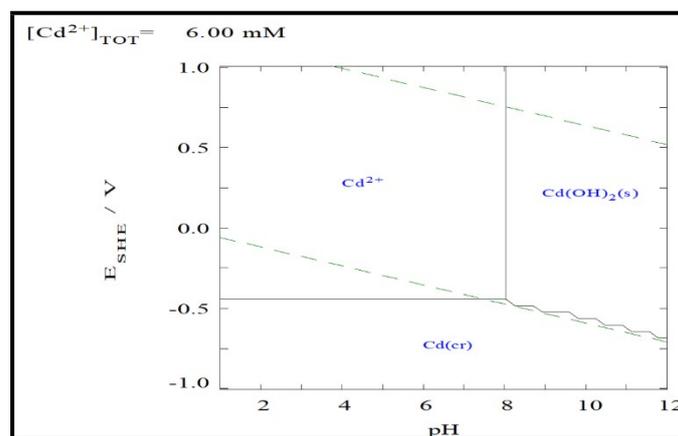
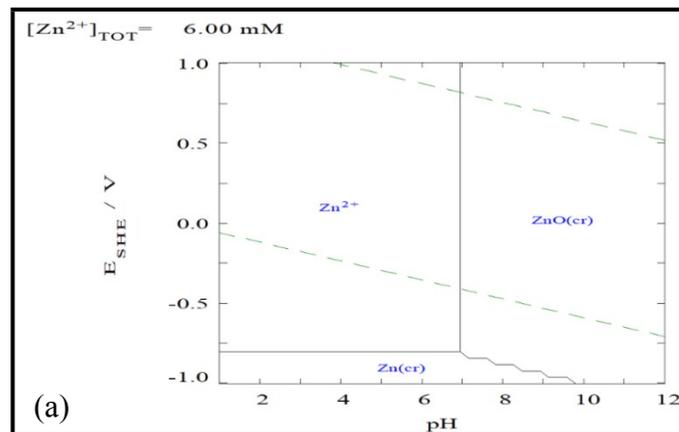
To investigate heteroaggregation of PS NPs with bentonite clay colloids, cryo TEM was performed. A drop of PS NPs (10mg/L) and bentonite clay colloid (50 mg/L) in presence of NaCl (40 mM) mixture was placed onto the carbon coated 300 mesh copper grid. The excess solution was removed using blotting paper. The grid containing sample was plunged into liquid ethane. The grid was placed onto cryo holder that was finally placed into the TEM instrument and imaging was completed.

SEM imaging using lyophilised samples

The PS NPs (10 mg/L), bentonite clay colloid (50 mg/L) and NaCl (40 mM) 4ml mixture was lyophilised (FreeZone - Labconco) at -84°C and vacuum ranging between 0.028 to 0.08 mBar. The freeze-dried sample powder was used to obtain SEM images.

Eh-pH Speciation modelling of heavy metals

Unlike commonly present ions like- Ca^{2+} , Na^+ and Mg^{2+} , metal ions generally have higher ionic potential and change in environmental parameters alter their speciation. For example- below pH 7, zinc is in +2 form while can speciate in zinc hydroxide in alkaline condition. A considerably different scenario can be observed in case of mercury (Hg) which remains in elemental form in relevant environmental conditions. The speciation can change the aggregation behaviour of NPs in the aqueous environment. Therefore, to calculate Eh-pH speciation of the metal ions, MEDUSA-HYDRA software was used. Utilized metal ions concentration i.e. 6 mM was provided as input in HYDRA to obtain all the possible complexes. Further MEDUSA was used to get the graph for various species of metal ions in a range of Eh and pH.



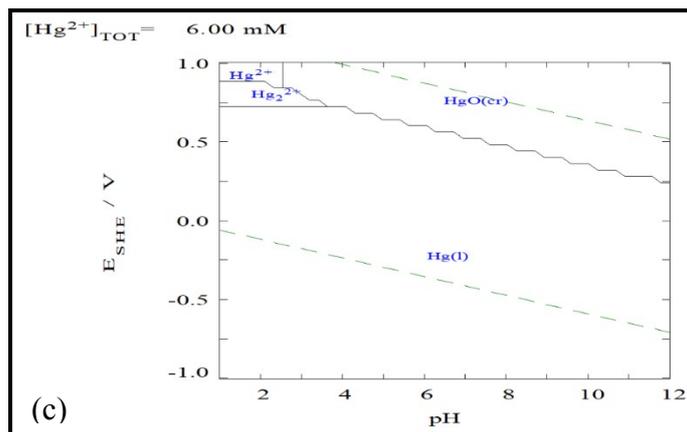


Figure S12: Speciation diagram of (a) Zinc II (b) cadmium II (c) Mercury II at 6 mM.

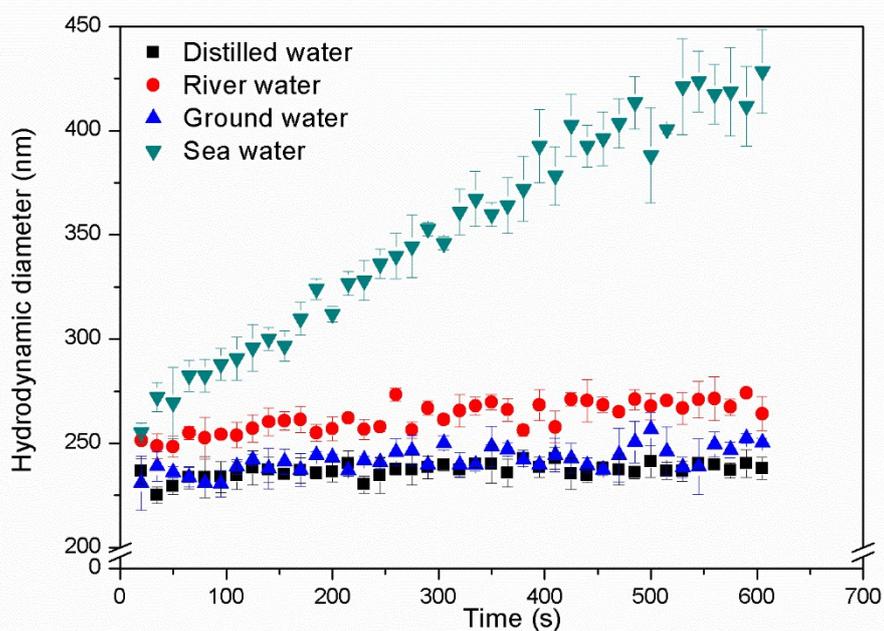


Figure S13: Rate of aggregation of PS NPs (10 mg/L) in RW, GW and SW at 25°C.

References

1. E. M. Hotze, T. Phenrat and G. V. Lowry, *Journal of Environmental Quality*, 2010, **39**, 1909-1924.
2. F. Babick, in *Suspensions of Colloidal Particles and Aggregates*, Springer International Publishing Ag, Cham, 2016, vol. 20, pp. 75-118.
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