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# Surface Modification of SiO<sub>2</sub> Nanoparticles to increase Asphaltene Adsorption

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## Abstract

The use of nanoparticle as asphaltene sorbent is a subject of great interest in the oil industry due to their usability in different steps in the crude oil processing. Nanoparticles of metals and nonmetals oxides as Fe<sub>2</sub>O<sub>3</sub>, NiO, SiO<sub>2</sub>, etc have been used for enhanced oil recovery, deasphalt or directly in crude oil as catalyst, finding a strong dependence of adsorptive properties and activity with the size and composition of the nanoparticles. Characteristics as hydrophobicity, net charge and polarizability of the nanoparticle could modify the affinity of the nanoparticles to different molecules present in the media, in our case to asphaltenes dissolved in non-polar organic solvents. Modification of nanoparticle surface producing changes in their activity by adsorbing different

molecules has proved to be a suitable way to change their interaction with specific molecules improving the affinity and doing more specific. This work present results in the use of surface modified silica nanoparticles ( $\text{SiO}_2$ ) to increase the asphaltene adsorptivity.  $\text{SiO}_2$  nanoparticles were modified by wet impregnation method with three different molecules. Chitosan ( $\text{SiO}_2\text{Q}$ ), Carboxymethyl Cellulose ( $\text{SiO}_2\text{CMC}$ ) and Polyethylene Glycol 200. ( $\text{SiO}_2\text{PEG}$ ). Surface modified nanoparticles showed an enhanced in the absorptivity compare with a raw nanoparticle. Kinetics and thermodynamic experiments were done showing a preferential interaction of the modified nanoparticles with the smallest asphaltene nanoaggregate generating a competitive process diminishing asphaltene aggregation.

## INTRODUCTION

Asphaltenes is considered the most aromatic and polar fraction in the crude oil. This fraction has been defined, in terms of solubility, as the fraction of crude oil insoluble in paraffin of low molecular weight (*n*-heptane). The adsorption of asphaltenes on solids is the result of favorable interactions of the asphaltene species or its aggregates with chemical species on or near to the mineral surface, different interaction forces, individually or in combination can be responsible for it. The adsorption onto surface depends strongly of the nature of the solvent and concentration of asphaltenes in the solution due to the aggregation tendency of the asphaltenes<sup>1-5</sup>. The major forces, which contribute to the adsorption process, include electrostatic (Coulomb), charge transfer, van der Waals, repulsion or steric interactions and hydrogen bonding. Since asphaltenes are a complex mixture of compounds the forces responsible for the adsorption or interaction with solvent the use of appropriated sorbent could help to subdivide the asphaltenes in fractions. Recently Adams<sup>6</sup> publish a well documented review about Asphaltenes adsorption, including the effect of sorbent nature, solvent and temperature, in this review clearly is observed the complexity of the phenomena and the influence of these variables in the adsorption process.

The liquid phase adsorption is, in general, a very complex phenomenon; in the case of asphaltenes, the formation of molecular aggregates in solution and posterior adsorption competes with low molecular weight species adsorption and could be interpreted as multilayer adsorption. Molecular interaction could induce aggregation, multilayer formation or adsorption onto surfaces, these process occur simultaneously in the media and contributes to the complexity in results interpretation. Castro et al<sup>7</sup> reported studies related to the prediction of adsorption isotherms of asphaltenes on porous surfaces, their develop a molecular thermodynamic approach for modeling of adsorption isotherms of asphaltene adsorbed on Berea sandstone, siltstone, bedford, dolomitic limestone rock and using a mathematical model for asphaltene precipitation and approach to quasi two-dimensional confined liquids. The authors applied the classical thermodynamic model for describe asphaltene adsorption and fit experimental data with theoretical models. In the used macro surfaces experimental results indicate the tendency of asphaltenes to Langmuir-type adsorption isotherm.

Adsorption of asphaltenes onto various minerals at nano scale has been the subject of many research works.<sup>1,2,6,8-11</sup> Nassar and co-workers have been done an extensive work in asphaltene adsorption onto different nanoparticles<sup>12-15</sup>. In these works, they report a Langmuir behavior in the adsorption thermodynamic with a maximum asphaltene adsorption in a range between 20 to 130 mg/g depending on nanoparticle composition. In other experiments and varying the properties of the media they could increase the maximum adsorption until 3 times due the changes in the asphaltene-asphaltene interaction and asphaltene-solid interaction by variations in the solubility

properties of the media. The adsorption capacity of nanoparticles in general is associated with size and composition. Additionally the tendency of nanoparticles to induce aggregates formation and adsorb it, could enhance the adsorptive capacity<sup>11,16-18</sup> of the nanoparticles showing a complex adsorption kinetics behavior.

Nanoparticle surface modification<sup>19-23</sup> is used to change the surface properties of the nanoparticle, and the interaction forces with solvent or particular molecules present in the media. Using different molecules, the surface of nanoparticle could be modified to change the wettability, acidity, interfacial tension or enhanced interaction with specific molecules present in the media. Several authors<sup>24-30</sup> have been employed surface modified nanoparticles to induce emulsion formation or break emulsions, by varying the surface activity and wettability of nanoparticles surface. This capability of the nanoparticles to change radically their properties could be used to enhance their adsorptive capability. In this work we produce SiO<sub>2</sub> nanoparticles (NPS) and modified their surface with three different molecules (Carboxymethyl Cellulose, Chitosan and Polyethylene Glycol 200) in order to enhance the adsorptivity of the NPS. and promote the adsorption of different kinds of components of asphaltenes. Based in the hypothesis that some sub fractions in the asphaltenes contribute preferentially with the aggregation, using nanoparticles with appropriate specificity to these sub fractions it's possible to diminish the aggregation and keep the asphaltenes well dispersed in the media. Kinetics experiments were done showing the low effect of asphaltene aggregation in solution in the adsorption. Equilibrium kinetics showed a linear increment with a saturation regime clearly as result of the increment in the interaction forces and adsorptive capacity of the functionalized surfaces.

## **MATERIALS AND METHODS**

### **Materials**

Materials required for the synthesis of nanoparticles, surface modification, and asphaltene precipitation are described as follow. Tetraethyl Orthosilicate (TEOS 98%), Ammonium hydroxide solution 31.5% (NH<sub>3</sub>), Absolute ethanol 99 %, Polyethylene Glycol 200 (PEG), Carboxymethyl Cellulose, Toluene, Tetrahydrofuran anhydro, Absolute ethanol 99 %, Acetic Acid glacial (100%) were obtained and used as received from the Aldrich Company. Chitosane was extracted from crustacean shells by the methodology proposed by Zhao et al<sup>31,32</sup> , in brief removal of proteins and the dissolution of calcium carbonate present in crab shells in high concentration permit the extraction of chitin. The resulting chitin is deacetylated in 40 % NaOH at 120 °C for 1-3 h. This treatment produces 87 % of deacetylated chitosan

### **Asphaltene precipitation**

Asphaltenes were precipitated from Furril Crude oil, a 21 API gravity medium crude oil, with 3.5% of asphaltenes, by a well-known method using a 40:1 heptane toluene mixture. The asphaltenes were washed three times to remove remain resins. Solutions were prepared by dissolving a desired amount of the asphaltenes in toluene.

## Nanoparticle Preparation

Silica nanoparticles were prepared by hydrolysis and condensation of TEOS in ethanol, and in presence of ammonia using a variation of the methodology proposed by Ismail et al<sup>33</sup>. First, solution containing appropriate quantities of absolute ethanol, ammonia and deionized water were stirred for 5 minutes to ensure complete mixing. Then a proper amount of TEOS in absolute ethanol was added to the above solution and the reaction proceeded at ambient temperature for 24 hours.

The surface of SiO<sub>2</sub> nanoparticles were modified by wet impregnation method, three different molecules were used, Chitosane (SiO<sub>2</sub>Q), Carboxymethyl Cellulose (SiO<sub>2</sub>CMC) and Polyethylene Glycol 200 (SiO<sub>2</sub>PEG). In each case 0,3 gram of nanoparticle were dispersed in 10 mL of 2000 ppm of each solutions and agitated with magnetic stirrer at 300 rpm for 36 hours at 40 C. After this time the solution was centrifuged at 5000 rpm to separate the nanoparticle from the solution and washed 3 times. Modified nanoparticles were dried at 110 C for 48 h and keep in a closed vial until use.

Nanoparticle size distribution was obtained by measuring a 0.02 wt % dispersion of nanoparticles in water in a homemade Dynamic Light Scattering (DLS) Instrument. Before measurement, nanoparticles solutions were passed through a 0.8 μm PTFE membrane filter. Thermo Gravimetric Analysis (TGA) of the nanoparticle dry powders were carried out under N<sub>2</sub> atmosphere at a heating rate of 10 °C/min up to 700 °C (Universal V4.5A, TA Instruments, U.S.A.)



## Adsorption Experiment

Batch adsorption experiments were carried out by mixing 10mL of asphaltenes solutions of different concentrations with fixed amount of approximately 0,3 grams of desired nanoparticles. The vials were sealed and left in a closed chamber saturated with toluene vapor at 25 C. The samples were shaken periodically to ensure reach adsorption equilibrium. After desired time the mixture is centrifuged at 5000 rpm to separate the nanoparticles from the liquid phase. The adsorption of asphaltenes onto nanoparticles was followed by the change in the concentration of solutions. UV-vis spectra were measured with a Ocean Optics USB2000 instruments with a 0.2 cm path cell. Absorbance at 550 nm was taken to avoid saturation at high concentrations. Calibration curve at this wavelength was done to establish the relationship of absorbance with a concentration in the range from 10 to 1000 ppm, this range assure a low preeminence of aggregates in the media.

The adsorbed amount of asphaltenes onto nanoparticle mass,  $Mads$  (mg/g), was calculated using the mass balance in eq 1

$$Mads = \frac{(C0 - Cs(t))V}{m} \quad (1)$$

where  $V$  is the sample volume (L),  $C0$  is the initial concentration of asphaltenes in the solution (mg/L),  $Cs(t)$  is the concentration of asphaltenes in the solution at a given

time,  $t$  (mg/L), and  $m$  is the mass of the nanoparticles (g). When the system reaches equilibrium,  $Mads_{eq}$  can be estimated from eq 1 by replacing  $Cs(t)$  with  $Ce$ , where  $Ce$  is the liquid equilibrium concentration

## RESULTS AND DISCUSSION

### Nanoparticle Characterization

A representative Scanning Electron Microscopy (SEM) photograph and the corresponding particle size intensity distribution histogram are depicted in Fig. 1a and b respectively. The DLS size intensity distribution plot shown a principal mean particle diameter at 20 nm with a half-width of 10 nm, which is not very different from the estimation obtained by SEM. A second maximum in the distribution with lower intensity appear at 200 nm attributed to few aggregates of nanoparticles, these aggregates are collections of smaller particles. This second peak can be understood with the stated in previous works<sup>34</sup> the intensity distribution has a nonlinear dependence with the size and low concentrations of relative big particles could show relative high intensity distribution values.

After the nanoparticle surface modification, the size intensity distribution shift to higher mean diameter, due to recovering of the nanoparticles with the modifier increasing the mean size in few nanometers. To evaluate the recovering of nanoparticles for the different compounds, thermogravimetric analysis (TGA) were done and are presented in Fig. 2 for SiO<sub>2</sub> (A), SiO<sub>2</sub>Q (D), SiO<sub>2</sub>CMC (B) and SiO<sub>2</sub>PEG (C) showing the capping effectivity of the method for the different modifiers. For pure SiO<sub>2</sub> (line A) the TGA curve

shown one step of 4% of decay starting at temperatures lower than 100 C this decay is due principally to release of occluded water in the mesoporous structure of the nanoparticle. For SiO<sub>2</sub>Q (line D) the TGA curve of the chitosan-silica composite is characterized by the decomposition region from 30°C to 200°C correspondent to water desorption followed by slow decomposition of the organic part of the composite adsorbed in the surface of the nanoparticle with a diminishing of 15% in mass. TGA curve for SiO<sub>2</sub>CMC (line B) and SiO<sub>2</sub>PEG (line C) shown a decay profile from 70 to 600 C mainly originates from the progressive desorption of the adsorbed molecules with a diminishing of 11 and 8% respectively. The TGA mass loss in each sample is consistent with the adsorption onto the surface of Quitosane (average 10.000 MW), CMC ( 240,2 MW) and PEG (200 MW).

## Asphaltene adsorption onto nanoparticles

The kinetic mechanism for the adsorption process could be modeled by a pseudo-second order kinetics described by equation 2, the experimental data presented in Figure 3 were fitted by using this model.

$$Mads(t) = \frac{k_2 * Mads_{eq}^2 * t}{1 + k_2 * Mads_{eq} * t} \quad (2)$$

Where  $Mads(t)$  and  $Mads_{eq}$  are the amount of asphaltenes adsorbed onto functionalized  $SiO_2$  nanoparticles (mg/g) at any time  $t$  (h) and in the equilibrium.  $k_2$  is the rate constants of pseudo second-order adsorption. It is easily shown that this equation leads to a typical saturation curve similar to the usual Langmuir isotherm (L-type curve). The curve for  $SiO_2$  (D) reached the saturation regime ( $Mads_{eq}$ ) at maximum adsorption ration of 3 mg/gr of nanoparticles in 24 hours. For surface modified nanoparticles the saturation regime is reached at 5, 7 and 14 mg/gr for  $SiO_2$ PEG (C),  $SiO_2$ Q (B) and  $SiO_2$ CMC (A) respectively. This first result demonstrated the feasibility of the surface coverage to increase the amount of adsorbate onto the surface, additionally this result in the case of raw  $SiO_2$  nanoparticles is consistent with experiments previously reported by Acevedo et al<sup>1,35</sup> in their study of the asphaltene adsorption at low concentration regime. For a wide range of concentrations, they found a low surface adsorption for low concentration and the adsorption increase exponentially at high solutions concentration. This behavior at high concentrations is clearly related with the formation of aggregates in the solution and posterior adsorption of the aggregates onto surface, which increase the effective mass adsorbed. In our experiment we guarantee low asphaltene concentration in solution to diminish aggregation adsorption effect and promote the adsorption of smallest aggregates or low molecular weight subfractions present in asphaltenes. Using the surface modifies nanoparticles the adsorption of these low molecular weight subfraction is clearly enhanced.

Relative high asphaltene concentration (more than 200 ppm) introduce the aggregation in solution phenomenon simultaneously with adsorption, to study the influence of asphaltene concentration in solution, the same experiment was done for different initial

concentration and the data is fitting with equation 2. This experiment is directed to corroborate the hypothesis that nanoparticles could adsorb only a low molecular weight molecules present in the asphaltenes due the small size in the sorbent Figure 4 shown the plot of fitted values of  $Mads_{eq}$  vs concentration in equilibrium. For  $SiO_2$  nanoparticles a constant value for  $Mads_{eq}$  is showed, this behavior corroborate that only the adsorption of the smallest units of asphaltenes in solution is presented reaching the saturation at lowers values of adsorbed mass. For modified nanoparticles the  $Mads_{eq}$  increase with the initial asphaltene concentration, in contrast with raw nanoparticles, the surface modification induce an increment in the number of active sites available for adsorption in presence of the same quantity of molecules in the media and discarding aggregate adsorption. The polar active groups exposed in the modified nanoparticles showed a high affinity to asphaltenes and increase the adsorptivity.

## Adsorption Isotherms

When the solution reach the equilibrium, the approximated Langmuir model can be described by the following expression:

$$Mads_{eq} = Mads_{max} * \frac{K * Ce}{1 + K * Ce} \quad (3)$$

where  $Mads_{eq}$  is the amount of asphaltenes adsorbed onto the nanoparticles (mg/g),  $C_e$  is the equilibrium concentration of asphaltenes in the solution phase (mg/L),  $K$  is the Langmuir equilibrium adsorption constant related to the affinity of binding sites (L/mg), and  $Mads_{max}$  is defined as the monolayer saturation capacity, representing the maximum amount of asphaltenes per unit mass of nanoparticles for complete monolayer coverage (mg/g). The values of  $K$  and  $Mads_{max}$  for each system were determined by fitting the experimental data with equation 3. In Figure 5 the plot of experimental data fitted are depicted.

Results from the fitted values shown a good correlation for the  $SiO_2$ ,  $SiO_2Q$  and  $SiO_2CMC$ . The plot shown an enhancement in the interaction of modified nanoparticles compare with raw material, this effect is observed as a faster growing in the curve and an increment in the adsorbed mass at the equilibrium. For  $SiO_2PEG$  the model does not fit in the range of concentrations used may be due the slow interaction rate for this nanoparticles with the asphaltenes.

## **CONCLUSIONS**

Asphaltene adsorption onto  $SiO_2$  nanoparticles raw and with surface modifications were studied. The results showed an enhancement in the adsorptive properties of nanoparticles after surface modification. The magnitude of the enhancement depends strongly with the molecular properties of capping molecules for CMC a 10 times enhancement is achieved. A growing number of active groups in the capping molecules

enhance in the same way the adsorptivity of nanoparticles. The results shown that nanoparticles preferentially adsorb the smaller aggregates of asphaltenes reducing the tendency to aggregate in solution and subsequent adsorption of aggregates onto surface. This results shown the possibility to increment adsorptive capacities of nanoparticles by modifying their surface with adequate molecules. Additionally the results demonstrate that nanoparticles only adsorb a low molecular weight molecules present in asphaltenes, this fact have a great importance for the asphaltene stabilization in the crude oil.

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## FIGURES

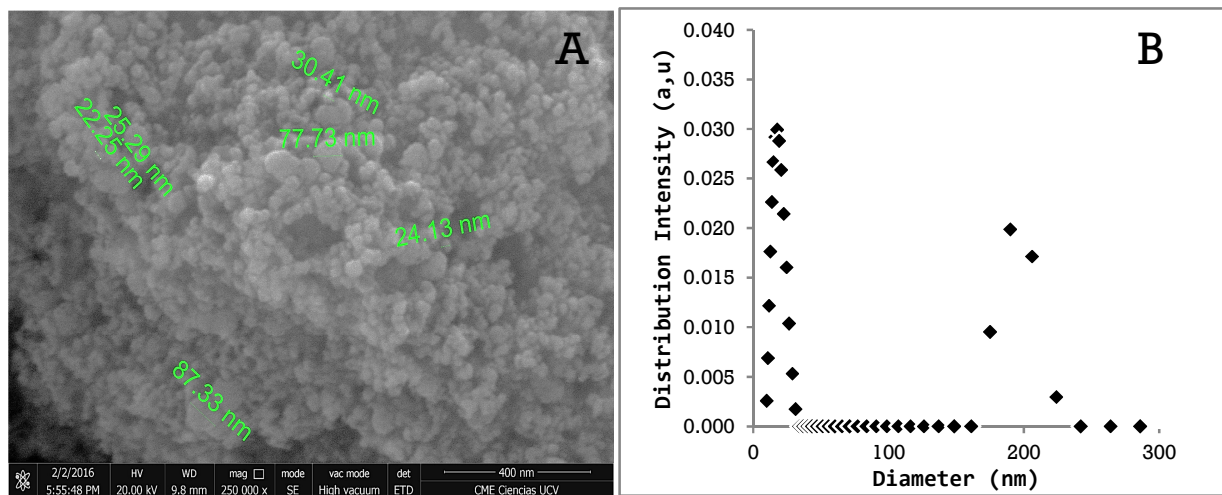


Figure 1. SEM image of SiO<sub>2</sub> nanoparticle (A) and DLS plot with size distribution Intensity (B).

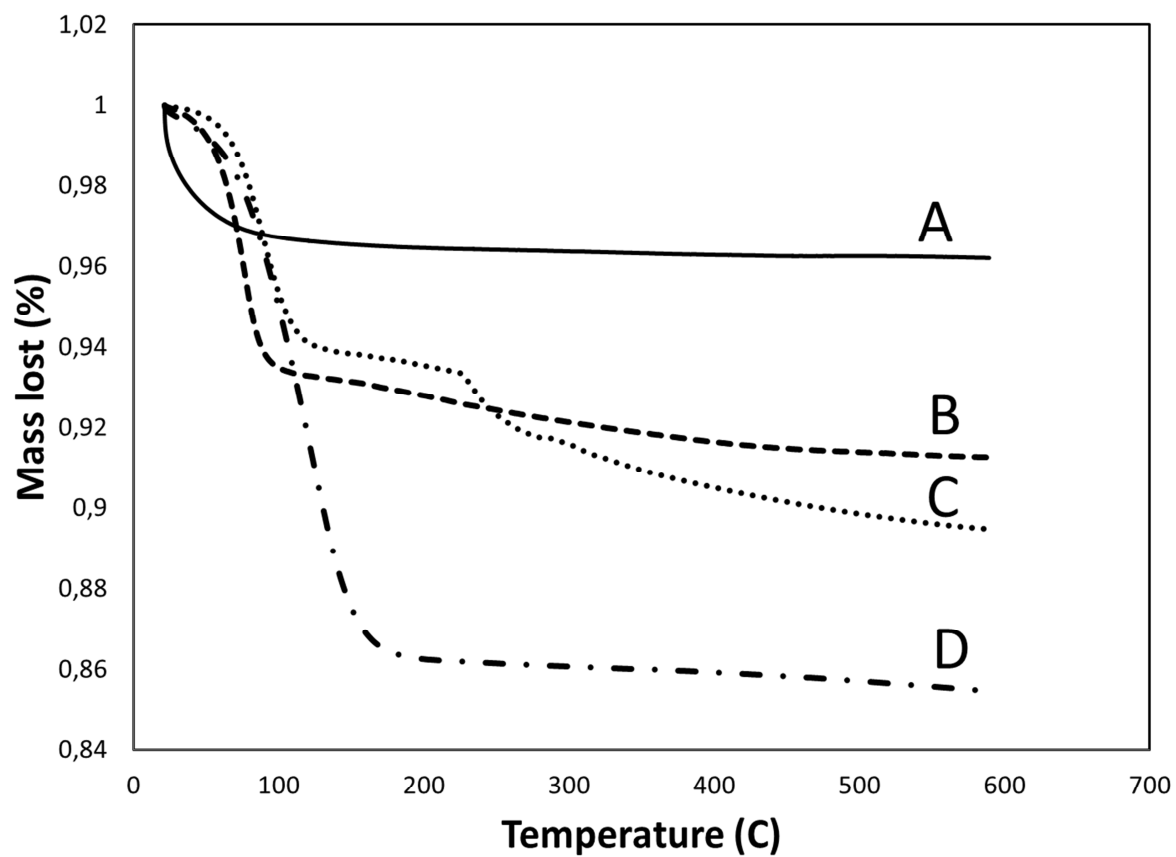


Figure 2. Termogravimetric analysis (TGA) for SiO<sub>2</sub> (A), SiO<sub>2</sub>CMC (B), SiO<sub>2</sub>PEG (C) and SiO<sub>2</sub>Q (D),

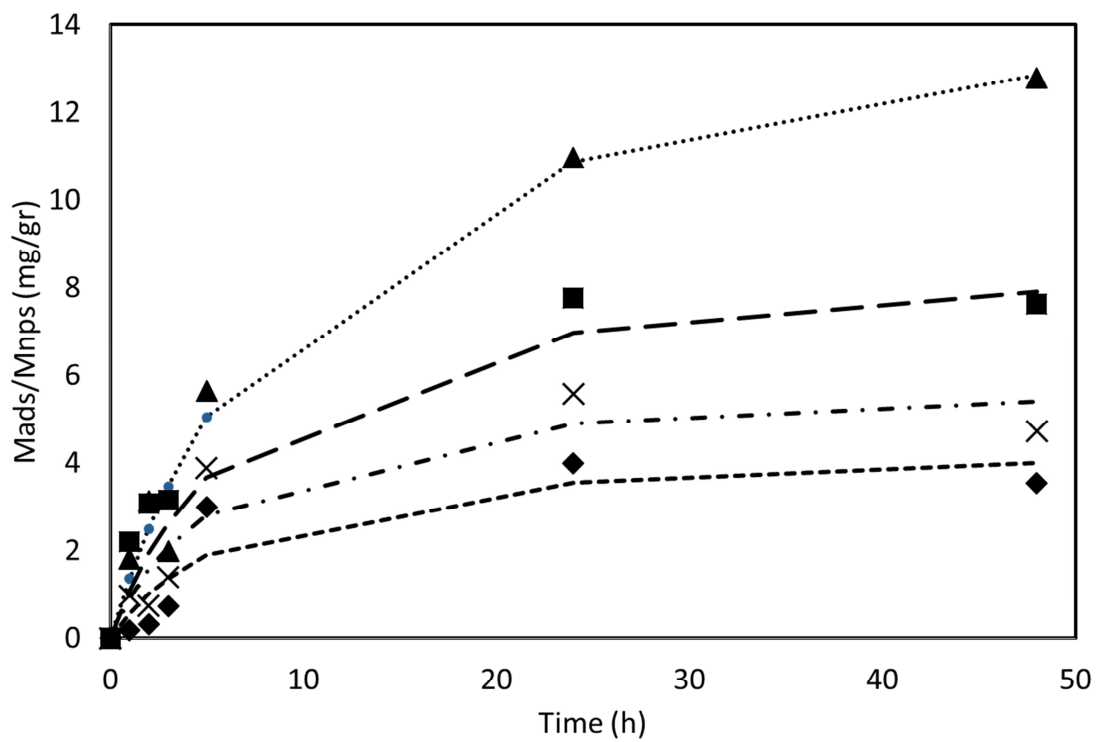


Figure 3.  $M_{ads}(t)/M_{ads\_eq}$  of asphaltenes vs time for different nanoparticles  $SiO_2$  (diamonds)  $SiO_2PEG$  (X),  $SiO_2Q$  (squares) and  $SiO_2CMC$  (triangles)

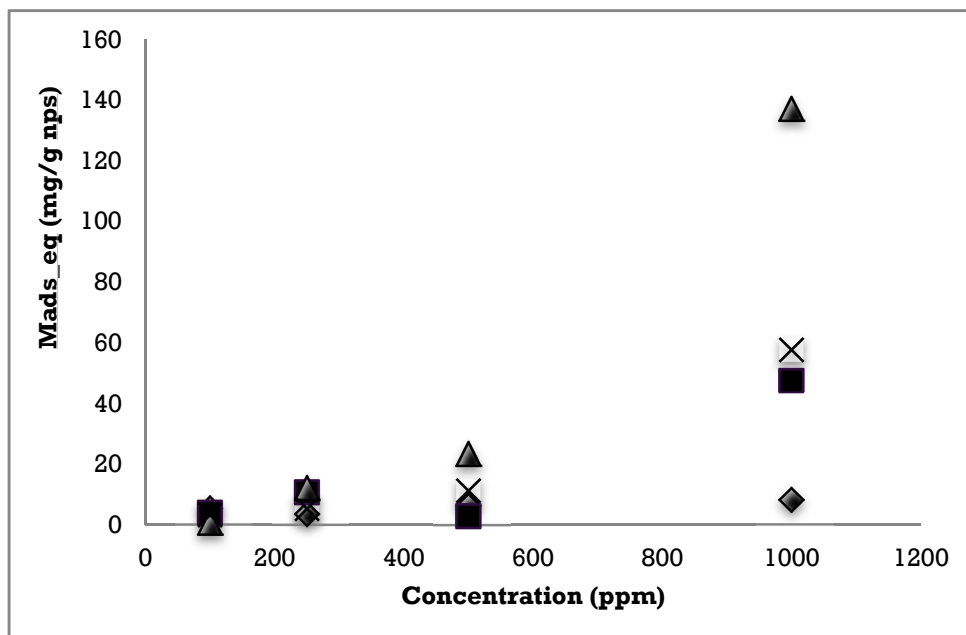


Figure 4. Plot of fitted values of  $Mads_{eq}$  vs concentration in equilibrium for SiO<sub>2</sub> (diamonds) SiO<sub>2</sub>PEG (X), SiO<sub>2</sub>Q (squares) and SiO<sub>2</sub>CMC (triangles).

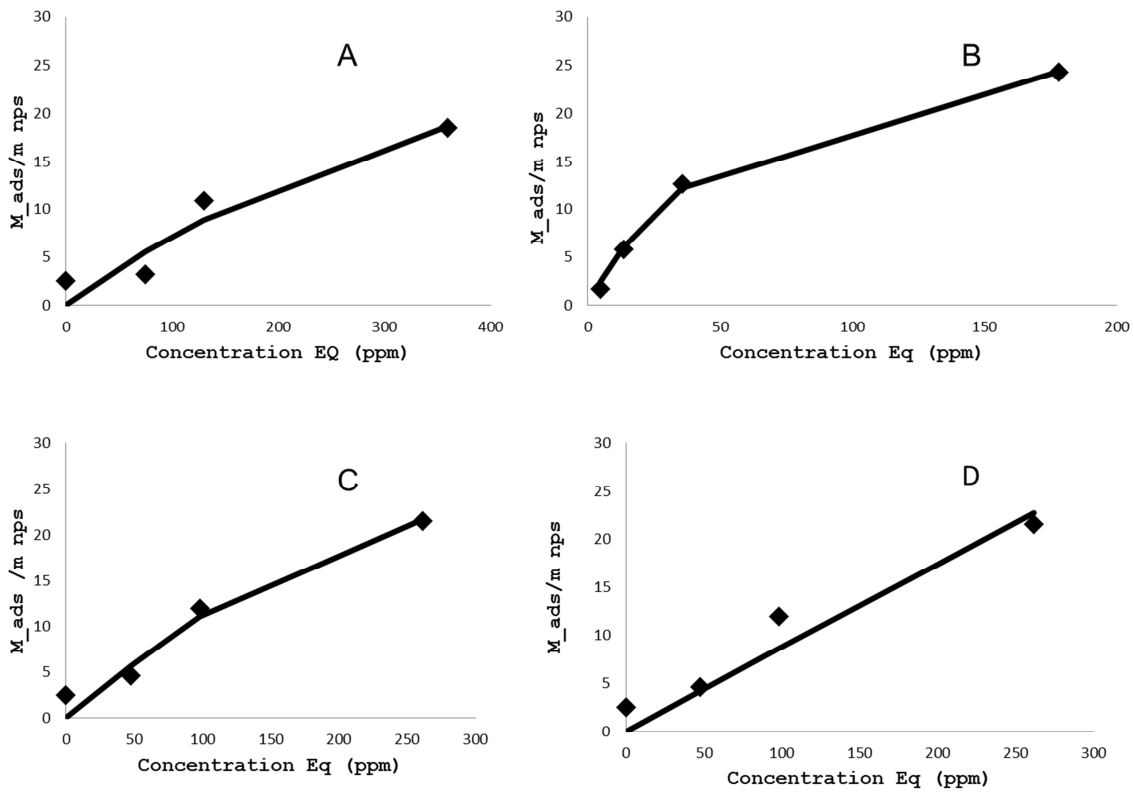


Figure 1. Plot of thermodynamic experimental data fitted with equation 3 for SiO<sub>2</sub> (A), SiO<sub>2</sub>CMC (B), SiO<sub>2</sub>Q (C) and SiO<sub>2</sub>PEG (D)