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CHEMICAL INHIBITOR ADSORPTION AND DESORPTION CHARACTERISTICS OF COMMON GRAVEL PACK SANDS UNDER STATIC AND DYNAMIC CONDITIONS

Adsorption of Chemical Inhibitors on Gravel Pack

Gbenga Folorunso Oluyemi

School of Engineering, Robert Gordon University, Aberdeen; AB10 1FR; UK

Phone: +44(0)1224262421; Fax: +44(0)1224262444; Email: g.f.oluyemi@rgu.ac.uk

Abstract

In fields or wells with active programmes of scale and corrosion management via chemical inhibitor injection, the performance of the injected chemical inhibitor species in terms of their adsorption and desorption characteristics is very crucial to the success of the chemical injection programme. Benchmarks for measuring inhibitor performance include rapid, relatively steep adsorption isotherms and slow, relatively less steep desorption isotherms.

The adsorption and desorption characteristics of three different pack sands taken as reservoir formation analogues were investigated using static and dynamic laboratory tests. Specifically the investigation focussed on petrophysical and grain parameters controls on adsorption and desorption characteristics of these sands.

Correlation of adsorption intensity with sand uniformity coefficient exhibited a direct relationship for the static model whilst it exhibited an inverse relationship for the dynamic model. Contrastingly correlation of adsorption strength with uniformity coefficient exhibited

an inverse relationship for the static model and a direct relationship for the dynamic model. Integration of correlation coefficients from the adsorption/desorption data with adsorption intensity, adsorption strength and adsorption capacity showed that Freundlich model was better suited to modelling the adsorption/desorption characteristics of the gravel pack sands.

Keywords: adsorption, desorption, chemical inhibitor, commercial pack sands, static and dynamic conditions

1.0 Introduction

Formation of scale minerals in reservoir formations and process systems is a common flow assurance related problem encountered in the oilfield. Scale formation and deposition in reservoir formations can cause significant permeability impairment and blockage of perforations and screen openings. In process systems and equipment such as tubings, pipes, valves, chokes pumps, separators etc., it can restrict flow and cause equipment malfunction. In extreme cases, it can cause complete shut-down of well and process equipment. Corrosion of downhole and surface process equipment is another flow assurance related problem which can lead to a total well shutdown. To deal with scale and corrosion problems, the oil and gas industry uses both reactive and preventative approaches. However in recent times there appears to be a substantial shift towards preventative approaches in dealing with the challenges posed by scale formation and deposition in formation and process systems. This is due to the increasing complexity of oilfield environments and the associated difficulties and cost of operating in these complex environments. The most common preventative approach to scale and corrosion mitigation uses chemical inhibitors squeeze treatment. Chemical inhibitor squeeze treatment involves dissolution of a chemical inhibitor in a carrier fluid and ‘forceful’ injection of the fluid stock into the producing formation rock through the production well in a staged process that includes pre-flush, main treatment, over-flush and well shut-in (Kerver,

1965; Kahrwad, 2008). The injected inhibitor adsorbs on the surface of the formation rock during the injection with substantial adsorption taking place during shut-in. The adsorbed inhibitor then desorbs into the produced formation water streams as the well is opened and put back on production, inhibiting scale formation by delaying mineral crystal nucleation and retarding crystal growth (Van Rosmalen, 1983; Kahrwad, 2008). This process is made possible by the attachment of the inhibitor molecules to active growth and nucleation sites of scale crystals (Patroni Zavala et al., 2008)

Evaluation and qualification of chemical inhibitors prior to field application is a common practice in the oil and gas industry. The basis for this practice is the fundamental belief founded on field experience which supports the notions that no one chemical inhibitor may work for two different fields or wells even when they appear to have similar formation and fluid characteristics; and that pre field application evaluation of chemical inhibitors should be conducted on a case by case basis.

Pre field application evaluation usually involves laboratory static and dynamic flow tests. With static tests, the compatibility of the chemical inhibitor and the reservoir fluid is determined whilst with dynamic tube blocking flow test, the minimum inhibitor concentration (MIC) of the chemical inhibitor is determined. Using formation rock core or its analogue as substrate in a core flood test the adsorption and desorption isotherms of the inhibitor-formation rock interactions are obtained. The usual criteria for evaluating chemical inhibitor performance on the basis of these tests are (see Figure 1):

1. Very rapid adsorption rate and high adsorption concentration during injection defined by steep adsorption isotherms
2. Very slow desorption rate and longer desorption time during well production defined by a relatively less steep desorption isotherms described as extended squeeze life. The

amount of adsorbed concentration released during the entire desorption process must represent a substantial percentage of the total adsorbed concentration.

3. A desorption isotherm maintained above the MIC for as long as possible to minimise the number of squeeze treatments applied over the field life.

How long the adsorbed inhibitor desorbs into production fluid streams in concentrations above the MIC depends on the adsorptive capacity, volume of treated formation and formation adsorption characteristics (Kerver, 1965).

A laboratory study conducted by Kerver (1965) on a range of real reservoir formation cores (using a corrosion inhibitor) has shown that clay mineralogies adsorb unusually large amount of inhibitor but desorb far lesser amount over a very long production time. The conclusion from this work was that inhibitor species adsorbed on clay are mostly irretrievable regardless of the length of production time. Gdanski and Funkhouser (2005) and Gdanski (2008) gave more direct laboratory evidence of adsorption and desorption characteristics of siderite (FeCO_3) and family of alumino-silicate minerals of which most clay mineralogies are members. The alumino-silicates minerals considered include quartz, feldspars, kaolinite and albite classified as silica-type surfaces; and muscovite, illite, smectite and chlorite classified as alumina-type surfaces. Evidence presented in these works appears to rank siderite as having better adsorption and desorption characteristics than the alumino-silicate group members. All silica-type surface minerals are believed to have low desorptive capacities except kaolinite; however, kaolinite release capacity is also believed to be very low. Whilst the alumina-type surface minerals have high adsorptive capacities, the strength of adsorption on their surfaces is relatively weak. The adsorbed inhibitor species may therefore be lost into the fluid streams as quickly as they are adsorbed. However, laboratory and field application evidence presented by Flemming et al (2008) appears to suggest that the presence of kaolinite

stabilised with a fixation agent in the reservoir rock can significantly enhance adsorption and desorption characteristics of reservoir rock.

Generally, by extrapolation, formation rocks with substantial natural clay mineralogies would appear to be good sites for excellent adsorption. However, to achieve longer squeeze life and keep the inhibitor concentrations above the MIC in reservoirs defined by these lithologies, more volume of inhibitor than necessary would be required. The key physical properties of clay minerals which define their adsorption and desorption characteristics appear to be their large surface area and pore size distribution. Their Large surface areas tend to promote their adsorptive capacities whilst their relatively low porosity (microporosity) tends to hamper their desorptive capacities. These properties can be applied in a similar fashion to evaluate the adsorption and desorption characteristics of sand. It does appear therefore that structural make up and petrophysical properties of the formation rock will be valuable for developing adsorption-desorption correlations.

In unconsolidated reservoir rocks producing substantial volume of sand, the eroding effects of moving sand particles and the changing petrophysical properties such as porosity, permeability, grain size distribution etc. may therefore affect adsorption and desorption characteristics of the formation. The eroding effects may strip the formation of the already adsorbed inhibitor species or reduce the surface area of sand available for adsorption causing reduction in the amount of adsorption. Similarly, the changing petrophysical properties may accelerate desorption faster than is required to keep inhibitor concentration above MIC.

Previous works have concentrated their focus on investigating chemical inhibitor performance in sand laden fluid transported via steel pipes (Ramachandran et al., 2004; Fielder, 2000). Binks et al. (2011) investigated how the effectiveness of corrosion inhibitor used to protect steel against corrosion was reduced by the presence of synthetic silica sand. By measuring the equilibrium adsorption isotherms of the inhibitor species on the steel and sand surface, they

were able to develop a quantitative correlation between sand concentration and surface concentration of inhibitor. Synthetic sand used in this study was 100% silica and may exhibit physical characteristics significantly different from real formation sand which in almost all cases would contain additional silicate minerals such as mica and feldspars. Fielder (2000) used both laboratory test and field evaluation and analysis approaches to investigate effects of suspended fines such as calcium carbonate and kaolinite on the adsorption and precipitation behaviour of phosphonate and polymeric scale inhibitors. Both solid laden and non-solid laden static and dynamic tests carried out revealed substantial impact of the suspended solids on the polymeric inhibitor performance. The study concluded that the suspended particles acted as competing alternative sites of inhibitor adsorption, competing with the rock surface for the inhibitor species in solution.

The current work is focused on qualitative and quantitative evaluation of the adsorption and desorption characteristics of common oilfield gravel packs. It is intended that this would help provide valuable inputs for enhanced optimisation of chemical inhibitor injection programme in wells with gravel pack completions and allow for integration of chemical inhibitor performance into the overall field optimisation programme.

2.0 Theoretical framework

Though there are a number of adsorption and desorption models which are applicable for the modelling of the adsorption and desorption characteristics of chemical inhibitors, however the most widely used ones are the Freundlich and Langmuir isotherms. However, it appears Freundlich isotherm is more trusted to accurately model the adsorption and desorption behaviour of these chemicals (Gdanski, 2008; Flemming et al. 2008) perhaps because the shape of its isotherm is often found to be consistent with the adsorption mechanism of these chemicals. Combined Freundlich and Langmuir adsorption model has been reportedly used in

the fields of Hydrology and groundwater transport for modelling the adsorption of Arsenic on metal oxides (Jeppu and Clement, 2012; Raul et al., 2003).

2.1 Freundlich adsorption model

Freundlich adsorption model is a semi empirical model (Sohn and Kim, 2005) originally developed to describe the adsorption of organic materials from aqueous solution onto activated carbon. The mathematical form of the model is as given in equation (1).

$$\Gamma = kC^n \quad (1)$$

Where, Γ is the concentration of the species from the solution adsorbed on the adsorbent in mg/g; C is the concentration of the species remaining in solution in mg/l; k is adsorption constant in l/mg and n is adsorption intensity. n ranges from 0 to 1 and is dependent on a number of factors such as temperature, concentration and pH (Jeppu and Clement, 2012). As n approaches 1, the Freundlich model assumes a linear form (Turiel et al., 2003; Umpleby et al., 2001) as depicted in Figure 2.

The Freundlich isotherm equation assumes that the adsorbent has a heterogeneous surface composed of adsorption sites with different adsorption potentials.

Freundlich model can be linearised via logarithmic transformation to obtain the equation presented in equation (2).

$$\Gamma = \log k + n \log C \quad (2)$$

2.2 Langmuir adsorption model

Unlike Freundlich model, Langmuir adsorption model was developed based on thermodynamic principles (Sohn and Kim, 2005). The mathematical form of the model is presented in equation (3).

$$\Gamma = \frac{\Gamma_{max}BC}{1+BC} \quad (3)$$

Where, Γ is the concentration of the species from the solution adsorbed on the adsorbent at equilibrium in mg/g; C is the concentration of the species remaining in solution in mg/l; B is adsorption affinity constant related to the adsorption strength or energy in l/mg and Γ_{max} is the adsorption capacity of the system or maximum amount of adsorbate that can be adsorbed on adsorbent in mg/g; it is a measure of the total binding sites available per gram of adsorbent. Figure 3 shows a typical Langmuir isotherm showing the adsorption capacity at equilibrium condition.

In the same vein, Langmuir model can be linearised to obtain the equation presented in equation 4.

$$\frac{1}{\Gamma} = \frac{1}{B\Gamma_{max}} \frac{1}{C} + \frac{1}{\Gamma_{max}} \quad (4)$$

3.0 Laboratory experimental implementation

3.1 Materials and equipment

Three different sizes of commercial pack sand namely 40/60, 16/30 and 12/20 sands were used as substrates. The sands were selected because they fall within the size range most often used in gravel packing. The grain size distributions of these sands were analysed using the traditional sieve analysis technique. Figure 4 shows the grain size distributions for all the commercial sands; the sands were generally well sorted with their d_{50} ranging from 350 μm to 1100 μm . The fluids used were a brine containing 292 ppm of phosphonate inhibitor and a phosphonate inhibitor free brine.

3.2 Procedures

The following procedures implemented in two stages were used for the laboratory experimental work. The procedures are similar to the standard laboratory procedures often employed for evaluation and qualification of scale inhibitor prior to field application.

Stage 1: static test - 500 cm³ of each of the three commercial sands was poured into a separate one-litre beaker. 400 cm³ of brine dosed with phosphonate inhibitor was then added to each beaker to completely submerge the sands. The beakers were left for 1.5 hours to allow reasonable adsorption of the scale inhibitor species onto the sand adsorbent, at the end of which 4 ml sample of the brine was collected from each beaker. Further samples of the brine were collected at 3, 4.5, 24 and 48 hours. The effluent samples were analysed using ICP analytical technique.

Stage 2: dynamic test - 1000 g of 40/60 commercial sand was weighed and packed into a cylindrical Perspex sand pack chamber which was later attached to a benchtop flow system (Figure 5). The sand was then saturated with ordinary brine at 5 ml/sec for 20 mins after which it was saturated with the inhibitor dosed brine at the same flow rate. Samples of the effluent were collected at 30 seconds interval. After completely saturating the sand with the inhibitor solution, the sand pack chamber was shut in and left for 24 hours to allow for the adsorption of the inhibitor onto the sand adsorbent. At the end of shut in period the sand was flushed with inhibitor free brine at 5 ml/sec; effluent samples were also taken during the flushing. This procedure was repeated for the 16/30 and 12/20 commercial sands. The effluent samples were similarly analysed using ICP analytical technique.

4.0 Presentation of results

Adsorption and desorption rate profiles with respect to time are a very useful tool for evaluating adsorption rate of chemical scale inhibitors (adsorbate) on formation sand

adsorbents (Kerver., 1996; Flemming et al., 2008). On the other hand, Freundlich and Langmuir adsorption isotherms are the most widely used models for obtaining adsorption and desorption models for a range of adsorbate-adsorbent systems (Kahrwad et al., 2008; Patroni Zavala et al., 2008). The static and dynamic tests' results are therefore presented in form of adsorption and desorption rate profiles and fitted Freundlich and Langmuir models. The 'static' and 'dynamic' adsorption and desorption rate profiles are presented in form of normalised concentration versus time.

Linearised forms of both Freundlich and Langmuir models presented in equations 2 and 4 respectively were fitted into the 'static' and 'dynamic' laboratory data to develop static and dynamic desorption/adsorption models of the chemical inhibitor with respect to all the three sands. For Freundlich model fitting, log-log plots of adsorption ($\log \Gamma$) against concentration in solution ($\log C$) were used; whilst for Langmuir model fitting, plots of inverse of adsorption ($1/\Gamma$) against inverse of concentration in solution ($1/C$) were used.

5.0 Discussion of results

5.1 Adsorption and desorption isotherms

Figure 6 (a and b) presents the 'static' adsorption and desorption profiles respectively whilst Figure 7 presents the 'dynamic' adsorption and desorption rate profiles in a composite form. The adsorption and desorption rates for both the static and dynamic adsorption and desorption isotherms are equal and exactly opposite of each other at equilibrium.

The static adsorption and desorption rates of the chemical inhibitor with respect to the three commercial sands were very high as shown in Figure 6. The adsorption rate with respect to the 12/20 and 16/30 sands was similar and exhibited a slightly steeper slope than adsorption rate with respect to 40/60 sand. In the same vein, both 12/20 and 16/30 sands reached equilibrium condition faster than the 40/60 sand as shown in the figure. Against this

background, it appears that the adsorption and desorption characteristics of 12/20 and 16/30 sands were very similar to each other but slightly different from that of 40/60 sand. This relationship is similar to the pattern of relationship in the grain size distribution characteristics of the three sands (Figure 4).

The dynamic adsorption and desorption rates of the chemical inhibitor with respect to the three sands were also very high. The adsorption profiles of the three sands were in fact similar to each other as seen from the composite adsorption-desorption profiles in Figure 7. However, whilst the desorption profiles with respect to 16/30 and 40/60 sands were similar and steeper; the desorption profile for the 12/20 sand was slightly less steep.

5.2 Freundlich and Langmuir adsorption models

Figures 8 (a and b) presents the Freundlich and Langmuir models respectively for the ‘static’ chemical inhibitor adsorption with respect to the three sands. The correlation coefficients of the Langmuir fits were generally better for all the sands as shown in Table 1 suggesting that Langmuir isotherm provided better fits for the static adsorption data. However, it is also obvious the strength/energy of adsorption was generally very low for the Langmuir fitted data, being approximately zero for the three sands. Although better fits were generally achieved with Langmuir isotherm for all the sands, nonetheless it appears both Freundlich and Langmuir isotherms are suitable for modelling the static experimental data with respect to developing static adsorption and desorption models for the three sands.

Similarly, Figure 9 (a and b) presents the Freundlich and Langmuir models respectively for the ‘dynamic’ chemical inhibitor adsorption with respect to the three sands. However in this case, in contrast to the static adsorption, the Freundlich model provided better fits as evidenced by the higher correlation coefficients for each of the sands as presented in Table 2. The Langmuir correlation coefficient (R^2) values obtained for 16/30 sand especially for the static modelling case were however not consistent with the magnitudes of the adsorption

strength/energy and adsorption capacity; and were somewhat deceptive. In addition, they were generally inconsistent between the static and dynamic modelling cases i.e. Langmuir correlation coefficients were generally higher for the static case and vice versa for the dynamic case. On this basis, correlation coefficients could not be used alone in the evaluation of the two adsorption models to determine their suitability for modelling the adsorption/desorption characteristics of the three sands. It was therefore important that the correlation coefficient values were integrated with other key model parameters such as the adsorption strength/energy, adsorption intensity and adsorption capacity to obtain results that were truly reflective of the models' behaviour. With the application of this integration approach to all the sands, the Freundlich model appeared to show better modelling prospects for the adsorption/desorption characteristics of the sands (Tables 1 and 2).

5.3 Adsorption intensity and sand uniformity coefficient.

Adsorption intensity of chemical inhibitor adsorbate on sand sorbents relates to the constant “n” in the Freundlich equation. From the general theory of adsorption and desorption, this constant would obviously depend on factors intrinsic and extrinsic to the adsorbent. Intrinsic factors would include surface chemistry and pore structure of adsorbent whilst extrinsic factors would include environmental factors such as temperature and pressure in the process vicinity of the adsorbent; and the nature of the adsorbates (Babi et al., 2011; Vieira and Beppu, 2006). On the other hand, uniformity coefficient is a unique formation grain size distribution parameter that describes the measure of grain size differentiation in sand. Uniformity coefficient is given as a ratio of the d_{60} to d_{10} of sand and has a value of 1 if there is little or no differentiation in the sand size with all the sand particles exhibiting the same size. In order to understand the correlation between adsorption intensity (constant n) and sand uniformity coefficient, the fitted values of adsorption intensity for static and dynamic Freundlich models were plotted against the corresponding sand uniformity coefficient as

shown in Figure 10. The figure shows rather intriguingly different relationships between adsorption intensity and uniformity coefficient for the static and dynamic models. Whilst for the static model, adsorption intensity increased with increasing uniformity coefficient; for the dynamic model, it decreased with increasing uniformity coefficient. In addition adsorption intensity was also found to be generally higher for all the sand adsorbents under the static test condition. Sand stratification phenomenon and flow dynamics relating to static and dynamic test conditions respectively are a plausible explanation for this.

Stratification of the sand adsorbents in accordance to the individual grain specific gravity in brine was possible in the static test though the degree of stratification may be insignificant if directly correlated with the uniformity coefficient of the sands which was generally close to 1. The adsorption capacity of granular activated carbon (GAC) has been reported to have been enhanced by stratification through prevention of premature desorption (Babi et al., 2011). In the same vein, it was possible that during the static test, stratification of sand adsorbents helped to enhance the sand surface and increase the adsorption bond between the adsorbate and the sand adsorbent. In contrast, the chances of stratification of the sand adsorbents in the dynamic test were very remote as the sands were well distributed in the test chamber and the flow rates used were not high enough to cause redistribution or stratification of the sands. Nonetheless, even small flow rates could potentially upset any equilibrium within the system and reduce the strength of the adsorbate adsorption.

5.4 Adsorption strength and sand uniformity coefficient

Adsorption strength of the sand adsorbents relates to the constant terms k and B for Freundlich and Langmuir models respectively. This property would also depend on the same intrinsic and extrinsic factors highlighted for adsorption intensity. Plot of adsorption strength versus Uniformity Coefficient were also obtained to investigate the possible influence of Uniformity Coefficient on the adsorbent adsorption strength; these plots are shown in Figure

11. The figure shows that while the adsorption strength increases with uniformity coefficient and is generally high for the dynamic tests, it reduces with uniformity coefficient and is generally low for the static tests.

This result agrees with previous studies on the removal of dye and heavy metals from contaminated surface water via static and dynamic adsorption and desorption. In particular the explanation based on continuously changing concentration gradient at the interface of the adsorption surface provided by Filipkowska and Rodziewicz (2009) and Gupta et al. (2001) may also account for the static/dynamic adsorption/desorption behaviour pattern obtained in this study. In the case of the dynamic tests, the concentration gradient is believed to increase at the interface of the adsorption surface as the inhibitor specie flowed through the sand pack. In contrast however, for the static case, the concentration gradient is believed to decrease at the adsorption surface interface with time.

5.5 Application to inhibitor squeeze design in gravel pack completions

Gravel pack completions are known to have commercial pack sands acting as a filter between the formation and the wellbore. The petrophysical and mineralogical characteristics of these sands can be significantly different from that of the formation. This difference in properties means that the adsorption/desorption characteristics of the formation would be different from that of the gravel pack sand.

In order to achieve full optimisation of inhibitor squeeze treatment, it is proposed that the adsorption and desorption characteristics of the gravel pack sand should be evaluated alongside that of the formation. This would allow for the evaluation of the effects and impact of the adsorption/desorption behaviour of gravel pack on the overall adsorption/desorption characteristics of the gravel packed well or formation. With this proactive approach, field operators can obtain fairly accurate design information about their squeeze jobs such as the volume of squeeze, squeeze life, frequency of treatment etc. in gravel packed wells to enable

the design of more reliable field life squeeze treatments for their wells or fields. The major benefits of this include reduced cost of treatment and reduced downtime.

6.0 Conclusions

Knowledge of adsorption and desorption characteristics of gravel pack sands has been shown to be very valuable in the integration of chemical inhibitor performance into the overall field optimisation programme. Adsorption and desorption characteristics of three different commercial gravel pack sands (12/20, 16/30 and 40/60), which find great application in sand control completions, have been evaluated in terms of their adsorption and desorption characteristics.

The adsorption intensity was found to be generally higher for all the sand absorbents under the static test condition. This increased with increasing Uniformity Coefficient for the static model; whilst for the dynamic model, it decreased with increasing uniformity coefficient. In contrast the adsorption strength increased with Uniformity Coefficient for the dynamic model and vice versa for the static model.

The integration of the correlation coefficients with adsorption strength/energy, adsorption intensity and adsorption capacity suggests that Freundlich models would be more suitable for modelling the adsorption/desorption characteristics of the sands.

In summary, the study has shown that the adsorption/desorption characteristics of gravel pack sands will be different from that of the formation sands and that having adequate knowledge of these characteristics is important for the design and optimisation of inhibitor squeeze treatment.

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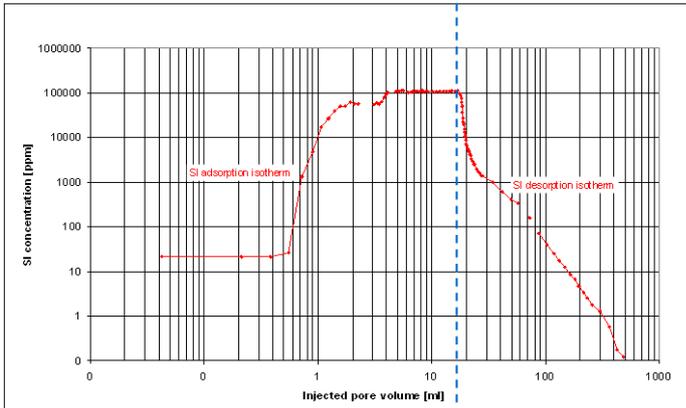


Fig.1 An example plot of SI adsorption and desorption isotherms from laboratory dynamic adsorption and desorption test

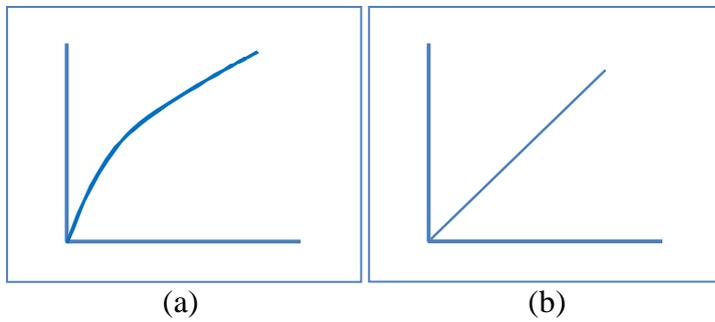


Fig. 2 Freundlich isotherms (a) when $n < 1$ and (b) when $n = 1$

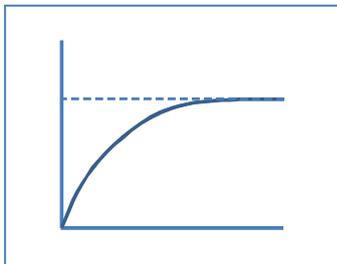


Fig. 3 Langmuir isotherm; the dashed line depicts the position of adsorption capacity at equilibrium condition

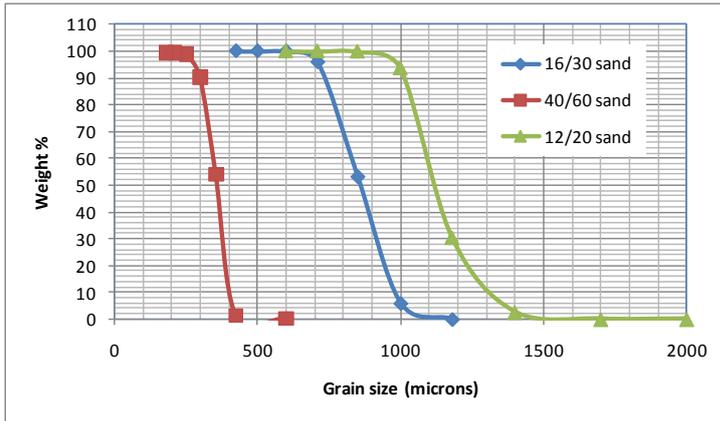


Fig. 4 Grain size distribution of the 40/60, 16/30 and 12/20 commercial sands

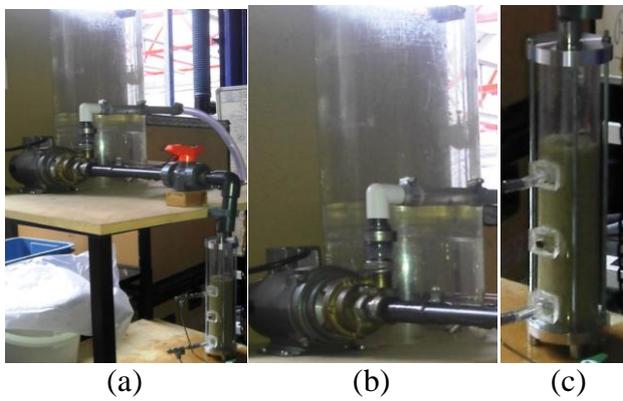


Fig. 5 Images of the dynamic test set up showing (a) the entire set up, (b) the fluid storage chamber connected to a variable rate pump and (c) the Perspex sand pack

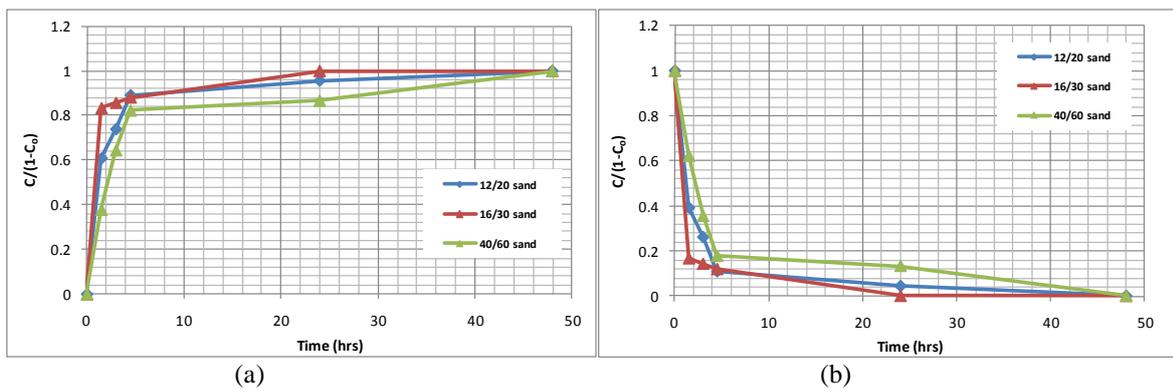


Fig. 6 Static (a) adsorption and (b) desorption profiles

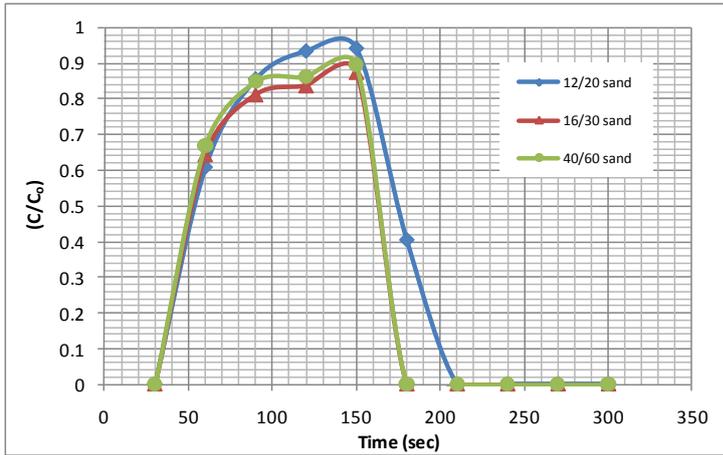


Fig. 7 Composite dynamic adsorption and desorption profiles

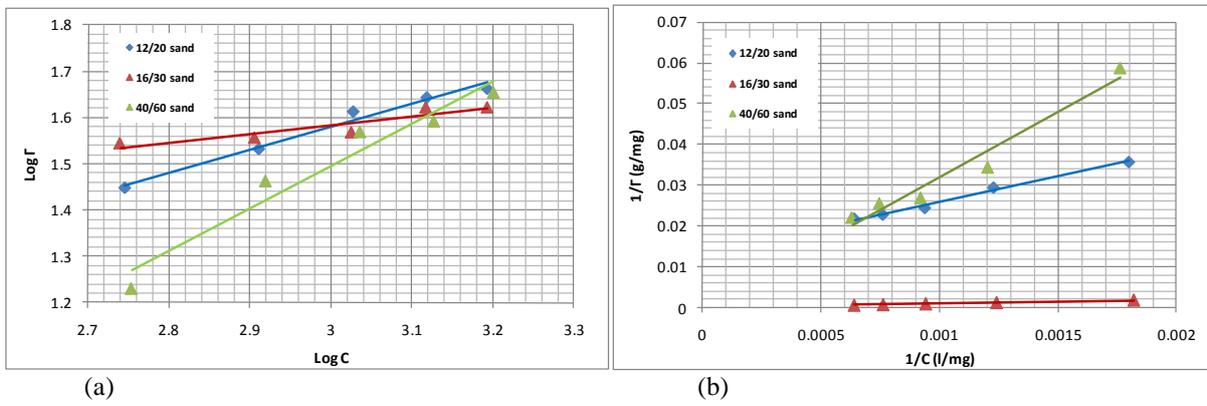


Fig. 8 Fitted static (a) Freundlich and (b) Langmuir models

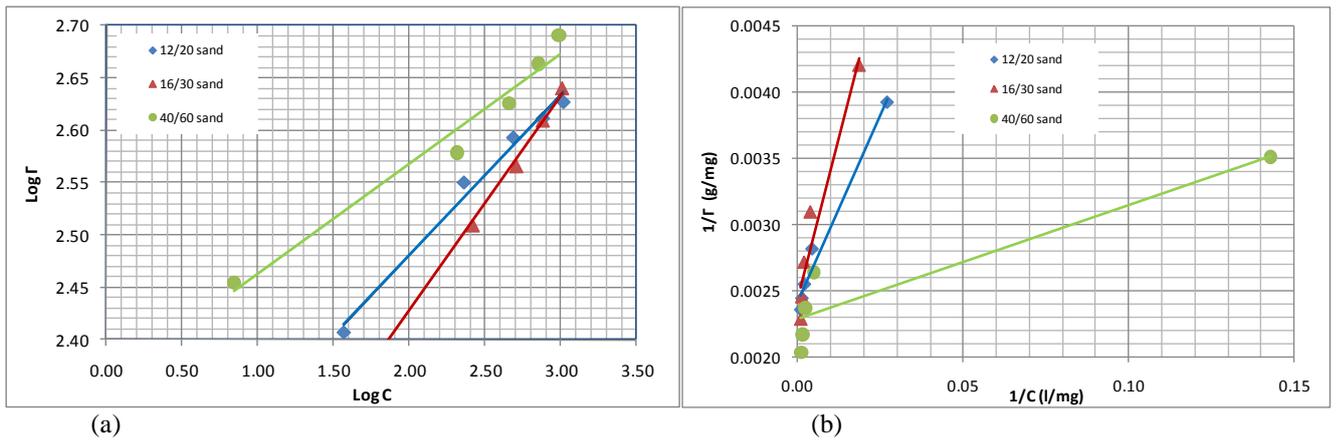


Fig. 9 Fitted dynamic (a) Freundlich and (b) Langmuir models

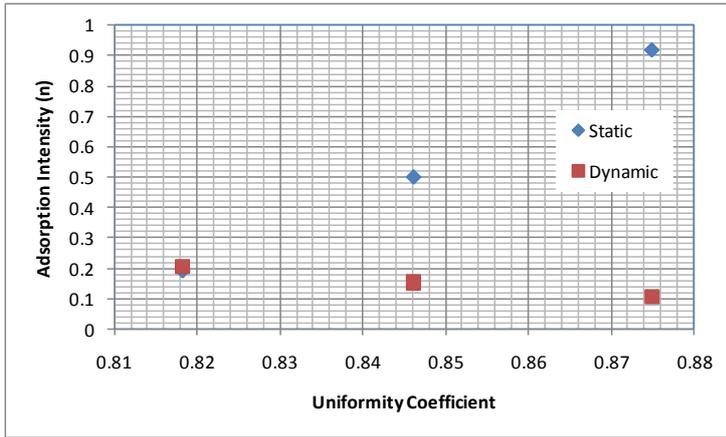


Fig. 10 Plot of adsorption intensity obtained from the Freundlich fits of the dynamic adsorption data against Uniformity Coefficient

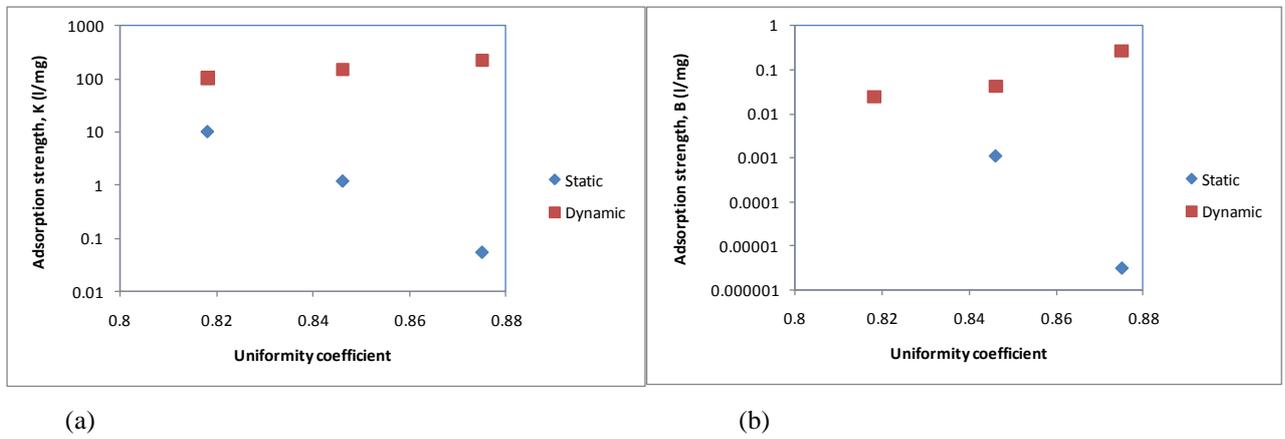


Fig. 11 plot of (a) Freundlich adsorption strength, K and (b) Langmuir adsorption strength, B against Uniformity Coefficient obtained for both static and dynamic data

Table 1 Freundlich and Langmuir model parameters and correlation coefficients from the static test models of phosphonate chemical inhibitor adsorption on 12/20, 16/30 and 40/60 commercial sands

| Commercial gravel sands | Freundlich model parameters | | | Langmuir model parameters | | |
|-------------------------|-----------------------------|--------|----------------|---------------------------|----------------------------|----------------|
| | k (l/mg) | n | R ² | B (l/mg) | Γ _{max} (mg/g) | R ² |
| 12/20 | 1.1951 | 0.5009 | 0.9808 | 0.001072 | 72.6 | 0.9914 |
| 16/30 | 10.1064 | 0.1931 | 0.8409 | 0.000000 | 0.0 | 0.9753 |
| 40/60 | 0.0553 | 0.9173 | 0.9465 | 0.000003 | 1000.0 | 0.9943 |

Table 2 Freundlich and Langmuir model parameters and correlation coefficients from the dynamic test models of phosphonate chemical inhibitor adsorption on 12/20, 16/30 and 40/60 commercial sands

| Commercial gravel sands | Freundlich isotherm model | | | Langmuir isotherm model | | |
|-------------------------|---------------------------|--------|----------------|-------------------------|----------------------------|----------------|
| | k (l/mg) | n | R ² | B (l/mg) | Γ _{max} (mg/g) | R ² |
| 12/20 | 148.9 | 0.1538 | 0.9868 | 0.0425 | 416.7 | 0.9761 |
| 16/30 | 104.5 | 0.2045 | 0.9975 | 0.0244 | 416.7 | 0.9303 |
| 40/60 | 227.8 | 0.1052 | 0.9677 | 0.2644 | 434.8 | 0.8656 |