The inhibition of crystal growth of gypsum and barite scales in industrial water systems using green antiscalant

D. E. Abd-El-Khalek, B. A. Abd-El-Nabey, Mervat A. Abdel-kawi, Sh. Ebrahim and S. R. Ramadan

ABSTRACT

Mineral scale is a major flow assurance problem in industrial water systems. The antiscale properties of sunflower (*Helianthus annuus*) seed extract for $CaSO_4$ and $BaSO_4$ scales were investigated using NACE and conductivity tests, respectively. Comparative studies between the extract and 1-hydroxyethane-1,1-diphosphonic acid (HEDP), as commercial antiscalants, were done. The results revealed that the inhibition of $CaSO_4$ scales using sunflower seed extract reached 100%, while HEDP achieved a maximum inhibition of 88%. Moreover, the maximum inhibition of $BaSO_4$ scale in the presence of the extract was 84% compared with 86% in the presence of HEDP. Also microscopic examination showed that both inhibitors modified $CaSO_4$ and $BaSO_4$ crystals.

Key words | green antiscalant, gypsum and barite, HEDP, sunflower seeds

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INTRODUCTION

Industrial water systems operated on poorly treated feed water are often plagued by deposition of undesirable materials on equipment surfaces (Amjad *et al.* 2014). Water scaling on heat exchangers and petroleum production equipment surfaces is often the persistent problem in cooling water systems, boilers, secondary oil recovery, and desalination plants (Abdel-Gaber *et al.* 2008). However, although carbonates are common types of scales, sulfate scales are far more difficult to remove once they form on equipment surfaces (Amjad 1994).

To mitigate the problem of scaling, a number of chemical formulations have been used as inhibiting compounds which are able to suppress scale precipitation. The influence of polymeric additives containing the –COOH group on both the rate and crystal modification of gypsum has been the subject of numerous investigations (Öner *et al.* 1998; Dogan *et al.* 2000; Senthilmurugan *et al.* 2010; Amjad 2012). Results of these studies reveal that these polymers are effective gypsum scale inhibitors and the inhibition increases with the acid content of the polymer (Dogan *et al.* 2000).

In addition, phosphonate-containing molecules have been investigated for $BaSO_4$ (Jones *et al.* 2003; Wang *et al.* 2005) and $CaSO_4$ (Amjad *et al.* 2014; Dogan *et al.* 2016) inhibition. Also, various techniques are used to elucidate the mechanism of interaction between EDTA and barium sulfate surfaces (Jones *et al.* 2007). It is shown that complexion with metal ions is not sufficient to explain the inhibition of barite crystallization but that other processes such as chemisorption must also occur.

Because of the fact that scale deposits are crystalline with a surface charge which is either directly or indirectly pH dependent, the chemical additives depending on the

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extent of ionization of their functional groups cause changes in the distribution of electrical charges on the surface of the suspended particles, thus determining the stability of the respective suspensions (Amjad *et al.* 2014). The use of chemical compounds in a variety of applications is conditioned by environmental and health concerns. Accordingly, during recent years, industrial requirements for chemical compounds refer not only to their efficacy but to safety as well. The requisites for these compounds should focus on non-mutagenic, non-carcinogenic products with characteristics more environmentally acceptable than systems currently in use. Thus, some green antiscalants have been tested and evaluated (Li *et al.* 2006; Martinod *et al.* 2009; Wang *et al.* 2013). Currently plant extracts are employed as scale inhibitors in order to develop new cleaning chemicals for a green environment (Abdel-Gaber *et al.* 2008, 2011, 2012; Castillo *et al.* 2009; Abd-El-Khalek *et al.* 2016). Plant extracts are viewed as a rich source of natural chemical compounds that can be extracted by simple procedures at low cost. It has been reported that extract of sunflower (*Helianthus annuus)* seeds is rich in lipids and amino acids which contain many functional groups and have surface active properties (Evon *et al.* 2007). Moreover, protein macromolecules are expected to enable more elaborate control of crystal morphology and structure (Qi *et al.* 2000).

This work aims to examine the efficiency of sunflower seed *(Helianthus annuus*) extract as a green inhibitor of calcium sulphate and barium sulfate scales for industrial water application. The antiscalant performance of the extract was compared with the performance of the commercially available antiscalant HEDP (hydroxyethylidene-1,1-diphosphonic acid).

MATERIALS AND METHODS

Preparation of solutions

Double distilled water and analytical reagent-grade NaCl, $BaCl_2$, Na_2SO_4 and $CaCl_2$ and HEDP were used for preparing solutions. Stock solution of sunflower seed (*Helianthus annuus*) extract was obtained by drying the leaves for 2 hours in an oven at 70 °C and grinding to powdery form. A 5 g sample of the powder was refluxed in 100 mL distilled water for 1 hour. The refluxed solution was filtered to remove any contamination. The concentration of the stock solution was determined by evaporating 10 mL of the filtrate and weighing the residue. The concentration of the stock solution was expressed in terms of grams per litre.

NACE test for calcium sulfate scaling

The test method is described in the NACE Standard (TM 0374-2001) 'Laboratory Screening Tests to Determine the Ability of Scale Inhibitors to Prevent the Precipitation of Calcium Sulfate' (Miksic *et al.* 2007). For the test, synthetic brines were prepared: calcium brine: 7.5 g/L NaCl + 11.0 g/L $CaCl_2.2H_2O$ and sulfate brine: 7.5 g/L NaCl + 10.66 g/L Na_2SO_4.

Solutions for each test were connected in the test cell with different concentrations of sunflower seed extract or HEDP. Testing cells were placed in the water bath set at 71 °C for 72 hours. After that the concentration level of calcium ions was determined in the solution by titration with EDTA and murexide indicator.

Using these data, the percentage of scale inhibition was calculated:

$$\% \text{ Inhibition} = 100 \times (C_a - C_b):(C_c - C_b)$$

where $C_a = Ca^{2+}$ concentration in the treated sample after precipitation; $C_b = Ca^{2+}$ concentration in the blank after precipitation; $C_c = Ca^{2+}$ concentration in the blank before precipitation.

Conductivity test for $BaSO_4$ scaling

This test is based upon the solution conductivity measurements while barium sulfate is being precipitated from barium chloride solution by the addition of sodium sulfate in the presence of different concentrations of the inhibitor. The supersaturation point, *S*, is a key point in homogeneous nucleation. When the ionic product is beyond this point, the homogeneous nucleation rate increases suddenly, and this results in precipitation and scaling (Drela *et al.* 1998; Abdel-Gaber *et al.* 2008). Supersaturation point *S* is represented by the maximum volume of sodium sulfate after which precipitation occurs. The test setup has been described previously (Drela et al. 1998; Abdel-Gaber et al. 2008). A solution of 0.5 mL of 0.1 M $BaCl_2$ was added to the appropriate volume of the stock solution of sunflower seed extract or HEDP, and then the mixture was made up to 100 mL by distilled water. The conductivity of the stirred solution was measured during titration by 0.01M Na_2SO_4 using an HQ14d conductivity meter. The titrating solution was added in portions of 0.2 mL each. Measurements were done at $25.0 \pm 0.1\,^{\circ}C$.

FTIR spectrum

A Fourier transform infrared (FTIR) spectrometer (FTIR LX 18-5255 Perkin Elmer) was used for characterizing the sunflower extract. The spectra were recorded in the wavenumber range of 4,000–400 cm^{-1}. The extract sample was ground with KBr and the powdered mixture was pressed in a hydraulic press to form a translucent disk through which the beam of the spectrometer could pass.

Microscopic examination

The morphology and crystal lattices of the scales were observed with an optical microscope (Axioskop 40 Zeiss), and a scanning electron microscope (SEM; JEOL-5300 scanning microscope). Prior to SEM examination, scale crystals were sputter-coated with a thin film of gold under vacuum.

RESULTS AND DISCUSSION

FTIR and functional groups

Figure 1 illustrates the FTIR spectrum of the sunflower seed extract. As is seen, a broad band at 3,374 cm^{-1} was observed, and this band can be attributed to the stretching of the

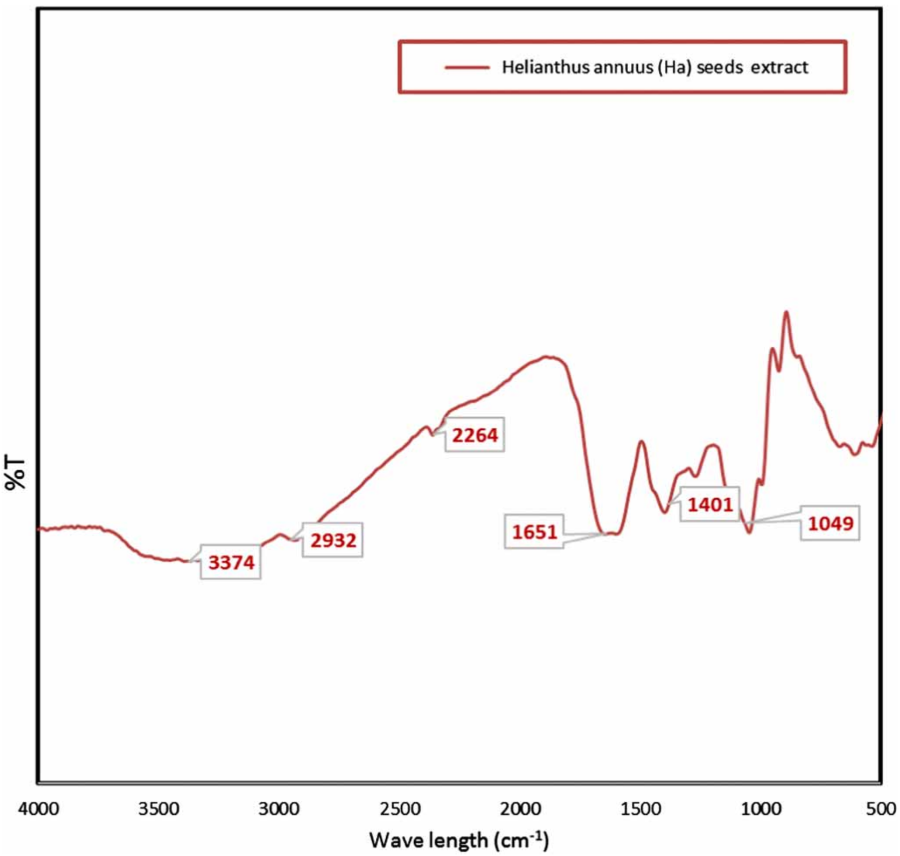

Figure 1 | FTIR spectrum of sunflower (*Helianthus annuus*) seed extract.

hydroxyl group, or N-H broad band. The appearance of the N-H band's vibration at 3,300–3,500 cm^{-1} is an indication of the presence of amine groups (Etemadi *et al.* 2017) as a result of the presence of amino acids in the *Helianthus annuus* extract (Evon *et al.* 2007). The band at 1,651 cm^{-1} is probably attributed to the $C=O$ bond of the carboxylic group. In addition, the peak at 2,932 cm^{-1} is assigned to C-H bending, while the peak at 1,049 cm^{-1} can be attributed to the C-O ether band. Also, the peak at 2,264 cm^{-1} is assigned to the $C\equiv N$ band. It is reported that the studied extract is rich with flavonoids, triterpenoids, oils and amino acids (Evon *et al.* 2007; Dwivedi & Sharma 2014) which act as sources of carboxyl and amine groups in addition to phenolic structures.

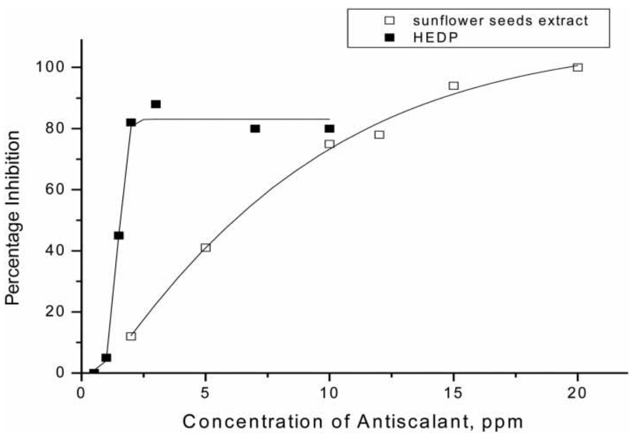

Figure 2 | Variation of percentage inhibition of calcium sulfate scales with concentration of sunflower seed extract and HEDP.

Calcium sulfate scaling

The NACE experiment was used to test the efficiency of sunflower seed extract as a $CaSO_4$ scale inhibitor. Figure 2 shows the variation of percentage inhibition of calcium sulfate scale with concentration each of sunflower seeds and HEDP. As shown, increasing the concentration of plant extract increases the percentage of calcium sulfate scale inhibition. It is clear that in the presence of low concentrations of the inhibitors (less than 10 ppm), HEDP is more efficient, while at higher concentration, the efficiency of sunflower seed extract exceeds HEDP and reaches 100% at 20 ppm of the extract.

Figure 3 shows photographs of $CaSO_4$ crystals after precipitation in the absence and presence of the optimum concentrations of sunflower seed extract and HEDP. As is seen, in the absence of antiscalant, gypsum crystals are thin tubular cells and needles exhibiting monoclinic symmetry (Issabayev *et al.* 2018), whereas crystals grown in the presence of additives are markedly modified with a lack of tubular-cell-shaped gypsum and of reduced size. The morphology changes indicate that scale inhibitors significantly damage the crystalline structure of calcium sulfate, which may result from coordination between functional groups and Ca^{+2} ions. Amino acids which are extracted from sunflower seeds (Evon *et al.* 2007; Zhang *et al.* 2017), in addition to phosphonate groups in HEDP, might exert strong interaction with Ca^{2+} ions (Hoang 2015).

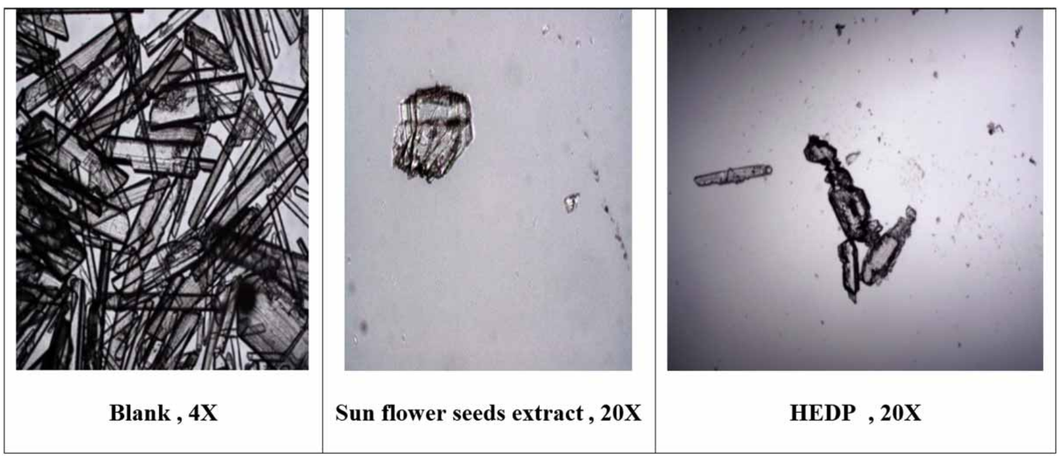

Figure 3 | Photographs of $CaSO_4$ crystals after precipitation in the absence and presence of scale inhibitors at their optimum concentrations.

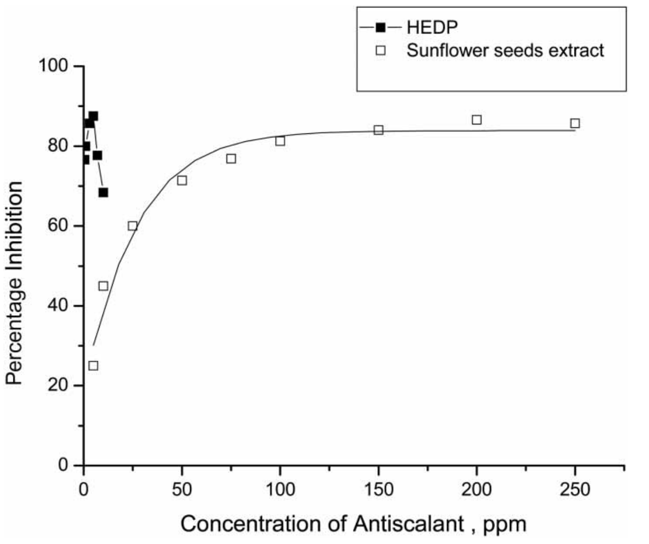

Figure 4 | Variation of percentage inhibition of barium sulfate scales with concentration of sunflower seed extract and HEDP.

Barium sulfate scales

Figure 4 shows the variation of percentage inhibition of barium sulfate scales with concentration of sunflower seed extract and HEDP. Percentage of scale inhibition was calculated from the following equation:

$$\%\ \text{scale inhibition} = (S_{in} - S_o)/S_{in}$$

where S_o = supersaturation point in the absence of scale inhibitor and S_{in} = supersaturation point in presence of scale inhibitor.

As is seen, the percentage inhibition of $BaSO_4$ scales increases linearly with extract concentration. A plateau region is observed at 100 ppm of the extract with 83% inhibition; after this concentration, no notable increase of the inhibition is observed. Moreover, maximum inhibition in the presence of HEDP is 86% at 5 ppm, and further increase of the concentration decreases its efficiency. It is clear that HEDP acts as a threshold inhibitor, while the influence of the extract may be attributed to change of the ionic strength and/or it may form a stable complex with cations and/or anions and reduce supersaturation (Amjad 1994). However, the tested extracts have high optimal concentrations; they could be promising green antiscalants with regard to eutrophication caused by phosphorus polymers.

Figure 5 shows photographs of $BaSO_4$ crystals after precipitation in the absence and presence of sunflower seed extract and HEDP. As is seen, pillow-shaped barium sulfate scales were observed in the absence of the examined antiscalants (Jones *et al.* 2007). These crystals were modified by the addition of the extract and HEDP with reduction of their size. The observed change in morphology may be explained in terms of the surface adsorption of scale inhibitors on the growing $BaSO_4$ crystals (Amjad 1994). The adsorption could take place via (i) electrostatic attraction between the charged particles and the charged chemical constituents of the extract, (ii) dipole-type interaction between unshared electron pairs in the extracted molecules and growing particles, (iii) π-interaction with particle surfaces and (iv) a combination of all of the above (Schweinsgberg *et al.* 1988; Abdel-Gaber *et al.* 2008). A combination of all of the above cases of adsorption can arise because of the chemical constituents of sunflower seed extract, which contains many functional groups. Therefore, the inhibition properties of the extract largely depend on the carboxylic acid groups, which have a noticeable inhibition effect on barite crystallization through strong interaction with the growing $BaSO_4$ particles (Qi *et al.* 2000).

CONCLUSION

An approach to fighting sulfate scales has been provided by using sunflower seed extract as a novel green antiscalant. The results revealed that the extract inhibits the precipitation of both barium and calcium sulfate. In comparison with HEDP, the extract has a value of percentage inhibition of barium sulfate near to that of HEDP with a notable difference in their optimum concentrations. However, sunflower seed extract is a more efficient inhibitor than HEDP for calcium sulfate scale precipitation. Also microscopic examination showed that both inhibitors modified $CaSO_4$ and $BaSO_4$ crystals. Carboxyl and amine groups in addition to phenolic structures that are extracted from sunflower seeds may have important roles in sulfate crystal growth suppression.

However, the tested extract has higher optimal concentration; it can be considered as an alternative to non-green

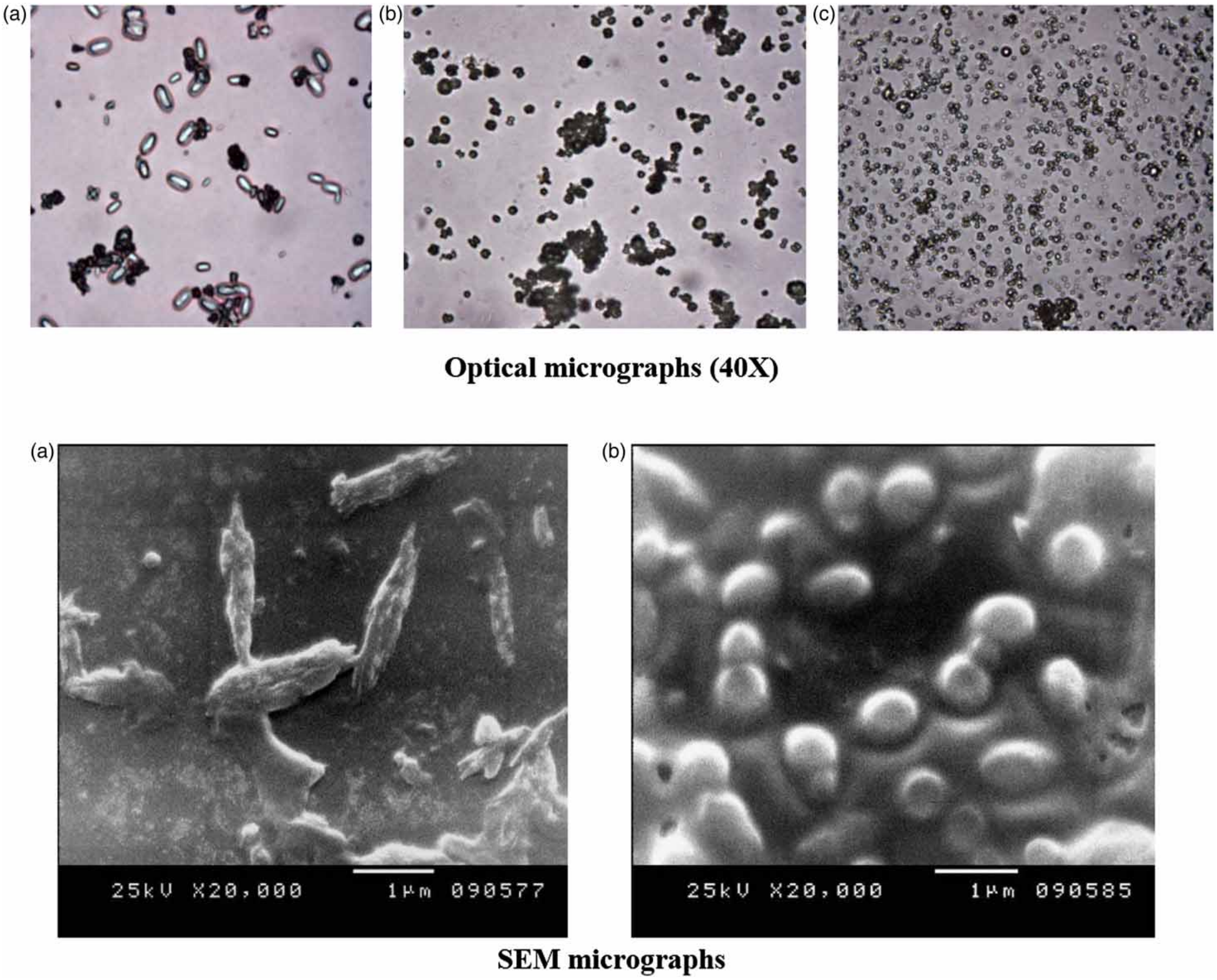

Figure 5 | $BaSO_4$ crystals after precipitation in the absence and presence of scale inhibitors at their optimum concentration: (a) blank, (b) in the presence of sunflower seed extract and (c) in the presence of HEDP.

technologies especially in food and pharmaceutical industries and desalination plants, with regard to eutrophication caused by phosphorus polymers.

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