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## SCIENTIFIC PAPER

# STUDY OF ESSENTIAL OILS ADSORPTION ON THREE PHOSPHATE FERTILIZERS

Nejib BENALI<sup>\*1,3</sup>, Houcine BEN DAOUD<sup>1</sup>, Manel FARHATI<sup>1</sup>, Chedly TIZAOU<sup>2</sup>, Mehrez ROMDHANE<sup>1</sup>.

1. *Environment, Catalysis and Process analysis (ECAP), National School of Engineering of Gabes, P.O. Box 6029- 1975 Gabes, Tunisia. Tel: +216 58901537*
2. *College of Engineering, Swansea University, Swansea SA1 8EN, United Kingdom*
3. *Institut supérieur des études technologiques de Gafsa, Campus universitaire, Gafsa 2112*

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\* [benali\\_nejib@yahoo.fr](mailto:benali_nejib@yahoo.fr), [houcine.bendaoud@yahoo.fr](mailto:houcine.bendaoud@yahoo.fr), [manelfarhati@yahoo.fr](mailto:manelfarhati@yahoo.fr), [c.tizaoui@swansea.ac.uk](mailto:c.tizaoui@swansea.ac.uk), [mehrez.romdhane@laposte.net](mailto:mehrez.romdhane@laposte.net)

**ABSTRACT:** In this paper, we report the study of essential oils adsorption on three phosphate fertilizers: mono-ammonium phosphate, di-ammonium phosphate and triple super phosphate with the aim to prepare a bi-function product which can be used as a fertilizer and bio-pesticides. Essential oils were isolated by steam distillation from *Eucalyptus salubris* and *Artemisia herba.alba* and analysed by GC-MS and GC-FID. About 12 and 22 constituents were identified and quantified in these oils, respectively. The kinetic adsorption study of essential oils showed that DAP and TSP exhibited high adsorption capacities compared with MAP (DAP (0.143 g/g) and TSP (0.139 g/g) for *Eucalyptus salubris* essential oil and (DAP (0.135 g/g) and TSP (0.134 g/g) for *Artemisia herba-alba* essential oil). The adsorption isotherms of all identified components in the *Eucalyptus salubris* essential oil were determined and the Langmuir and Freundlich models were used to describe the experimental data. Langmuir model fitted well the isotherms of the majority of the essential oil components (1,8-cineole,  $\alpha$ -pinene,  $\beta$ -Pinene, isopinocarveol,  $\beta$ -eudesmol,  $\alpha$ -phellandrene, Pinocarvone, P-cymene and Spathulenol) and only Terpineol and Globulol isotherm data followed the Freundlich model. The selectivity was affected by the abundance of each component in the crude essential oil and the polarity of terpenic components.

**Key words:** Adsorption; di-ammonium phosphate; Essential oil; isotherms; mono-ammonium phosphate; triple super phosphate fertilizers.

## Highlights

- Essential oils adsorption by three fertilizers to combine fertilization/bio-pesticides functions.
- Effect of various operational parameters on the adsorption of essential oils by fertilizers.
- Modeling of essential oils adsorption isotherms by Langmuir and Freundlich models.
- Protect the bio-active compounds of essential oils against evaporation and degradation.

## INTRODUCTION

In modern agriculture, the use of pesticides is necessary to control pests. However, the excessive use of synthetic chemical pesticides has many harmful environmental and human health risks and the development over time of pest resistance to pesticides [1]. This led to the search for new harmless products with high efficiency. Natural products, such as essential oils and plant extracts, are excellent alternative to synthetic pesticides [1-3]. These products are eco-friendly, biodegradable and can act against pests through multi-effects including antifeedant, insecticidal, repellent, growth regulatory and antivector [4,5].

Many essential oils were particularly known for their important pest control properties such as those from eucalyptus (*Eucalyptus globulus*) [6,7], thyme (*Thymus vulgaris*) [8,9], vetiver (*Vetiveria zizanioides*), lemongrass (*Cymbopogon flexuosus*) [11,12], clove (*Eugenia caryophyllus*) [13] and rosemary (*Rosmarinus officinalis*) [14-17]. Essential oil from *Mentha* species is highly powerful against *Callosobruchus maculatus* and *Tribolium castanum*, common stored grain pests [10-18]. Also, peppermint essential oil (*Mentha piperita*) has a good repellent power against flies, ants, lice and moths [19,20]. Spearmint (*Mentha spicata*) [10] and basil (*Ocimum basilicum*) essential oils [10,20,21] can be successfully used in warding off flies. Other essential oil bearing plants like those from *Melaleuca leucodendron*, *Pelargonium roseum*, *Lavandula angustifolia*, *Mentha piperita* and *Juniperus virginiana* were also effective against various insects and fungal pathogens [1,4,5].

Eucalyptus and Artemisia essential oils have been reported to have great efficiency in pest control [22,23]. Indeed, Eucalyptus essential oil possesses a wide spectrum of biological activity including anti-microbial, fungicidal, insecticidal/insect repellent, herbicidal, acaricidal and nematocidal. [22-25].

While *Asteraceae* family contains some species such as Artemisia plants, whose essential oils has also insecticidal and repellent properties [26,28]. Indeed, *Artemisia herba-alba* essential oil blocks the asexual reproduction of some insects such as *Aspergillus niger* Tiegh, *Penicillium italicum* Wehmer and *Zygorrhynchus* sp [27]. Research studies on the chemical

compositions of *Artemisia* species demonstrated that *Artemisia herba-alba* had higher essential oils yield than other species [28,29].

Despite being effective insecticides and pesticides, essential oils do not however persist long in the environment and hence require continual reapplication to achieve the desired results. In order to overcome this issue and improve the stability of bioactive compounds of essential oils, several research studies have focused on the encapsulation of essential oils using different methods such as complex coacervation [30], co-precipitation [31], emulsification [32], molecular inclusion, co-crystallisation, and extrusion [33].

Despite being a well-established chemical engineering separation technique and simple to employ, adsorption has so far marginally studied for essential oils-based product formulation. The adsorption studies carried out so far on essential oils adsorption have mainly focused on the use of clays as adsorbing. Indeed, El Miz et al. [34,35], studied the adsorption of thymol (main component of thymus essential oil) on sodium bentonite (montmorillonite clay) [34], and Pillared clay (modified montmorillonite clay) [35] showing that the maximum amount adsorbed was 177 and 319 mg·g<sup>-1</sup> respectively with a good affinity of thymol to anionic clay sites.

Nguemtchouin et al. [36], have also used kaolin to study the adsorption of *Xylopiya aethiopica Dunal* (Annonaceae). They found that the amount of essential oil adsorbed was inversely proportional to the kaolin particle size and the treatment of kaolin with hydrogen peroxide increased the adsorption capacity.

Up today, in the better of our knowledge, there are no previous studies dealing with the adsorption of essential oils on fertilizers. The resulting products can be advantageous, first, because solid fertilizers are already available agricultural materials with acceptable sorption properties such as porosity and specific surface area [36-39]. Second, a fertilizer loaded with essential oils can provide dual effects: a fertilization and pest control.

This study will present for the first time new data on the adsorption of *Eucalyptus salubris* and *Artemisia herba.alba* essential oils on three different commercial fertilizers including

mono-ammonium phosphate (MAP), di-ammonium phosphate (DAP) and triple super phosphate (TSP) which are the most commercialized fertilizers in Tunisia.

## **MATERIAL AND METHODS**

### **Chemicals and reagents**

Chemical reagents used were purchased from Sigma-Aldrich-Fluka (Saint-Quentin, France). The three fertilizers (MAP, DAP, TSP) were purchased from the Tunisian Chemical Group.

### **Plant material and oil extraction**

Aerial parts of "*Artemisia herba-alba*" and "*Eucalyptus salubris*" were collected from the regions of El maadher-Menzel bouzeine (middle of Tunisia) and Orbata (south west of Tunisia) in the period of March 2013. These plant materials were air dried at room temperature until mass constant. A sample of 100g of each plant was subjected to hydrodistillation in 1L of distilled water during 4 hours in a glass Clevenger apparatus. The obtained essential oils were dried over anhydrous sodium sulphate and then stored at +4 °C until analyzed and used. The experiments were carried out in triplicate.

### **Chemical analyses of extracted oils**

GC-MS analyses were performed using a Hewlett–Packard 5973-6890 system operating in EI mode (70 eV) equipped with a split/splitless injector (250 °C), a split ratio 1/100, using a fused silica HP-5 MS capillary column (30 m x 0.32 mm (i.d.), film thickness: 0.25 µm). The column temperature program was from 45 °C (2 min) to 220 °C at a rate of 5 °C.min<sup>-1</sup> (2min). Helium was used as the carrier gas at a flow rate of 1.2 mL min<sup>-1</sup>. Linear retention indices for all components were determined using n-alkanes standards analyzed in the same previous conditions.

The identification of the components was based on comparison of their mass spectra with those of the Wiley Library [40], and those described by Adams [41], as well as by comparison of their retention indices with literature data [42].

Based on external calibration, quantification of essential oil components was performed using GC-FID under the same conditions with GC-MS (column, oven temperature, flow rate

of the carrier gas) using a Hewlett–Packard 5973-6890 system Cx gas chromatograph equipped with a flame ionization detection (FID) detector and DB-5MS capillary column (30 m × 0.32 mm, film thickness 0.25 μm). Injector and detector temperatures were set at 200 and 270 °C, respectively.

Diluted sample (1 mg in 10 mL petroleum ether) of 1 μL was injected in the split mode (ratio 1 : 10). Quantitative data were obtained electronically from FID area percent data without the use of correction factors.

### **Fertilizers characterization**

The three commercial fertilizers (MAP, DAP and TSP) were characterized as follows:

#### ***Moisture***

Moisture content was measured using the loss on drying method with drying apparatus by heating 2 g of fertilizer at 100 °C for 5 hours [43]. The moisture content is expressed as follow:

$$Mc (\% w/w) = \frac{m_i - m_f}{m_i} \times 100 \quad (1)$$

where  $m_i$  and  $m_f$  are the sample mass before and after drying respectively.

#### ***Determination of macronutrient fertilizers (N, P and K)***

The total nitrogen content was determined using the Kjeldahl method [43], using digestion flask and steam distillation apparatus, while the phosphorus content, which is expressed as a percentage of P<sub>2</sub>O<sub>5</sub>, was determined by gravimetric quinolinium phosphomolybdate method [43], using a Buchner flask, sintered glass funnel with porosity of 5 to 20 μm and filter crucible with porosity of 5 to 20 μm. Various forms of phosphorus present in fertilizers were first converted into orthophosphate which was then precipitated as quinolinium phosphomolybdate [(C<sub>9</sub>H<sub>7</sub>N)<sub>3</sub>H<sub>3</sub>PO<sub>4</sub>·12(MoO<sub>3</sub>)] after reaction with quimociac reagent in a boiling medium. The total phosphate content is expressed by Eq. 2. Potassium content of the fertilizers was also determined by gravimetric method using sodium tetraphenylborate solution (STPB) as reagent [43]. Potassium from sample is first extracted with water or ammonium oxalate and then precipitated as potassium tetraphenylborate with an excess of

sodium tetrphenylborate (STPB). The excess of STPB is back titrated with benzalkonium chloride (BAC) or quaternary ammonium chloride using Clayton yellow as indicator. The potassium content is expressed by Eq. 3.

$$\text{Total phosphate (as } P_2O_5 \text{) \%} = A \times \frac{3.207 (V1)}{V} \times \frac{1}{B} \times 100 \quad (2)$$

$$\text{Total potassium (as } K_2O \text{) \%} = A \times \frac{3.207 (V2)}{V} \times \frac{1}{B} \times 100 \quad (3)$$

where A is the mass (g) of the precipitate, B the mass (g) of analytical sample, V1 the predetermined volume (mL) of the sample solution (the equivalent of 10mg as  $P_2O_5$ ), V2 the predetermined volume (mL) of the sample solution (the equivalent of 15mg as  $K_2O$ ), V the volume (mL) of the sample solution, factor 3.207 is the quinolinium phosphomolybdate precipitate contains 3.207 percent  $P_2O_5$  on mass basis and factor 0.1314 is the potassium tetrphenylborate precipitate contains 0.1314 percent  $K_2O$  on mass basis.

### ***X-ray diffraction analysis***

The X-ray powder diffraction patterns of the studied fertilizers were recorded using a PANalytical X'Pert<sup>3</sup> Powder diffractometer equipped with Cu  $K\alpha$  radiation source ( $\lambda = 1.54178 \text{ \AA}$ ).

### ***Brunauer–Emmett–Teller surface area***

Brunauer–Emmett–Teller (BET) surface area and average pore size of the three studied fertilizers were determined from  $N_2$  adsorption/desorption isotherms at 78K using micrometrics ASAP 2020 surface Area and porosity Analyzer. The surface area was calculated using the multi-point BET method, and a relative pressure ( $P/P_0$ ) between 0.00115 and 0.56784 was applied.

Specific surface area was analyzed according to the BET method using Eq. (4)

$$A_s = (V_m / 22414) \times N_a \times \sigma \quad (4)$$

where  $A_s$  is the surface area of solids,  $V_m$  is the monolayer volume of the adsorbate and  $N_a$  is Avogadro number [44-46].

Pore volume was obtained from the t-plot method using Eq. (5)



$$V_p = (V_f / 22414) \times M / \rho_l \quad (5)$$

where  $V_f$  is the volume of gaseous nitrogen necessary to fill the pores,  $M$  is the molar volume of  $N_2$  and  $\rho_l$  is the liquid density

All calculations were performed using the program of Quantachrome Nova 2200e surface area analyzer.

### **Kinetics of essential oil adsorption and desorption by fertilizers**

Granulated fertilizer (MAP, DAP or TSP) was dried overnight under vacuum at 55 °C in a thermostatic bath to remove completely the moisture content [36-39]. A sample of each fertilizer was then immersed in pure essential oils with a liquid/solid ratio of 10mL/g. The samples were equilibrated in an overhead shaker at room temperature (25°C) and the change of the adsorbed amount of essential oil was determined by measuring the mass of solid samples after each 10 mn until saturation. The essential oil content of the fertilizer at each time  $t$  was calculated by Eq. 6.

$$A_c = \frac{m_t - m_s}{m_s} \quad (6)$$

where  $A_c$  is the adsorbed essential oil content (g/g),  $m_t$  is the total mass of sample at time  $t$  (g) and  $m_s$  is the mass of fertilizer (g).

Desorption kinetic of essential oil from each loaded-fertilizer was determined in open air by measuring the mass change over time of saturated fertilizers samples at constant room temperature.

The relative desorbed essential oil quantity in open air was calculated as follow:

$$D_q = \frac{m_{sat} - m_t}{m_s} \quad (7)$$

where  $D_q$  is the desorbed essential oil mass (g<sub>EO</sub>/g<sub>fertilizer</sub>),  $m_{sat}$  is the saturated mass of sample at equilibrium (g).

### **Effect of temperature on the desorption and desorption operation**

Kinetics of essential oils adsorption and desorption were studied as previously at three temperatures (-5, 15 and 25°C).

## Adsorption isotherms

Solutions of 0.1 mL of essential oil in 10 mL acetone were prepared to carry out the adsorption studies. In batch mode, a given mass of the fertilizer (0.1 ; 0.2; 0.3; 0.4; 0.5; 0.6;0.7;0.8; 0.9 and 1.0 g) was added to 2 mL of the solution and mixed thoroughly for three hours at room temperature (25°C). The adsorption time of three hours was sufficient to reach equilibrium as was found in a preliminary study.

The concentration of each component of the essential oil in the acetone solution was determined by GC-FID. Adsorption isotherms were determined using the peak area of each component of the essential oil before and after adsorption.

The sorbate concentration of each component,  $q_i$ , can be expressed as follow:

$$q_i = \frac{m_i}{m_{ad}} = \frac{V(C_{i0} - C_i)}{m_{ad}} \quad (8)$$

where  $m_i$  is the mass of each component adsorbed (mg),  $m_{ad}$  is the mass of adsorbent (g),  $V$  is the volume of the analyzed acetone solution sample (1 $\mu$ L),  $C_{i0}$  and  $C_i$  are respectively the concentrations of each component at time 0 and at time  $t$  determined by a calibration curve of the GC-FID peak areas.

## Statistical analysis

All data of kinetic of adsorption/desorption, effect of temperature and adsorption study were expressed as means  $\pm$  standard deviations (SD) of triplicate measurements. The confidence limits were set at  $p < 0.05$ . SD did not exceed 5% for the majority of the obtained values.

## RESULTS AND DISCUSSION

### Fertilizers characterization

Chemical and physical characteristics of the three studied fertilizers are summarized in **Table 1**. The results showed that the moisture content by mass is about 1.4, 1.3 and 4.6% respectively for MAP, DAP and TSP. The macronutrient grade of MAP, DAP and TSP are relatively high (11; 49; 0%mass for MAP, 18; 46; 0%mass for DAP and 0; 45; 15%mass for

TSP fertilizer). A notable property of these fertilizers is their aqueous solution pH, which is near neutral for DAP (pH 7.6) and TSP (pH 7.2) while MAP has an acidic character (pH=4.2).

### **X-ray diffraction analysis**

The EDXA analysis data, in **Figure 1**, present the elemental composition of MAP, DAP, and TSP fertilizers. It can be clearly seen that MAP (Figure 1a) DAP (Figure 1b) and TSP (Figure 1c) are composed of N, O, and P, primary elements of these fertilizers. The EDXA spectrum also shows the presence of Ca in the TSP fertilizer, which confirms its chemical composition.

### **BET surface area**

The adsorption-desorption isotherms of N<sub>2</sub> at 78K on the three fertilizers show a Langmuir curve type. This means that occasionally a fall in slope occurs after the first inflection. This is probably due to association of the solute in the gas phase, with increase in partial pressure the solute-solute attraction begins to increase more rapidly than the substrate-solute attraction. The distribution of pore size is regular and the increase in the adsorption of N<sub>2</sub> for TSP and DAP in comparison to the MAP, is possibly due their higher porosity. Relevant data obtained for the three studied fertilizers are presented in **Table 1**. TSP present a higher surface area ( $S_{\text{BET}}=1.43 \text{ m}^2/\text{g}$ ) and pore volume ( $V_p=0.33 \text{ cm}^3/\text{g}$ ) compared to DAP ( $S_{\text{BET}}=0.78 \text{ m}^2/\text{g}$  and  $V_p=0.18 \text{ cm}^3/\text{g}$ ) and MAP ( $S_{\text{BET}}=0.09 \text{ m}^2/\text{g}$  and  $V_p=0.0198 \text{ cm}^3/\text{g}$ ). These differences in  $S_{\text{BET}}$  and  $V_p$  between MAP, DAP and TSP can be explained by the structural morphology of these fertilizers. Indeed, mono-ammonium phosphate (MAP) tends to produce crystals of needle form while the di-ammonium phosphate (DAP) results in more granular forms of crystals which are of conical shape [37-39]. The later crystal form allows to DAP a higher  $S_{\text{BET}}$  and  $V_p$  than those of MAP.

TSP which is characterized by the highest values of  $S_{\text{BET}}$  and  $V_p$  is manufactured by adding phosphoric acid to phosphate rock. Specific surface and the average diameters of the pores of TSP are more related to the phosphate rocks particles. Indeed, the studied TSP is produced using Tunisian phosphate which is mesoporous solid and is characterized by a large specific surface area (about  $17.50 \text{ m}^2/\text{g}$ ) [47].

## Chemical analyses of essential oils

Essential oils were extracted from *Artemisia herba-alba* and *Eucalyptus salubris* plants materials with extraction yields of  $1.08 \pm 0.02\%$  (w/w, dry matter) and  $1.03 \pm 0.03\%$  (w/w, dry matter), respectively.

The components identified in the studied essential oils and their percentage compositions are summarized in **Table 2**. A total of 22 compounds have been identified representing more than the 90% of the total *Artemisia herba-alba* essential oil. For *Eucalyptus salubris*, a total of 13 peaks were detected from the GC/MS analysis of the essential oil.

GC-MS analysis showed six major components (higher than 5%) in *Artemisia herba-alba* essential oil:  $\alpha$ -thujone (27.99%),  $\beta$ -thujone (15.66%), 1,8-cineole (12.22%), 1,5,8-*p*-menthatriene (10,32%), dillapiole (5.77%) and chrysanthenyl acetate (5.05%). Many other minor components were detected in these essential oils such as: (+) spathulenol (3.61%), *p*-cymene (2.66%), camphor (2.53%), and sabinol (2.30%). This  $\alpha$ -thujone oil type has being described in oils from Tunisia [48], Morocco [49] and Algeria [50].  $\beta$ -thujone and  $\alpha$ -thujone have been found to be the major constituents in some *Artemisia herba-alba* oils from Tunisia [51,52] and Morocco [53].

For further comparison, the composition of *Artemisia herba alba* essential oil dominated by thujones was found in Morocco [54-55] and Algeria [56-58]. Camphor-type oils were reported in Spain [59], Morocco [55], Algeria [56,58] and Egypt [60]. Chrysanthenone was reported as an important component in essential oil hydrodistilled from Spanish [61], Moroccan [54,62] and Algerian species [56,58,62]. *Cis*-chrysanthenyl acetate was found to be the major component in some oils from Morocco [54,62] and Algeria [56]. More recently, the chemical variability of *Artemisia herba-alba*, observed in Tunisian areas (North-Western, Center and South-Eastern of Tunisia) showed various compositions dominated either by a single component ( $\alpha$ -thujone, camphor, chrysanthenone or *trans*-sabinyl acetate) or characterized by the occurrence, of two or more of these compounds at appreciable contents [63]. By contrast, the present composition of the essential oil, with 1,5,8-*p*-menthatriene

(10.32%) as a major component, can be considered as a new chemotype of *Artemisia herba alba* growing wild in South-Western of Tunisia.

The insecticidal propriety of *Artemisia herba alba* essential oil are mainly attributed to monoterpenoids [64] which are typically volatile and rather lipophilic compounds that can penetrate into insects rapidly and interfere with their physiological functions [64-66]. Due to their high volatility, they have fumigant action which is very important in controlling the stored-product insects.

Five major components were identified in *Eucalyptus salubris* essential oil: 1,8-cineole (47.79%), *p*-cymene (13.94%),  $\alpha$ -pinene (11.05%), (+) spathulenol (6.70%) and *trans*-pinocarveol (5.90%). 4-terpineol (4.18%),  $\beta$ -eudesmol (2.51%), globulol (1.93%) and many other minor components were identified in these essential oil.

Compared to the literature, chemical composition of the studied *Eucalyptus salubris* essential oil showed some differences [67,68].

Comparing the chemical compositions of essential oil of *Eucalyptus salubris* growing in the South-Western of Tunisia [69] to our studied essential oil, it's showed that the percentage of 1,8-cineole was relatively lower than that reported in literature which ranged between 60 to 70%. Moreover, in our essential oil extracted from leaves of *Eucalyptus salubris*, the proportions of  $\alpha$ -pinene,  $\beta$ -pinene,  $\alpha$ -phellandrene and *trans*-Pinocarveol were more important than these reported in literature. *Eucalyptus salubris* essential oil from Marrakech, Morocco was reported by ZRIRA et al. [70] to contain the same major components as those in our *Eucalyptus* essential oil with some differences in percentage compositions. Indeed, the Moroccan *Eucalyptus salubris* essential oil showed a higher percentage of oxygenated monoterpenes, mainly the 1,8-cineole component (72.9%). Whereas, oxygenated sesquiterpenes are predominant in our essential oil due to the remarkable higher proportions of spathulenol (6.70%), globulol (1.93%) 4-Terpineol (4.18%) and  $\beta$ -Eudesmol (2.51%).

*Eucalyptus salubris* essential oil biological activities reported in literature can be related to the presence of oxygenated compounds and especially 1,8-cineole [71]. Thus, an interesting correlation was found between the concentration of this component and the inhibition of *B.*

*subtilis*, *P. aeruginosa*, *C. albicans* and *M. ramannianus* with a correlation of 0.99, 0.97, 0.79 and 0.78 respectively [71].

A correlation between the insecticidal effect and *Eucalyptus* essential oils contents of 1,8-cineole and *p*-cymene was found on *M. domestica* *A. aegypti* larvae *A. albopictus* *L. longipalpis* *S. zeamais* and many others insects [72,73].

### **Kinetics of essential oil adsorption and desorption by fertilizers**

The adsorption kinetics of *Artemisia herba-alba* and *Eucalyptus salubris* essential oils in the three studied fertilizers are represented in **Figure 2**. It can be observed that the DAP and TSP have greater adsorption capacities compared to MAP. Although, slightly slower kinetics are observed for TSP compared to DAP and their equilibrium adsorption capacities were similar (**DAP (0.135 ± 0.004 g/g)** and **TSP (0.134 ± 0.001 g/g)** for *Artemisia herba-alba* essential oil and an equal quantity of *Eucalyptus salubris* essential oil of **0.114 ± 0.005 g/g** with the two fertilizers). **Figure 2** also shows that the saturation times of DAP and TSP were about 2 and 3 hours, respectively. A much lower adsorption equilibrium capacity was observed with MAP (**0.111 ± 0.002** and **0.0891 ± 0.003 g/g** with *Artemisia herba-alba* and *Eucalyptus salubris* essential oils, respectively). Therefore, the kinetics of *Artemisia herba-alba* essential oil adsorption by MAP were significantly slower compared to DAP and TSP.

The differences in adsorption capacities of the studied fertilizers can be attributed to the differences in their physical and chemical properties (Table 3). Indeed, the chemical bonds of the adsorbed molecules are carried out with interaction sites in adsorbents molecules. Considering the chemical formulas, the DAP has a number of interaction sites about twice that of TSP with a specific surface area close to half. This justifies the obtaining of similar adsorption capacities. In addition, MAP, which has been found to be the least adsorbent of essential oil, is characterized by both a specific surface area and a number of interaction sites lower than those of the TSP and DAP.

Desorption kinetic of *Artemisia herba-alba* and *Eucalyptus salubris* essential oils from the three studied fertilizers is represented in **Figure 3**. Desorption kinetics show that the three

studied fertilizers: DAP; MAP and TSP have a slow kinetics (2.5 days). The desorption of the studied essential oils from saturated samples of TSP, DAP and MAP were conducted in an open air atmosphere at the same temperature and pressure. The change in time of the essential oils content of the three fertilizers (**Figure 3**) indicates a slow kinetic desorption profiles. Compared to DAP and TSP desorption profiles, MAP desorption was shown to be faster. This can be attributed either to the essential oils content of the saturated adsorbents (which is in the order: TSP>DAP>MAP) and sorption physical properties (MAP have the lowest values of  $S_{BET}$  and  $V_p$ ).

Besides, given the significant biological activity of *Eucalyptus salubris* essential oil [73], and since TSP is the most widely marketed fertilizer in Tunisia as well as being relatively inexpensive compared to the other fertilizers, the study will mainly focus in the next sections on the adsorption of *Eucalyptus salubris* essential oil on TSP.

The kinetics of TSP adsorption and desorption with *Eucalyptus salubris* essential oil were studied at three temperatures (-5, +5 and +25°C). Results given in **Figures 4** confirm the exothermic aspect of essential oils adsorption by the fertilizers. Indeed, the amount adsorbed increases significantly with decreasing temperature evolving from  $0.902 \pm 0.002$  g/g at 25 °C to  $0.967 \pm 0.001$  g/g at 5°C and reached  $1.221 \pm 0.004$  g/g at -5 °C. The Arrhenius equation was used to fit the experimental data and from which the activation energy,  $E_a$ , was determined; a value of  $E_a$  equal to -8.3 kJ/mol was obtained. The low value of  $E_a$  indicates that the essential oil interaction with the fertilizers may proceed through van der Waals type interactions.

## **Modelling of adsorption kinetics**

### ***Pseudo first and second order models***

The modelling of batch adsorption kinetics of essential oil by the fertilizers was studied using the Lagergren pseudo-first order and pseudo second order models [74,75].

The first-order kinetic equation can be written as:

$$\frac{dq_t}{dt} = k_1 \times (q_e - q_t) \quad (9)$$

After integration and applying the initial condition  $(q_e - q_t) = q_e$  at  $t = 0$ , Equation 10 is obtained:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 \times t \quad (10)$$

The pseudo-second-order kinetics can be expressed by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (11)$$

where:  $q_e$  and  $q_t$  are the adsorption capacities at equilibrium and at time  $t$ , respectively ( $\text{g}\cdot\text{g}^{-1}$ ),  $k_1$  ( $\text{L}\cdot\text{min}^{-1}$ ) and  $k_2$  ( $\text{g}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$ ) are the rate constants of pseudo first-order and pseudo second-order adsorption, respectively [76,77]. The pseudo first-order adsorption rate constant,  $k_1$ , can be determined from the slope of a plot of  $\ln(q_e - q_t)$  versus  $t$  while the pseudo-second-order adsorption rate constant,  $k_2$ , can be determined from the intercept of a plot of  $t/q_t$  versus  $t$ . The best fit of the experimental data by either models, as determined by how close the correlation coefficient  $R^2$  to 1, will define which of the models best describe the adsorption process. **Figure 5** shows the plots using the two models for the adsorption of *Eucalyptus salubris* essential oil on the three fertilizers while Table 3 provides the parameters of each model and the values of the correlation coefficient  $R^2$ . The results given in **Table 4** show that the correlation coefficients  $R^2$  for to the pseudo-second order adsorption model have higher values as compared to the pseudo-first order model for the three studied fertilizers. Thus, the pseudo second order model is more suitable to describe the adsorption of essential oils on the fertilizers.

### ***Adsorption mechanism***

To achieve a better understanding of the mechanisms and rate controlling steps affecting the kinetics of adsorption, the kinetic experimental results were fitted to the Weber and Morris's intra-particle diffusion model [78]. In this model, the evolution of the amount adsorbed versus time is expressed as:

$$q_t = (k_{id} \times t^{1/2}) + C \quad (12)$$

where:  $k_{id}$  is the rate constant for intra-particle diffusion and  $C$  is a constant that is function of the boundary layer thickness. If  $C=0$  then the adsorption process is controlled by intra-particle



diffusion. If no then the adsorption process is controlled by mass transfer in the boundary layer and if multi-linear plots were obtained then a combination of diffusion and film mass transfer influence the adsorption process [79].

A plot of  $q_t$  versus  $t^{0.5}$  for *Eucalyptus salubris* essential oil adsorption is shown on **Figure 6**. The line in the first linear part passes through the point (0,0) indicating that pore diffusion controls the adsorption process and the film resistance may be neglected, whereas the horizontal lines present the equilibrium being reached [79].

In the present work, a multi-components adsorption is considered. Furthermore, the study of adsorption of each essential oil component, especially those exhibiting higher biological activities is very interesting to control the essential oil-fertilizer produced.

### **Adsorption of essential oil components**

Adsorption isotherms of *Eucalyptus salubris* essential oil components by TSP are shown in **Figure 7**. The change of the adsorbed amount of each essential oil compound with his equilibrium concentration showed variable adsorption capacities which decreased in the order: *1,8-cineole* > *p-cymene* > *spathulenol* > *isopinocarveol* > *pinocarvone* >  $\alpha$ -*pinene* > *globulol* > *terpineol* >  $\beta$ -*eudesmol* >  $\alpha$ -*phellandrene* >  $\beta$ -*pinene*. The most adsorbed components are the terpenes *1,8-cineole* and *p-cymene* which are the major constituents of the essential oil (47.79% and 13.94% respectively).

The majority of essential oil components were partially adsorbed by TSP in the studied adsorbent mass range except  $\beta$ -*eudesmol*,  $\alpha$ -*phellandrene* and  $\beta$ -*pinene* which are totally adsorbed.

The variability of the adsorbed amounts of the essential oil components can be explained by the affinity differences exhibited by the essential oil components to TSP. This affinity is related to their physical and chemical properties such as molecule polarity and their concentration in the crude essential [35,36]. Oxygenated monoterpenes represent 63.6% of total amount of essential oil adsorbed on TSP while lower quantities of monoterpenes hydrocarbons and oxygenated sesquiterpenes were adsorbed (24.65% and 11.73% of the total adsorbed amount, respectively). These results show a correlation between the adsorbed

amount of each compound and their concentrations in the crude essential oil (oxygenated monoterpenes: 58.89%, monoterpenes hydrocarbons: 28.70% and oxygenated sesquiterpenes: 11.15%). Furthermore, the oxygenated monoterpenes (*1,8*-cineole, isopinocarveol, pinocarvone and terpineol) and sesquiterpenes (spathulenol) which are high polar components were showed to be the most adsorbed compounds (Table 5). Whereas, the most abundant non polar monoterpene hydrocarbons: *p*-cymene (13.94% in the crude essential oil) is well adsorbed compared to the other monoterpenes ( $\alpha$ -pinene,  $\alpha$ -phellandrene and  $\beta$ -pinene).

Moreover oxygenated sesquiterpene: spathulenol (6.70% in the crude essential oil) is well adsorbed since it's a high polar component (Table 5).

The selectivity was affected by the abundance of each component in the crude essential oil (*1,8*-cineole (2294 mg/g), *p*-cymene (639 mg/g) and  $\alpha$ -pinene (381 mg/g)) which are the major constituents of the pure essential oil (47.79%, 13.94% and 11.05% respectively).

These results are similar with others cited in the literature. Indeed, some interested studies that focus on the study of essential oils adsorption on clays have shown that the selectivity was affected by the abundance of each component in the crude essential oil and the polarity of terpenic components. El Miz et al. [34], studied the adsorption of essential oil components of *Lavandula angustifolia* on sodium modified bentonite. They have shown that the most adsorbed components of these oil are: 2- $\beta$  pinene,  $\alpha$ -thujon, camphor, linalool, fenchol (*Z E*) and  $\alpha$ -farnesene which are the most abundant of the considered essential oil. In the other hand, they conclude that the selectivity of adsorption was affected by the polarity of terpenic components (2- $\beta$  pinene, 1,8-cineol and  $\alpha$ -thujon were adsorbed in larger amounts than some others monoterpene hydrocarbons).

In other research, El Miz et al [35], were studied the adsorption of thymol (main component of thymus essential oil) on sodium bentonite (montmorillonite clay), and Pillared clay (modified montmorillonite clay) [35], and have showed that the equilibrium adsorption of thymol increases with the increase of initial thymol concentration showing the adsorption process to be dependent on the initial concentration of sorbet. The maximum amount

adsorbed was 177 and 319  $\text{mg}\cdot\text{g}^{-1}$  respectively indicating a good affinity of thymol for anionic clay sites [35].

MMG. Nguemtchouin et al [36], studied the adsorption of essential oil components of *Xylopia aethiopica* (Annonaceae) by kaolin. They founded that the selectivity was affected by the abundance of each component in the crude essential oil; sabinene,  $\beta$ -pinene,  $\beta$ -phellandrene and  $\alpha$ -pinene which are the most adsorbed were the most abundant compounds (23.90%, 27.90%, 15.91% and 11.10% respectively), while  $\alpha$ -terpinene (2.22%) was the less adsorbed in all case. The selectivity of adsorption was affected by the polarity of terpenic components; germacrene D and terpinen-4-ol were adsorbed in larger amounts than some monoterpene hydrocarbons.

Regarding the differences between the amounts of essential oil constituents on TSP fertilizer and in order to enhance the design of an adsorbent system of fertilizer loaded with essential oil, it is necessary to know the most appropriate adsorption model.

### ***Fitting of adsorption isotherms***

Langmuir and Freundlich isotherm adsorption models were tested for their ability to describe the experimental results [80,81]. The adsorption Langmuir model is based on the assumption that the maximum amount adsorbed corresponds to a saturated monolayer of solute molecules on the surface of the adsorbent, without interaction between the adsorbed molecules side [81]. The linear expression of the Langmuir model is given by Eq. (13):

$$\frac{C_{ei}}{q_{ei}} = \frac{1}{K_{Li} \times q_{mi}} + \frac{1}{q_{mi}} \times C_{ei} \quad (13)$$

where  $q_{ei}$  ( $\mu\text{g}/\text{g}$ ) and  $C_{ei}$  ( $\mu\text{g}/\text{mL}$ ) are respectively the amount adsorbed of each essential oil compound per unit mass of fertilizer and essential oil concentration of the component at equilibrium,  $q_{mi}$  is the maximum amount adsorbed of the essential oil component per unit mass of the fertilizer requisite to form a complete monolayer on the surface bound at high  $C_{ei}$ , and  $K_{Li}$  is a constant related to the affinity of the binding sites ( $\text{mL}/\mu\text{g}$ ).

A plot of  $C_{ei}/q_{ei}$  vs  $C_{ei}$ ,  $q_{mi}$  and  $K_{Li}$  are determined from the slope and the intercept.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor  $R_L$  that is given by Eq. (14):

$$R_L = \frac{1}{1 + (K_L \times C_0)} \quad (14)$$

where  $C_0$  is the highest initial concentration of adsorbate ( $\mu\text{g/mL}$ ), and  $K_L$  ( $\text{mL}/\mu\text{g}$ ) is Langmuir constant. The value of  $R_L$  indicates the form of the isotherm to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ), or irreversible ( $R_L = 0$ ).

The second studied model is Freundlich model which is an empirical equation based on the distribution of solute between the solid phase and aqueous phase at equilibrium [80]. The Freundlich model can be expressed by Eq. (15)

$$q_{ei} = k_{fi} \times C_{ei}^{(1/n_i)} \quad (15)$$

Where  $q_{ei}$  is the amount adsorbed of each essential oil component at equilibrium,  $C_{ei}$  is the equilibrium concentration of each essential oil compound in solution,  $k_{fi}$  and  $n_i$  are empirical constants. The linear form of Eq. (15) is:

$$\ln(q_{ei}) = \ln(k_{fi}) + (1/n_i) \times \ln C_{ei} \quad (16)$$

$k_{fi}$  can be defined as adsorption or distribution coefficient and represents the quantity of each compound adsorbed onto the adsorbent for a unit equilibrium concentration ( $\mu\text{g}\cdot\text{g}^{-1}$ ) in accordance with Halsey [82], the relationship between  $k_{fi}$  and  $q_{mi}$  is:

$$k_{fi} = \frac{q_{mi}}{C_{0i}^n} \quad (17)$$

Where  $q_{mi}$  is the maximum adsorption capacity of each essential oil component. The slope  $1/n_i$ , ranging between 0 and 1, is a measure for the adsorption intensity or surface heterogeneity [74], A plot of  $\ln(q_{ei})$  vs  $\ln(C_{ei})$  enables the empirical constants  $k_{fi}$  and  $1/n_i$  to be determined from the intercept and slope of the linear regression. The two common isotherm models have been tested in the present study: Langmuir and Freundlich models.

Applicability of the isotherm equations was compared in **Table 6** by judging the correlation coefficient,  $R^2$  [35,36].

The Langmuir constants  $q_{mi}$  and  $K_{Li}$ , the Freundlich constants  $n$  and  $K_{fi}$  and the correlation coefficient  $R^2$  for the two models are presented in **Table 6**. These results indicate that the Langmuir model fits well the adsorption isotherms of most of the *Eucalyptus salubris* essential oil components. Based on these results, Langmuir model is showed to fit well the experimental data of the components *1,8-cineole*,  $\alpha$ -pinene,  $\beta$ -pinene, isopinocarveol,  $\beta$ -eudesmol,  $\alpha$ -phellandrene and pinocarvone with a correlation coefficients  $R^2$  close to 1 ( $>0.95$ ) can conform to this model. The adsorption of other compounds mainly *p-cymene*, terpineol, spathulenol and globulol is well fitted by Freundlich model.

According to the obtained results, TSP presented the highest adsorption capacity for *1,8-cineole* with  $q_m=2294,97 \mu\text{g}\cdot\text{g}^{-1}$ ,  $K_L=100$  and  $K_f=6,580$ ; then *p-cymene* with  $q_m=639,21\mu\text{g}\cdot\text{g}^{-1}$ ,  $K_L= 70$  and  $K_f=1,685$ .  $\alpha$ -pinene, spathulenol, pinocarvone, isopinocarveol and terpineol have respectively  $q_m=381,06 \mu\text{g}\cdot\text{g}^{-1}$ ,  $q_m=320,28\mu\text{g}\cdot\text{g}^{-1}$ ,  $q_m=253,31 \mu\text{g}\cdot\text{g}^{-1}$ ,  $q_m=253,31 \mu\text{g}\cdot\text{g}^{-1}$  and  $133,93 \mu\text{g}\cdot\text{g}^{-1}$ .

## CONCLUSION

Essential oils of *Eucalyptus salubris* and *Artemisia herba* adsorption on the three studied fertilizers DAP, MAP and TSP showed that DAP and TSP exhibited higher adsorption capacities and slower desorption kinetics as compared to MAP. The adsorption kinetics of all identified components in *Eucalyptus salubris* essential oil showed that the terpenes: *1,8-cineole* and *p-cymene* were more adsorbed than the other components. The variability of the adsorbed amounts of the essential oil components can be explained by the abundance of each component in the crude essential oil and the affinity of compounds which is related to their physical and chemical properties such as molecule polarity.

The experimental adsorption data were fitted by Langmuir and Freundlich models at low values of equilibrium concentration. Adsorption isotherms of the terpenic compounds of *Eucalyptus salubris* essential oil on TSP was fitted with Langmuir model like: *1,8-cineole*,  $\alpha$ -

pinene,  $\beta$ -pinene, isopinocarveol,  $\beta$ -eudesmol,  $\alpha$ -phellandrene, pinocarvone, *p*-cymene and spathulenol, and Freundlich model like :terpineol and globulol. This study has shown that fertilizers commonly used in agriculture can be used as media for the slow release of essential oils and hence have potential as an alternative technology to synthetic pesticides for the control of pests.

## FIGURE CAPTIONS

**Figure 1.** Energy Dispersive X-ray Analysis (EDXA) spectra of the fertilizers; a) Mono-Ammonium Phosphate MAP; b) Di-Ammonium Phosphate DAP; and c) Triple Super Phosphate TSP.

**Figure 2.** Adsorption kinetics of a) *Artemisia herba-alba* and b) *Eucalyptus salubris*; Used symbols: ◆ - TSP; ▲ - MAP; ■ - DAP

**Figure 3.** Desorption kinetics of a) *Artemisia herba-alba* and b) *Eucalyptus salubri*; Used symbols: ◆ - TSP; ▲ - MAP; ■ - DAP

**Figure 4.** Effect of temperature on the a) adsorption and b) desorption kinetics of *Eucalyptus salubris* essential oil on Triple Super Phosphate (TSP); Used symbols: ◆ - (-5 °C); ■ - (+5 °C); ▲ - (+25 °C)

**Figure 5. a)** Pseudo-first-order and **b)** Pseudo-second-order kinetics for adsorption of *Eucalyptus salubris* essential oil on fertilizers; Used symbols: ◆ - TSP; ▲ - MAP; ■ - DAP

**Figure 6.** Intraparticle diffusion for adsorption of *Eucalyptus salubris* essential oil on fertilizers; Used symbols: ◆ - TSP; ▲ - MAP; ■ - DAP

**Figure 7.** Adsorption isotherms of *Eucalyptus salubris* essential oil components on Triple Super Phosphate (TSP) plotted at different x-axis scales of concentration (g/L) a) 0 to 0.16; (b) 0 to 0.045; (c) 0 to 0.02

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**Table 1. Chemical and physical characterization of the fertilizers**

	<b>MAP</b>	<b>DAP</b>	<b>TSP</b>
<b>Chemical formula</b>	(NH <sub>4</sub> )H <sub>2</sub> PO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> .H <sub>2</sub> O
<b>Total nitrogen, %mass</b>	11	18	-
<b>Total phosphates as P<sub>2</sub>O<sub>5</sub>, %mass</b>	49	46	45
<b>Ca, %mass</b>	-	-	15
<b>pH</b>	4.2	7.6	7.2
<b>Moisture, %mass</b>	1.4	1.3	4.6
<b>Particle size (mm)</b>	1 – 4	1 – 4	1 – 4
<b>Average pore size (μm)</b>	69.8	7.7	4.2
<b>BET surface area (m<sup>2</sup>/g)</b>	0.09	0.78	1.43
<b>Pore volume (cm<sup>3</sup>/g)</b>	0.0198	0.1800	0.3284

**Table 2. Essential Oil composition of the aerial parts of *Artemisia herba-alba* and *Eucalyptus salubris***

peak N°	RI	Compound	<i>Artemisia herba-alba</i>	<i>Eucalyptus salubris</i>
			Composition (%)	Composition (%)
1	931	$\alpha$ -Thujene	-	1.14
2	936	$\alpha$ -pinene	0.70	11.05
3	940	$\beta$ -pinene	-	0.87
4	998	$\alpha$ -phellandrene	-	1.70
5	1018	1,5,8-p-menthatriene	10.32	-
6	1025	p-cymene	2.66	13.94
7	1030	1,8-cineol	12.22	47.79
8	1110	$\alpha$ -thujone	27.99	-
9	1114	$\beta$ -thujone	15.66	-
10	1123	Chrysanthenone	1.77	-
11	1141	trans-Pinocarveol	-	5.90
12	1143	Sabinol	2.30	-
13	1144	Camphor	2.53	-
14	1141	Verbenol	1.87	-
15	1160	Pinocarvone	-	1.01
16	1168	Borneol	0.71	-
17	1177	4-Terpineol	-	4.18
18	1227	Nordavanone	0.63	-
19	1262	chrysanthenyl acetate	5.05	-
20	1474	germacrene-D	0.91	-
21	1476	$\gamma$ -Selinene	1.13	-
22	1494	bicyclogermacrene	0.59	-
23	1523	davana ether	0.67	-
24	1576	(+) spathulenol	3.61	6.70
25	1578	Globulol	-	1.93
26	1622	dillapiole	5.77	-
27	1651	$\beta$ -Eudesmol	-	2.51
28	1655	1,3-cyclopentadiene	1.49	-
29	1841	5-amino-1-ethylpyrazole	0.55	-
30		Others	-	1.26
<b>Total</b>			<b>99.13</b>	<b>99.99</b>
Total identified			<b>93.36</b>	<b>98.73</b>
Monoterpenes hydrocarbons			13.68	28.70
Oxygenated monoterpenes			70.73	58.89
Total monoterpenes			<b>84.41</b>	<b>87.58</b>
Sesquiterpenes hydrocarbons			2.63	-
Oxygenated sesquiterpenes			9.38	11.15
Total sesquiterpenes			<b>12.01</b>	<b>11.15</b>


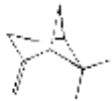
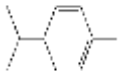





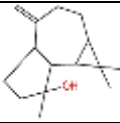
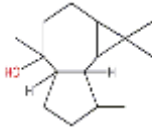
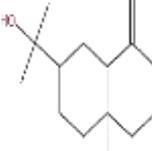
**Table 3. Physical and chemical properties of fertilizers and differences in essential oils adsorption capacities.**

Fertilizer	chemical formula	structural formula	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$V_p$ (cm <sup>3</sup> /g)	Adsorbed amount of Essential oil (gEO/g)	
					<i>Artemisia herba-alba</i>	<i>Eucalyptus salubris</i>
<b>MAP</b>	(NH <sub>4</sub> )H <sub>2</sub> PO <sub>4</sub>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HO}-\text{P}-\text{O}^- \text{NH}_4^+ \\   \\ \text{HO} \end{array}$	0.09	0.0198	0.111 ± 0.002	0.0891 ± 0.003
<b>DAP</b>	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	$\left[ \begin{array}{c} \text{O} \\ \parallel \\ \text{O}^--\text{P}-\text{O}^- \\   \\ \text{OH} \end{array} \right] \left[ \text{NH}_4^+ \right]_2$	0.78	0.1800	0.135 ± 0.004	0.114 ± 0.005
<b>TSP</b>	Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> .H <sub>2</sub> O	$\left[ \begin{array}{c} \text{O} \\ \parallel \\ \text{HO}-\text{P}-\text{O}^- \\   \\ \text{OH} \end{array} \right]_2 \left[ \text{Ca}^{2+} \right]$	1.43	0.3284	0.134 ± 0.001	0.114 ± 0.005

**Table 4. Pseudo-first-order, pseudo second order and intraparticle diffusion model adsorption rate constants.**

	Pseud first order kinetic			Pseudo second order kinetic			Intraparticle diffusion model		
	$q_e$ ( $g \cdot g^{-1}$ )	$k_1$ ( $g \cdot g^{-1} \cdot min^{-1}$ )	$R^2$	$q_{e2}$ ( $g \cdot g^{-1}$ )	$k_2$ ( $g \cdot g^{-1} \cdot min^{-1}$ )	$R^2$	$K_{int}$ ( $min^{-1}$ )	C	$R^2$
<b>TSP</b>	0.2432	2.1463	0.938	0.1393	12.79	0.989	0.0883	0.002	0.993
<b>DAP</b>	0.0739	1.1764	0.898	0.1373	12.45	0.999	0.1	0.004	0.971
<b>MAP</b>	0.1729	1.1256	0.833	0.1152	18.69	0.942	0.055	0.003	0.995

**Table 5: Chemical properties of *Eucalyptus salubris* essential oil compounds.**

Compound	<i>Eucalyptus salubris</i>	chemical formula	structural formula
	Composition (%)		
$\alpha$ -pinene	10.47	C <sub>10</sub> H <sub>16</sub>	
$\beta$ -pinene	0.82	C <sub>10</sub> H <sub>16</sub>	
$\alpha$ -phellandrene	1.61	C <sub>10</sub> H <sub>16</sub>	
p-cymene	13.21	C <sub>10</sub> H <sub>14</sub>	
1,8-cineole	45.28	C <sub>10</sub> H <sub>18</sub> O	
trans-Pinocarveol	5.59	C <sub>10</sub> H <sub>16</sub> O	
Pinocarvone	0.96	C <sub>10</sub> H <sub>14</sub> O	
4-Terpineol	3.96	C <sub>10</sub> H <sub>18</sub> O	
(+) spathulenol	6.35	C <sub>15</sub> H <sub>24</sub> O	
Globulol	1.83	C <sub>15</sub> H <sub>26</sub> O	
$\beta$ -Eudesmol	2.38	C <sub>15</sub> H <sub>26</sub> O	

**Table 6: Isotherm parameters for adsorption of *Eucalyptus salubris* essential oil on TSP.**

Compound	Langmuir model				Freundlich model		
	$q_m$ (th) ( $\mu\text{g}\cdot\text{g}^{-1}$ )	$q_m$ (exp) ( $\mu\text{g}\cdot\text{g}^{-1}$ )	$K_L$ ( $\text{dm}^3\cdot\text{g}^{-1}$ )	$R^2$	n	$K_f$ ( $\text{dm}^3\cdot\text{g}^{-1}$ ) <sup>1)</sup>	$R^2$
<b>1,8-Cineole</b>	2500.000	2294.97	100	0.982			
<b><math>\alpha</math>-Pinene</b>	238.095	381.06	105	0.967			
<b><math>\beta</math>-Pinene</b>	37.594	35.15	1330	0.971			
<b>Para-cymene</b>					0.626	1.685	0.947
<b>Isopinocarveol</b>	263.158	253.31	190	0.977			
<b><math>\beta</math>-eudesmol</b>	92.593	92.84	0.011	0.999			
<b><math>\alpha</math>-phellandrene</b>	83.333	80.85	2000	0.996			
<b>Pinocarvone</b>	263.158	253.31	190	0.977			
<b>Terpineol</b>					1.298	1.161	0.990
<b>Spathulenol</b>					1.746	0.939	0.979
<b>Globulol</b>					4.762	1.022	0.986

$K_L$ , direct measure for the adsorption intensity;  $q_{m(\text{exp})}$  and  $q_{m(\text{th})}$  limited adsorption capacity;  
 $K_f$ , adsorption or distribution coefficient Freundlich model and;  $R^2$  correlation coefficient.



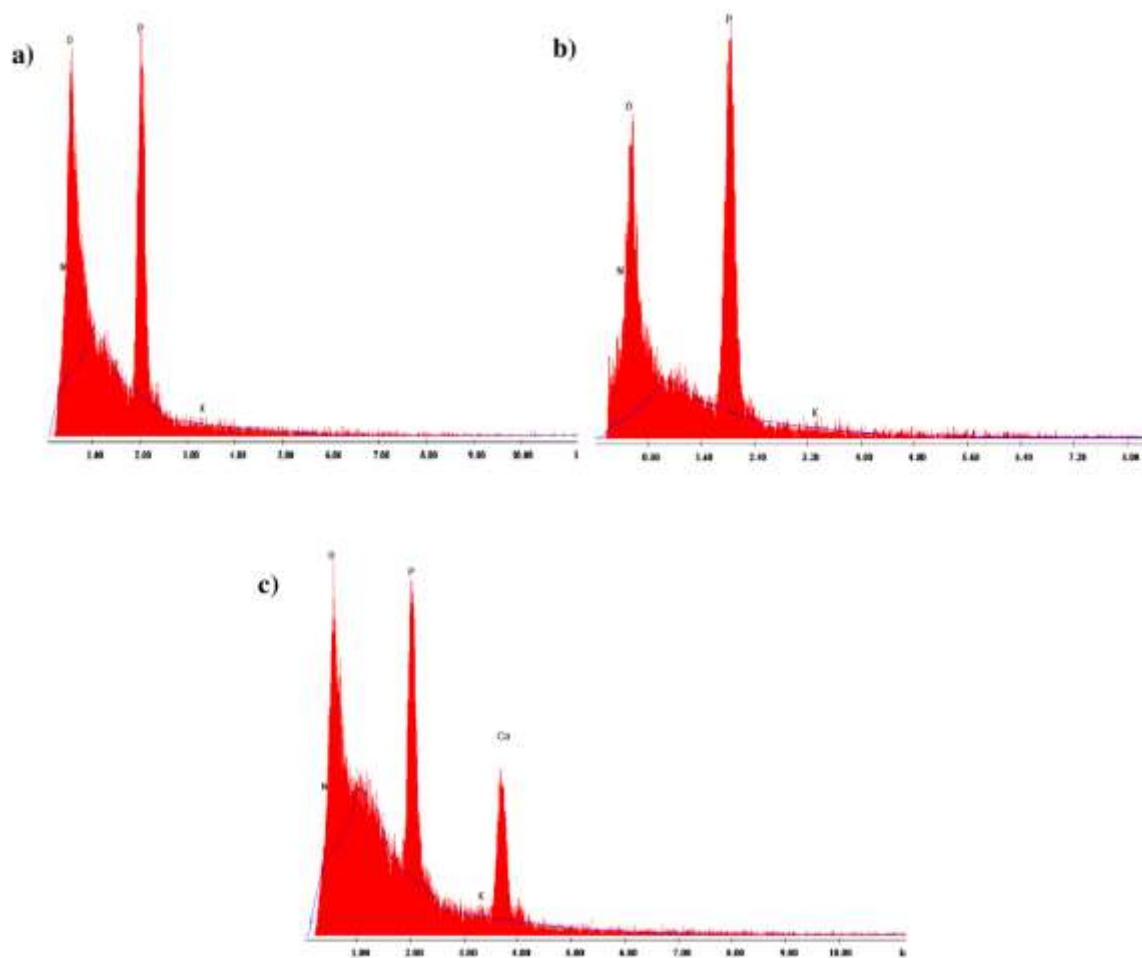


Figure 1.

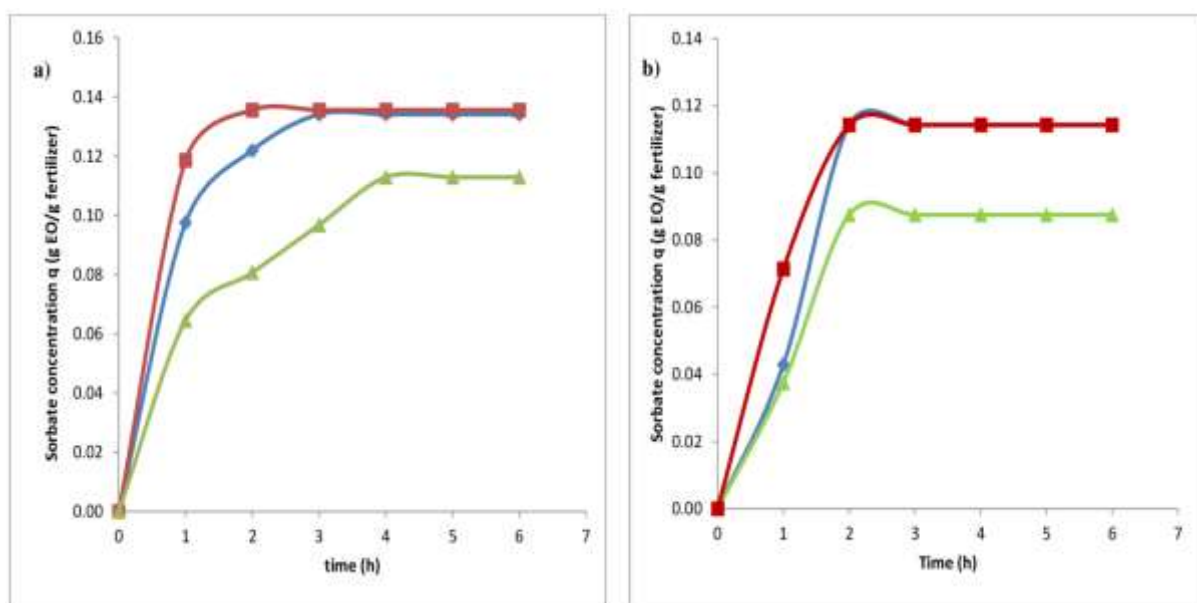


Figure 2.

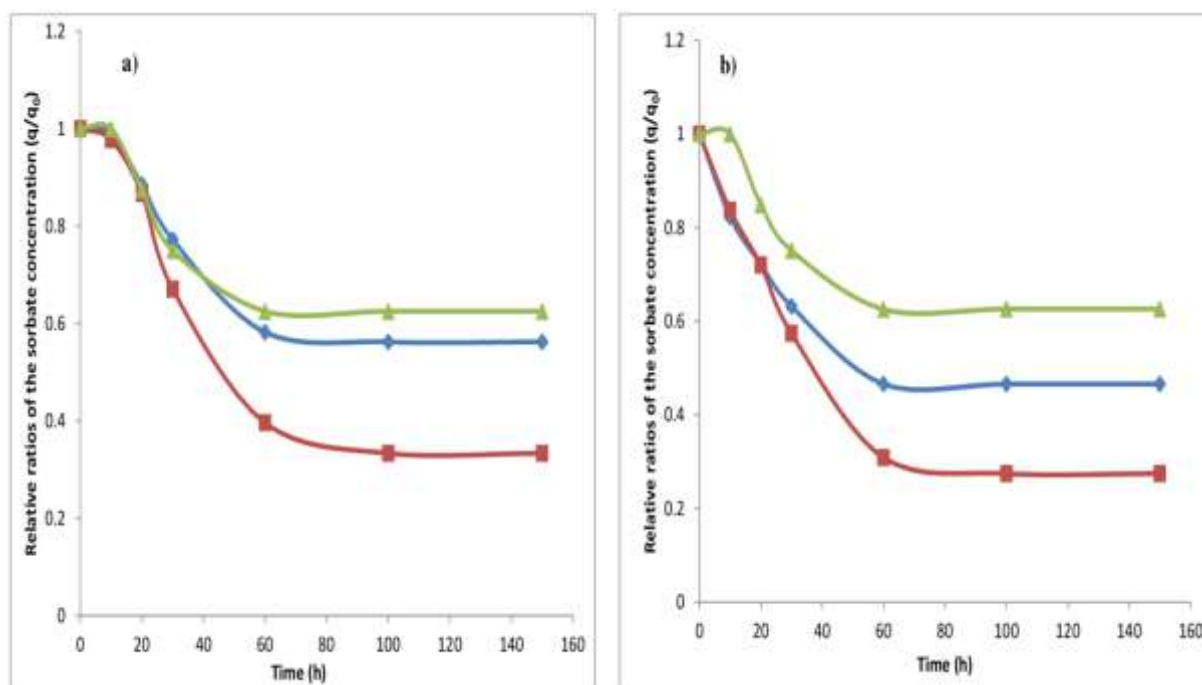


Figure 3.

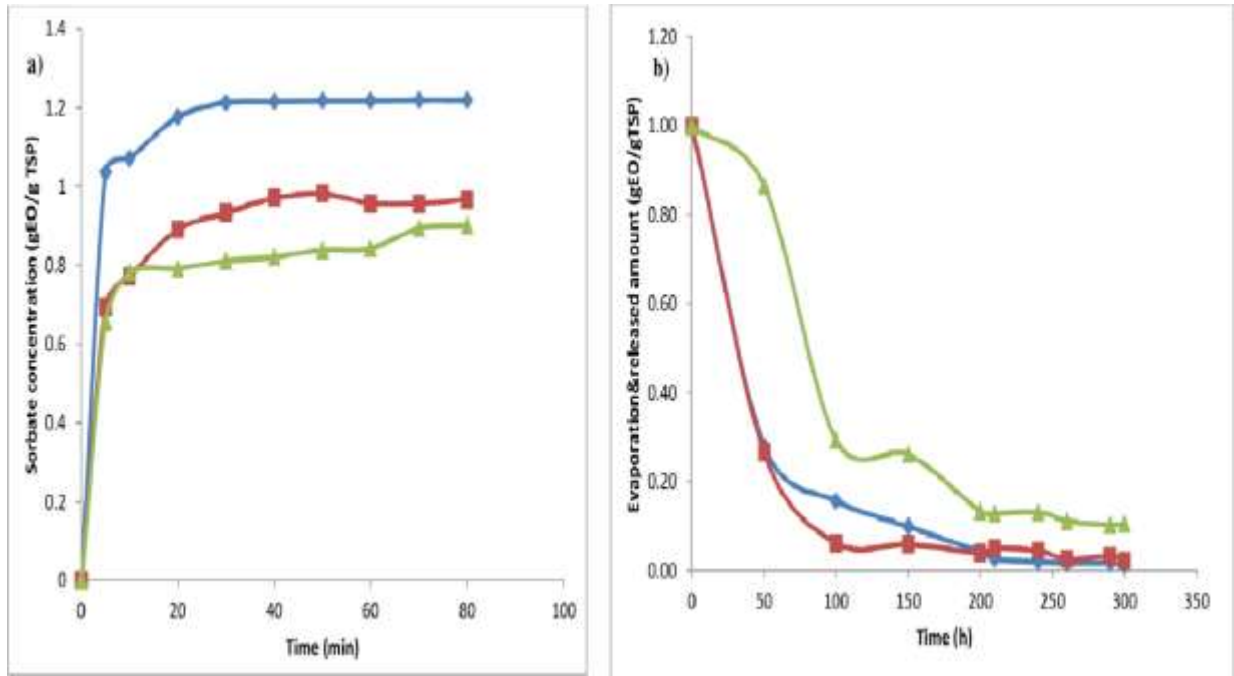


Figure 4.

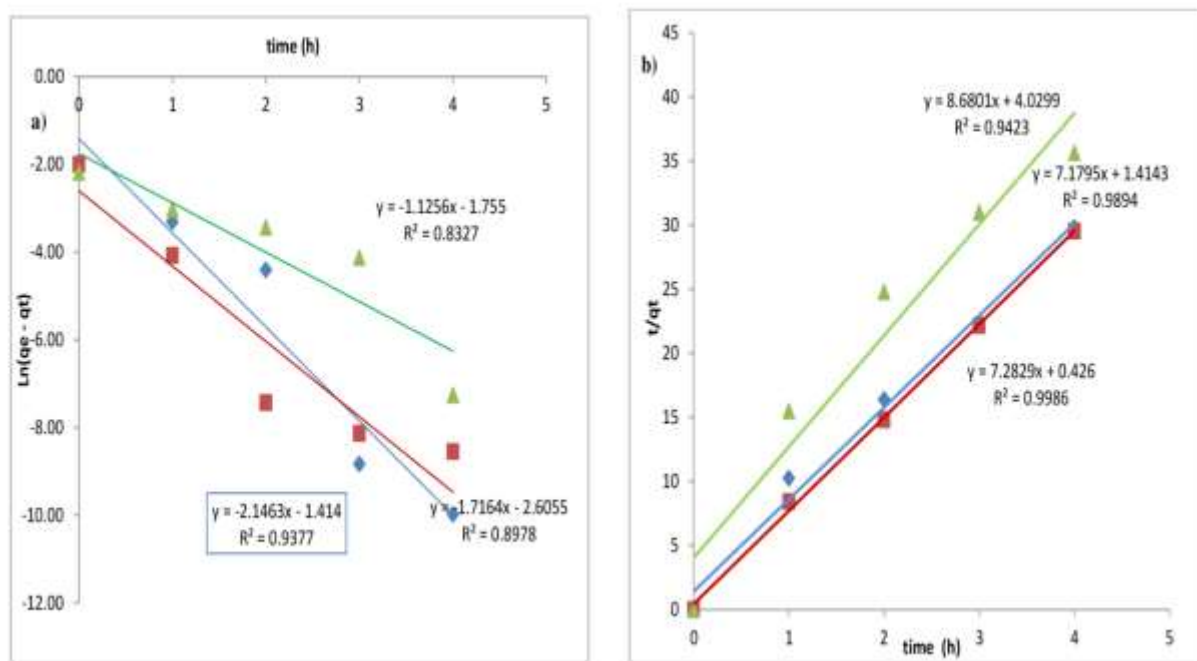


Figure 5.

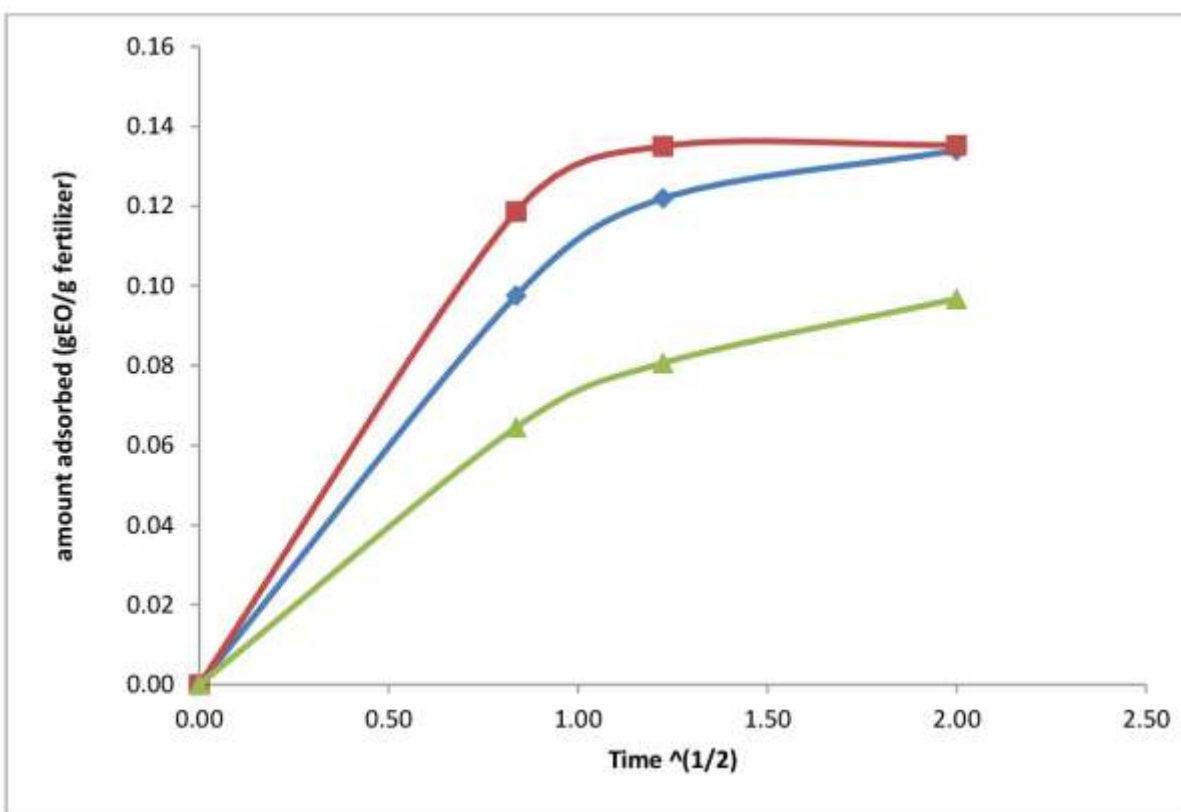


Figure 6.

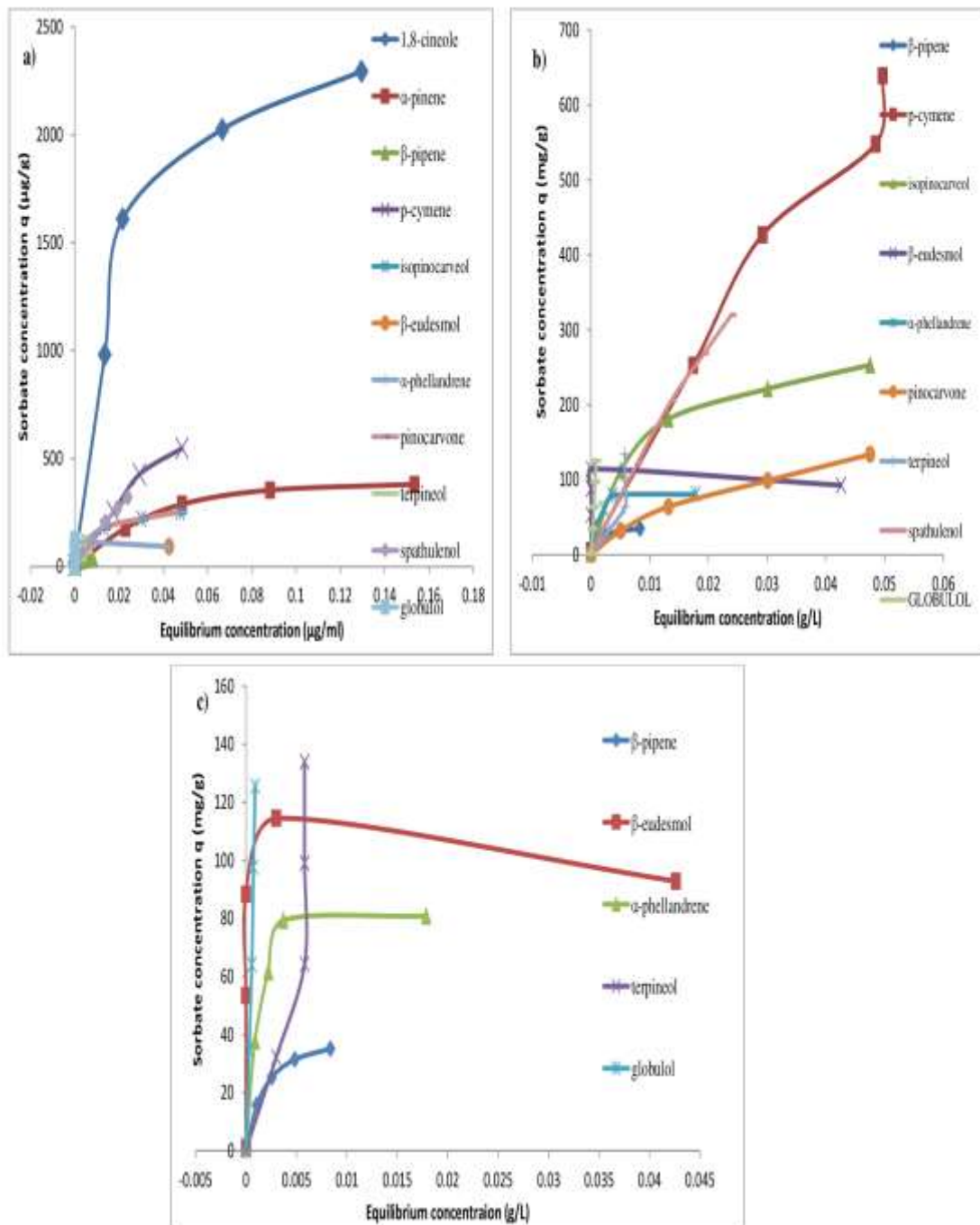


Figure 7.