Research Paper   Open Access

Extraction of Pb(II) from aqueous solutions using silica fume immobilized two quinoline derivatives

Asmaa M. Abdel Rahim[a,b*]

aDepartment of Chemistry, College of Science, University of Hafr Al Batin, P.O. Box 1803, Hafr Al Batin, 31991, Saudi Arabia
bChemistry Department, Faculty of Science, Minia University, Minia, Egypt
*Corresponding author: amoheyeldin@uhb.edu.sa

Abstract
Silica fume (SF) was modified with quinoline derivatives and used for the removal of Pb(II) from aqueous solution. SF and its phases were characterized by FT-IR and X-ray analysis. The effects of pH value, shaking time and amount of adsorbent were investigated. 8-hydroxy quinoline has the highest percentage of extraction and the maximum adsorption capacity which leading to choose it as the best one for removal of Pb(II).
Keywords*: Pb(II), quinoline derivatives, silica fume.*

I.   INTRODUCTION:

As a result of the success of the quinoline compounds to form stable complexes with metal ions and their complexes are sparingly soluble in water; this led to the possibility of their use as organic modifier on material surface to extract and removal of some toxic metal ions. Quinoline itself has few applications, but many of its derivatives i.e. 8-hydroxy quinoline (8HQ) and 2-hydroxy quinoline (2HQ) are useful in diverse applications. In fact, the nature of solid support whether organic [1, 2] or inorganic [3, 4] can control the stability, durability and mechanical properties. To increase its selectivity and loading capacity, it is needed to modification of its surface. In this context, silica fume (SF) could be modified with organic functional groups to obtain a new SF-based material capable of chelating heavy metal ions. The selectivity of these materials mainly depends on the structure of the immobilized organic compound and the positioning of the functional groups along the surface of the SF support [5]. Quinoline compounds are one of such suitable organic modifiers. It was pointed out that 8HQ was the best quinoline derivatives when use as modifier on SF surface, as it has applications for complexation of some of heavy metal ions [6, 7], and the nitrogen atom of heterocyclic ring and adjacent phenolic –OH group suitable for chelation with heavy metal ions [8].

Silica fume (SF), which is generated during silicon metal production from a blast furnace and historically considered as a waste product, is chosen as ideal solid supports for some reasons including: it is non-toxic and cheap. It has specific high surface area [9]. Also, this sub-micrometer particles with smooth surface is great negatively charged which is useful for binding with positively charged metal ion. Furthermore, silica or silica fume surface has been shown to strongly bind metal ion via surface complexation [10, 11]. In spite of all these advantages, there is no studies have been reported on using SF as SP-extractor for the determination of heavy metal ions and there are little papers used silica fumes after modification for these purposes [9, 12].

The solid phase extraction (SPE) method has emerged as a powerful tool for enrichment/separation of metal ions because of its various advantages over other methods, such as higher preconcentration factor, lesser waste generation, lower matrix effect, use of less toxic solvents, saving of time and cost, easiness of regenerability of a solid phase, and thereby more reusability. It can be used better than other methods such as liquid–liquid extraction (LLE) for preconcentration, separation and determination of metal ions such as lead [13–16]. Lead as a metal has been used for thousands of years due to its simple and ease of extraction and handling with, however it is a toxic metal and generally identified as an element of high toxicity due to environmental accumulation and high mobility [17, 18]. Lead as a poisonous metal can cause severe health problems for humans. It can attack almost all organs and systems in the human body with the main targets for lead toxicity are the nervous system, especially in young children as well as blood and brain disorders [19]. Its

poisoning is commonly a result of food or water contaminated with lead ingestion or may be caused by accidental ingestion of contaminated soil, dust, or lead based paint [20]. Water is one of the main sources of lead contamination for the general public. Even though the lead quantity in these samples is low, its presenting in the daily diet may have significant physiological effects [21]. The determination of lead ions at trace levels in water samples requires the use of highly sensitive and reliable analytical techniques [22]. This is what led to the use of SPE method direct determination and separation of lead from aqueous solutions. Various SP-extractors have been used for the separation and extraction of lead ions as its chelates, graphene [13], alumina-coated magnetite nanoparticles [15], multiwalled carbon nanotubes /poly(2-amino thiophenol) nanocomposites [16], SiO_2-nanoparticles [10, 11], silica-supported bis(diazoimine) ligand [27] and functionalized resin [28].

In the present work, a new simple SPE technique based on modification of SF with quinoline derivatives, and the influence of effective variables for selective extraction and separation of Pb(II) ions from real water samples has been optimized.

II.   Experimental

2.1. Materials and Methods

Silica fume (SF) was provided from the Ferrosilicon Company, Edfo, Egypt. Doubly distilled water (DDW) was used throughout all experiments. A stock solution of 0.1 M lead acetate was prepared by dissolving the appropriate amount of each salt in DDW. 0.01M of sodium salt of ethylene diamine tetra acetic acid solution was prepared by dissolving the appropriate amount of salt in DDW. A quinoline derivatives: 8-hydroxy quinoline (8HQ) and 2-hydroxy quinoline (2HQ) were analytical grade Merck. ACS reagent grade concentrated HCl and sodium hydroxide were obtained from Aldrich and used for justifying the pH values.

2.2. Apparatus

Solid phase extraction studies were carried out using batch equilibrium method. The pH measurements were made with Accumet® model 825 pH meter (Germany). Microwave oven Sharp REM20 (Korea) emitting 2.450 MHz microwave frequency using in modification of SF. The infrared spectra of SF and its modified phases before and after modification were obtained using FT-IR model 410 JASCO (Japan). JEOL X-ray diffractometer model JSX-60 PA. The analysis was run with Cu Kα radiation, Ni filtered ($\lambda = 1.54184$ Aº) at 35 Kv and 15 mA, under a normal scanning speed of 2º/1 minute, within the range of $2\Theta = 4º–100º$. Wrist Action mechanical shaker model 75 (manufactured by Burrell Corporation Pittsburgh. PA. U.S.A.). All measurements were performed at room temperature (25 ± 1ºC).

2.3. Modification of SF with quinoline derivatives using microwave technique

SF consists of very fine amorphous silica particles was first washed thoroughly with DDW and well dried before use. Then, equal weight ratio of SF and each quinoline compounds was irradiated at power 20.0 W for 5.0 min in a glass watch using a microwave oven. The products, SF loaded with 8HQ (SF-8HQ) and SF loaded with 2HQ (SF-2HQ) were then washed with DDW to remove the residues and excess of quinolines and left to dry for use [12].

2.4. Batch adsorption experiments

The percentage extraction of Pb(II) using SF and its new modified phases: SF-8HQ and SF-2HQ were determined in triplicate under static conditions by the batch equilibrium technique. 50.0 mg of each of the phases was added to a 0.5 mL of 0.1M of the Pb(II); the total volume was completed to 50.0 ml by DDW at pH range 2.0 – 6.0 in 100 mL measuring flask. For the pH adjustment, solutions of 1.0 M HCl and 1.0 M NaOH were used. This mixture was mechanically shaken for 30 min with all previous phases at room temperature to attain equilibrium. The phases were separated by filtration and washed with DDW; the unretained metal ion in the filtrate was determined by complexometric EDTA titration [12].

## III.   Result and discussion

3.1. Characterization of the adsorbent

3.1.1. FT-IR

The infrared spectral analysis has been carried out to understand the chemical bonding and it provides useful information regarding the molecular structure of the compound and describes the change that has occurred as a result of the modification process. The main bands in IR spectrum of silica fume (Fig. 1.a) could be seen as follows: the strong band centered at 1105 cm⁻¹ was attributed to asymmetric stretching frequency of υ(Si–O–Si), the band centered at 799 cm⁻¹ was due to symmetric stretching of υ(Si–O–Si), the band at 475 cm⁻¹ was due to the bending frequency of υ(O–Si–O) and a broad and strong overlapped band at around 3436 cm⁻¹ was due to υ(O–H) stretch [27]. Fig. 1.c, shows what happened after modification of SF with 8HQ, where the

band of SF which attributed to O–H stretch decreased in length and shifted to 3435 cm^{-1} and in 8HQ the band between 3590 and 3400 cm^{-1} which is due to hydroxyl group vibrations of the system which possess intra molecular hydrogen bonding [28]. Accordingly, in 8HQ the υ (–OH) absorption band is found at 3443 cm^{-1} in the measured FT-IR spectrum also decreased in length and the two bands in 8HQ molecule: 1579 and 1507 cm^{-1} which due to υ(C–O) stretching mode and υ(C=C) stretching, respectively decreased in length. The band of υ(C–O) stretching in 8HQ was found at 1279 cm^{-1} decreased in length and appeared adjacent to the υ(Si–O–Si), while the strong band centered at 1105 cm^{-1} in SF which attributed to asymmetric stretching frequency of υ(Si–O–Si) appeared with higher intensity. The bands at the range of 900-675 cm^{-1} due to υ(C–H) "oop" bending disappeared and replace by the band at 475 cm^{-1} that due to the bending frequency of υ(O–Si–O).

Finally, (Fig. 1.e) the spectrum of SF-2HQ, the bands at 3448 and 3253 cm^{-1} due to hydroxyl group not changed. The bands at 3000 and 2825 cm^{-1} due to υ(O–H) stretching and asym. C(sp^2)–H stretching decreased in length.
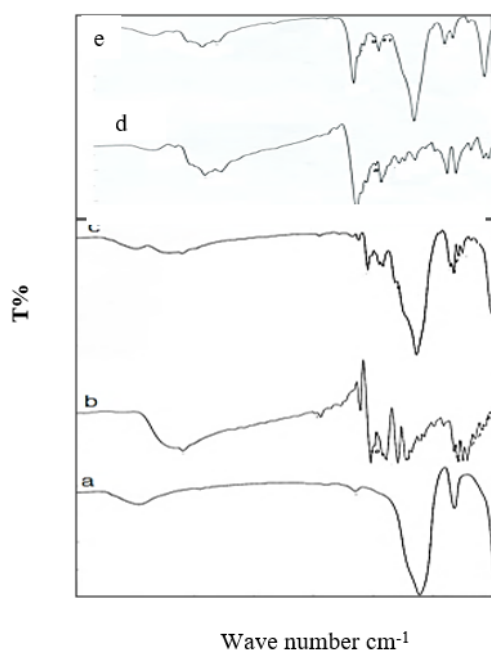
Figure 1: FT-IR spectra of SF, quinoline compounds and modified phases:(a) SF, (b) 8HQ, (c) SF-8HQ, (d) 2HQ and (e) SF-2HQ.

3.1.2. X-ray

The X-ray diffraction pattern of SF shows a broad hump in the range 15-25 2Ө. This indicates that SF is amorphous silica [29] that illustrated in (Fig. 2.a). From the X-ray diffraction spectra, it was cleared that after modification of SF with quinoline derivatives the intensity of the bands increased. But in the case of SF-8HQ (Fig. 2.b.), it has increasing in the number of the band and their intensity even after adsorption of Pb(II) than the other phases.
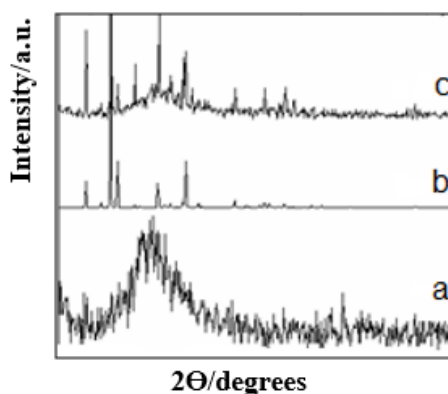
Figure 2: X-ray diffraction spectra of (a) SF, (b) SF-8HQ and (c) SF-2HQ

3.2. Extraction study in batch method

3.2.1. Effect of pH on metal extraction

Due to retain metal ions on a solid phase materials as metal ion-chelates, the pH of the aqueous solution is an important parameter. Therefore, experiments were carried out in this section to follow-up the possible contribution of reaction medium pH values on the determined metal adsorption capacity and extraction values. According to this, the effect of pH was investigated in the pH ranges of 2.0-6.0 with the model solution, keeping other parameters constant. The extraction values for Pb(II) are shown in (Fig. 3) which illustrated that the efficiency of SF-8HQ towards lead removal was higher than SF and the other phases in the same range of pH. The maximum lead adsorption capacity was found in the case of SF-8HQ.

On the other hand, in the case of SF-2HQ, at low pHs (2.0 and 3.0) the extraction of Pb(II) and the adsorption capacity values, few lead can be adsorbed. With increasing pH up to 6.0, the extraction of Pb(II) is also increased but not in the same percentage of SF-8HQ.
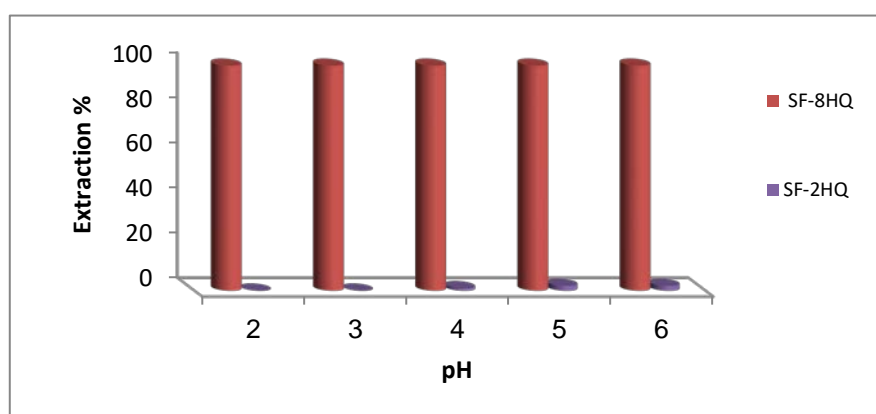

Figure 3: Effect of pH on Pb(II) extraction using SF-8HQ and SF-2HQ.

3.2.2. Effect of contact time and amount of adsorbent

Also, shaking time is an important factor in the process of evaluation of the sorbent, so batch adsorption experiment was conducted in order to determine the effect of contact time on the removal of Pb(II). It was carried out at different contact times 5.0 to 60.0 min using mechanical shaker with a fixed sorbent mass (50 mg), Pb(II) concentration (0.05 mmol) at a pH of (5.0) and 50.0 mL contact solution. As shown in (Fig. 4), for SF-8HQ first five minutes of shaking time is necessary for the maximum adsorption of Pb(II).
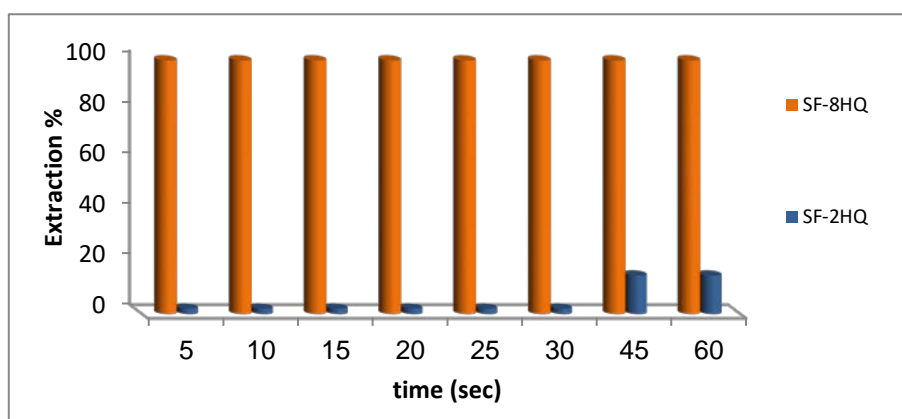

Figure 4: Effect of contact time on Pb(II) extraction using SF-8HQ and SF-2HQ.

As for the amount of adsorbent, (keeping all the other experimental variables, viz., pH (5.0) initial concentration (0.05 mmol), and contact time (30 min) were constant). (Fig. 5), presents the adsorbent weight profile versus Pb(II) adsorbed per unit mass. It may be observed that on increasing the adsorbent weight, the percentage extraction of Pb(II) increased until reached to constant value.

From previous results it is clear that, the highest percentage of extraction with SF-8HQ which is attributed to the nature of 8HQ because it well known chelating reagent.
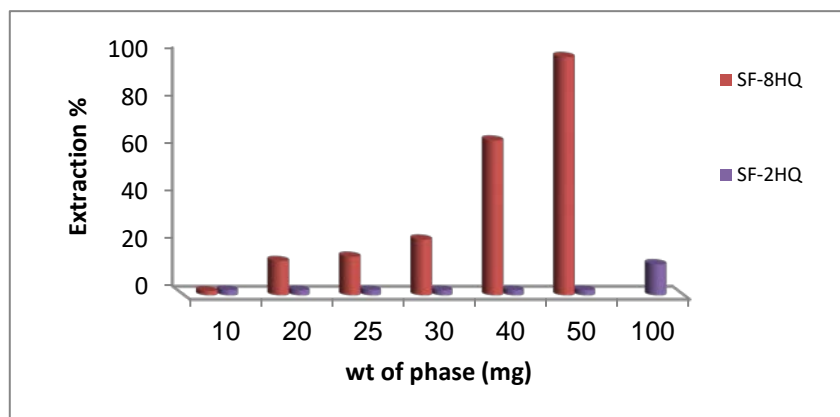

Figure 5: Effect of amount of adsorbent on Pb(II) extraction using SF-8HQ and SF-2HQ.

3.3. Conclusion

A new selective solid phase extractor (SF-8HQ) was obtained for extraction and removal of lead ions from aqueous solution with high percentage of extraction. This adsorbent was characterized by FT-IR and X-ray analysis.

References

[1].   V. Gurnani, A.K. Singh, B. Venkataramani, Cellulose based macromolecular chelator having pyrocatechol as an anchored ligand: synthesis and applications as metal extractant prior to their determination by flame atomic absorption spectrometry, Talanta, 61, 2003, pp. 889–903.

[2].   Y. Guo, B. Din, Y. Liu, X. Chang, S. Meng, J. Liu, Preconcentration and determination of trace elements with 2-aminoacetylthiophenol functionalized Amberlite XAD-2 by inductively coupled plasma-atomic emission spectrometry, Talanta, 62, 2004, pp. 207−2013.

[3].   S.A. Ahmed, Alumina physically loaded by thiosemicarbazide for selective preconcentration of mercury(II) ion from natural water samples, J. Hazard. Mater., 156, 2008, pp. 521−529.

[4].   E.M. Soliman, M.B. Saleh, S.A. Ahmed, New solid phase extractors for selective separation and preconcentration of mercury(II) based on silica gel immobilized aliphatic amines 2-thiophenecarboxaldehyde Schiff's bases, Anal. Chim. Acta, 523, 2004, pp. 133−140.

[5].   Damian Perez-Quintanilla, Alfredo Sanchez, Isabel del Hierro, Mariano Fajardo, Isabel Sierra. Solid phase extraction of Pb(II) in water samples using a new hybrid inorganic-organic mesoporous silica prior to its determination by FAAS. Microchim Acta (2009) 165:291-298.

[6].   Goswami A, Singh AK, Venkataramani B (2003) 8-Hydroxyquinoline anchored to silica gel via new moderate size linker: synthesis and applications as a metal ion collector for their flame atomic absorption spectrometric determination. Talanta 60:1141–1154

[7].   Khan S, Kazi TG, Kolachi NF et al (2010) Cloud point extraction of vanadium in pharmaceutical formulations, dialysate andparenteral solutions using 8-hydroxyquinoline and nonionic surfactant. J Hazard Mater 182:371–376.

[8].   Kumbasar RA (2009) Selective extraction of nickel from ammoniacal solutions containing nickel and cobalt by emulsion liquid membrane using 5,7-dibromo-8-hydroxyquinoline (DBHQ) as extractant. Miner Eng 22:530–536.

[9].   Yongchao Li, Tielong Li, Zhaohui Jin. Stabilization of Fe^0 nanoparticles with silica fume for enhanced transport and remediation of hexavalent chromium in water and soil. Journal of Environmental Sciences 2011, 23(7) 1211–1218.

[10].   Mohamed E. Mahmoud, Amr A. Yakout, Hany Abdel-Aal, Maher M. Osman. High performance SiO_2-nanoparticles-immobilized-penicillium funiculosum for bioaccumulation and solid phase extraction of lead. Bioresource technology. 106 (2012) 125-132.

[11].   Andreas E. K., Yiannis F., Constantine D. S. Silica-modified magnetic nanoparticles functionalized with cetylpyridinium bromide for the preconcentration of metals after complexation with 8-hydroxyquinoline. Talanta. 84 (2011) 834-839.

[12].   Salwa Ahmed, Ahmed Abdel Gaber, Asmaa Abdel Rahim, Novel solid phase-extractor based on functionalization of silica fume with 8-hydroxyquinoline for determination of pb(II) in water samples by square-wave adsorptive stripping voltammetry, 2019, Volume 4, Issue 4, 2019: 173-189.

[13].   Yukun Wang, Shuta Gao, Xiaohuan Zang, Jingci Li, Jingjun Ma. Graphene-based solid –phase extraction combined with flame atomic absorption spectrometry for a sensitive determination of trace amounts of lead in environmental water and vegetable samples. Analytical chimica acta. 716 (2012) 112-118.

[14].   Qun He, Dong Yang, Xiaoli Deng, Qiong Wu, Ruijun Li, Yunhui Zhai, Lijun Zhang. Preparation, characterization and application of N-2-Pyridylsuccinamic acid-functionalized halloysite nanotubes for solid-phase extraction of Pb(II). Water Research, Volume 47, Issue 12, 1 August 2013, Pages 3976-3983

[15]. Hossein Tavallali. Determination of Pb (II) in some real samples based on alumina-coated magnetite nanoparticles solid phase extraction method. International Journal of ChemTech Research. 3(2011) 1641-1646.

[16]. Mohammed Reza Nabid, Roya Sedghi, Akbar Bagheri, Mohammad Behbahani, Mohsen Taghizadeh, Hossein Abdi Oskooie, Majid M. Heravi. Preparation and application of poly(2-amino thiophenol)/MWCNTs nanocomposite for adsorption and separation of cadmium and lead ions via solid phase extraction. Journal of Hazardous Materials. 203-204 (2012) 93-100.

[17]. D.C. Adriano, Trace Elements in the Terrestrial Environment, in: Springer–Verlag, New York, 1986.

[18]. A. Safa O¨ zcan, O¨ zer Go¨k, Adnan O¨ zcan, J. Hazard. Mater. 161 (2009) 499.

[19]. World Health Organization, Guidelines for Drinking Water, WHO, Geneva, 1993.

[20]. D.M. Heil, Z. Samani, A.T. Hanson, B. Rudd, Water Air Soil Pollut. 13 (1999) 77.

[21]. C. Cabrera, Determination of lead in wine, other beverages and fruit slurries by flow injection hydride generation atomic absorption spectrometry with on-line microwave digestion. J. Anal. At. Spectrom. 9 (1994) 1423–1426.

[22]. Mena, C., Cabrera, C., Lorenzo, M., Lopez, C., 1997. Determination of lead contamination in Spanish wines and other alcoholic beverages by flow injection atomic absorption spectrometry. J. Agric. Food Chem. 45, 1812–1815.

[23]. M.C. Hennion. Journal of Chromatography A, 856 (1999) 3–54. Solid-phase extraction: method development, sorbents, and coupling with liquid chromatography.

[24]. Canrong Lin , Hongqing Wang, Yuyuan Wang, Zhiqiang Cheng . Talanta Volume 81, Issues 1–2, 15 April 2010, Pages 30–36 Selective solid-phase extraction of trace thorium(IV) using surface-grafted Th(IV)-imprinted polymers with pyrazole derivative.

[25]. Serhan U., Savas P., GoKhan C. and Ferhan T. solid phase extraction of Pb(II), Cu(II), Cd(II) and Cr(III) with syringe technique using novel silica-supported bis(diazoimine) ligands. Chemical engineering journal. 220 (2003) 420-430.

[26]. Sadegh K., Nadia N., Mohammed R. and Homayon A.P. A new functionalized resin and its application in flame atomic absorption spectrophometric determination of trace amounts of heavy metal ions after solid phase extraction in water samples. Microchemical journal 106 (2013) 147-153.

[27]. Silverstein R, Basseler GC, Morrill TC. Spectroscopic identification of organic compounds. 5th ed. New York: John Wiley and Sons: Inc.; 1998.

[28]. M. Rajasekaran1, P. Anbusrinivasan2 and S. C. Mojumdar. Growth, spectral and thermal characterization of 8-hydroxyquinoline. Journal of Thermal Analysis and CalorimetryAn International Forum for Thermal Studies. 2010.

[29]. Mostafa N Y, El-Hemaly S A S, Al-Wakeel E I, El-Korashy S A, Brown P W, 2001. Characterization and evaluation of the pozzolanic activity of Egyptian industrial by-products I: Silica fume and dealuminated kaolin. Cement and Concrete Research, 31(3): 467–474.