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Functionalization of Amberlite XAD-4 with 8-hydroxyquinoline chelator using aryldiazonium radical reaction and its application for solid phase extraction of trace metals from groundwater samples

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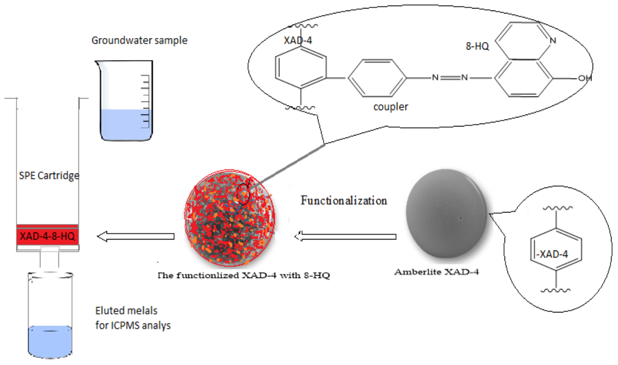
Graphical abstract



Abstract

In this work, the aryldiazonium salts radical addition method has been used successfully to anchor 8-hydroxyquinoline (8-HQ) moieties onto the surface of Amberlite XAD-4 beads. The nitroaniline aryldiazonium salt was generated (in-situ) and covalently grafted onto porous Amberlite XAD-4 by aid of hypophosphorous acid as a catalyst to facilitate the anchorage of 8-HQ chelator making use of the conventional diazo coupling. The successfulness of the synthesized chelating resin was confirmed by (ATR-IR), (TGA) and (XPS). The risen was packed into cartridges and used with standard solid phase extraction (SPE) apparatus for the extraction of trace metals; Co (II), Ni (II) and Cu (II) from groundwater samples prior to their measurement by (ICP-MS). The resin exhibited more than 90% enhancement in capacity exchange relative to the plain Amberlite XAD-4. Under the optimum conditions the sorption capacity of the sorbent was 0.366, 0.265 and 0.328 (mM/g) for Co (II), Ni (II) and Cu (II) respectively. The sorbent showed efficient performance when applied for SPE of trace metals from groundwater real samples from AlMadinah AlMumnawarah, Saudi Arabia.

Keywords: Solid phase extraction, Amberlite XAD-4, chelating resin, trace metals, ICP-MS, and groundwater.

1. Introduction

Heavy metals (HMs) are categorized as extremely toxic environmental pollutants (Srivastava and Goyal, 2010). They occur as natural constituents of earth crust, but many anthropogenic process accompanying the steadily growth of urbanization activities have increased the amount of heavy metals deposited onto earth surface several times above the background level from natural sources (Khan *et al.*, 2011). HMs possess crucial hazardous effects to biota, animal, and human being because of their toxicity, bio-accumulative and non-biodegradable nature (Bazrafshan *et al.*, 2015; Lichtfouse *et al.*, 2013). Frequently, HMs exist within very complex matrices at sufficiently low levels. Therefore, their accurate quantification is a challenging analytical task (Brown and Milton, 2005).

The truthful determination of trace analytes in distinct sample matrices is always a central objective for any analytical procedure, however, most of the available analytical techniques do not enable direct analysis. Therefore, an appropriate sample pretreatment step is usually required to separate the analytes from the matrix and preconcentrate them before their determination (Hu and He, 2012; Liu *et al.*, 2007; Wang *et al.*, 2003).

There are many procedures based on various separation concepts to separate trace elements from accompanying interferences. The choice of the suitable method depends on certain distinctive parameters including sample nature, concentrations of the analytes and the analytical techniques to be used in final measurement determine the adequate sample preparation method (Liu *et al.*, 2004). Examples of the common separation/extraction methods are; coprecipitation (Mendil *et al.*, 2015), ion exchange (Dabrowski *et al.*, 2004), electro-deposition (Armstrong *et al.*, 1996), cloud point extraction (Shemirani and Yousefi,

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2007), membrane filtration (Soylak *et al.*, 2007), solid phase extraction (SPE) (sometimes referred to as liquid–solid extraction) (Nickerson, 2011), adsorption (Liu *et al.*, 2007) and liquid–liquid extraction (LLE) (Korn *et al.*, 2006).

Among the numerous extraction and enrichment methods, SPE has become one of the most efficient multielement pre-concentration process for wide range of organic and inorganic analytes (Dabrowski, 1998; Huck and Bonn, 2000). Perhaps because SPE offers many advantages such as high recovery, short extraction time, low cost, simplicity and low consumption (or none) of organic solvents (Golshaei *et al.*, 2015; Liu *et al.*, 2007).

The ever continues research efforts in SPE provided science community with wide variety of (selective) SPE materials. Regularly, these materials prepared either by physical modifications (impregnation) or chemical modifications (chemical binding of selected moieties e.g., chelating agents for metals) to various solid supports, such as activated carbon, alumina, cellulose, silica gel, polyacrylate polymer and XAD resins, are useful substrates for the synthesis of SPE materials (Zhai *et al.*, 2010)

The commercially available Amberlite resins are very promising substrate for the design of chelating matrices due to their characteristic physical and chemical properties such as high surface area, porosity, purity and durability (Ahmad *et al.*, 2015). The well-known member of Amberlite XAD series; Amberlite XAD-4 which is a porous across-linked polystyrene divinylbenzene polymer, has found immense applications for the enrichment/separation of trace metals ions (Uzun *et al.*, 2001). Amberlite XAD resins have attracted much attention of researchers in the last few years for their appropriateness to be functionalized with broad range of specific chelating moieties.

The chelated resins showed good performance as SPE for preconcentration metal ions from various matrices in various applications (Gao *et al.*, 2010). Noticeably, most of the published chemical modification methods were based on the nitration step of phenyl ring with sulfuric and nitric acids followed by a diazo-coupling reaction (Jung *et al.*, 2010; Saxena and Meena, 2014).

The recently introduced chemical modification that uses the radical addition of aryldiazonium salts in presence of hypophosphorous acid as catalyst, is a very convenient approach for the addition of reactive functional group to the surface of carbon and other substrates. The obtained intermediate from radical addition reaction is amenable for the attachment of many moieties utilizing various chemical transformations like azo coupling scheme (Pandurangappa and Raghu, 2011).

Oxin chelating agents are very useful in analytical chemistry and radiochemistry applications, mainly for the extraction and fluorometric spectrophotometric determination of metal ions (Kosa *et al.*, 2012). 8-Hydroxyquinoline (8-HQ) is the most popular oxin chelators due to its capability to form stable complexes with many metal ions. 8-HQ and its derivatives are among the early chelating moieties that being successfully employed in the synthesis of chelating resins, due to their preferable chelating capacity for wide range of transition and heavy metals over alkaline earth cations (Wegscheider and Knapp, 1981).

A previous work in our laboratory showed that the chemical reduction of aryldiazonium salts method was a reliable approach for the covalent attachment of 8-HQ onto activated carbon (Alqadhi and Alsuhaimi, 2020). In this work, the method was proposed as green chemistry process for the chemical attachment of 8-HQ chelator onto amberlite XAD-4 substrate. The performance of synthesized metal chelator as SPE materials for sample preparation of trace metals from groundwater samples has been optimized.

2. Experimental work

2.1 Chemical reagents

All chemicals used in this work were of analytical reagent-grade and all working solutions were prepared in Millipore water ($\leq 18.2\ \Omega$). The solid support Amberlite XAD-4 (polystyrene divinylbenzene type, bead size 20-60 mesh and surface area of 750 m^2/g) were purchased from Sigma-Aldrich chemie GmbH (Darmstadt, Germany). The 4-nitroaniline, sodium hydrosulfite ($Na_2S_2O_4$), 8-Hydroxyquinoline and hypophosphorous acid were obtained from Acros Organics (Geel, Belgium), Sodium Nitrite ($NaNO_2$) was purchased from Loba Chemie (Mumbai, India). Hydrochloric acid and nitric acid from Panreac Quimica, SA (Barcelona, Spain) and ethanol from Fisher Scientific (Loughborough, UK).

Metals standard solutions were prepared from Elemental stock solutions 1mg/ml, Acros Organics (Geel, Belgium) by proper dilution. Ammonium acetate purchased from Sigma-Aldrich chemie GmbH (Darmstadt, Germany), buffer was prepared from ammonium acetate and purified by passing through a column of Chelex-100 from Bio-Rad (Hercules, CA, USA). The pH was adjusted to the required values with nitric acid, acetic acid from Sigma Aldrich (Darmstadt, Germany) or liquid ammonia from Panreac (Barcelona, Spain). Ultrapure water produced with a Millipore Milli-Q water purification system (Darmstadt, Germany). All the glassware which used in the experiments were soaked overnight into a 5% (v/v) nitric acid solution and rinsed thoroughly with purified water before usage.

2.2 Instrumentation and measurements

ICP-MS 7500 series, Agilent Technologies (Santa Clara, California, USA) was used for the determination of metal ions. The instrument preset at the standard operating parameters recommended by manufacturer. The pH measurements were done using a Basis pH meter HI 2211 pH/ORP meter (HANNA Instrument Company, Carrollton, Texas, USA).

IR spectra were recorded in the range of 400-4000 cm^{-1} using Thermo NICOLET 380 FTIR equipped with attenuated total reflection (ATR) accessory (Thermo-Fisher Scientific, Waltham, Massachusetts, USA). X-Ray photoelectron spectroscopy (XPS) for C1s, N1s and O1s were performed on CAE: Pass Energy 150.0 eV (Thermo Scientific, Waltham, Massachusetts, USA) equipped with Al K Alpha with a step size of 1 eV. Thermogravimetric analysis (TGA) was carried out under nitrogen atmosphere at a heating rate 10 °C/min using TA instrument, model SDT Q600, (Tokyo, Japan).

2.3 Preparation of 8-HQ-amberlite XAD-4 Chelating Resin

The 8-HQ-amberlite XAD-4 chelating resin was prepared using a simple three- step chemical transformation as shown follows:

Firstly, the 4-nitroaniline diazonium salt radical was generated in situ by dissolving 2g of 4-nitroaniline into 50 ml 1:1 solution of HCl: water. The solution was cooled in ice-bath and a cold solution of 2g $NaNO_2$ dissolved in water was added dropwise with continues stirring (Saylam *et al.*, 2014). Then a 20 g of amberlite XAD-4 was added and a 50 ml of hypophosphorous acid (H_3PO_2, 50% V/V in water) solution was added slowly. The solution was stirred at 0-5 °C for 2h. Then, filtered, washed with deionized water to remove any excess acid and finally washed with acetone to clean the product from any residual diazonium salt molecules. The functionalized XAD-4 was then vacuum dried for 24h before being used in the subsequent stage (Abiman *et al.*, 2008; Kempegowda and Malingappa, 2013; Wildgoose *et al.*, 2005).

In second step nitro groups on the surface of XAD-4 was reduced using 50 ml solution of 5% sodium hydrosulfite ($Na_2S_2O_4$) in a sealed flask at 45 °C for 24h to insure a maximum conversion of ($-NO_2$) groups into ($-NH_2$) groups. The product was filtered and washed with cold water to remove any excess of salt and used in the diazocoupling step (Fan *et al.*, 2007; Scheuerman and Tumelty, 2000).

In third step, the aminobenzyl-XAD-4 was diazotized for 1.5h at 0-5 °C with 50 ml of 2% (w/v) $NaNO_2$ in 1% acetic acid solution. Then filtered immediately, washed with cold water and a 50 ml of 1% 8-HQ solution in ethanol was added dropwise to the mixture for 4h with frequent mechanical shaking to allow the diazicoupling reaction to complete.

The obtained resin was filtered, washed with ethanol, water, 2% HCl solution and water until the filtrate showed no characteristic color. The chelator was then vacuum dried and stored in desiccator till the subsequent use (Fan *et al.*, 2007).

2.4 Chelator sorption performance

In order to evaluate the sorption capability of the synthesized metal chelator, it has been used a SPE sorbent for Co, Ni and Cu from standard solutions and groundwater real samples. These metal ions were chosen as a prove of concept.

2.5 Sorption capacity study

The sorption capacity (maximum amount of metal adsorbed per gram) of the prepared chelator; AXAD-4-8HQ was determined for Co, Ni and Cu in batch mode experiment.

This test was performed by placing 0.25 g of dry resin into 50 ml conical flask and 10 ml of 100 mg/L solution of each metal prepared in ammonium acetate buffer (0.2 M, pH 6) was added. The mixture was left to equilibrate overnight over a mechanical shaker. The solution was centrifuged and the amount of the remained metal ions in the supernatant solution were quantified against the original concentration using ICP-MS.

2.6 Effect of solution pH

The optimum pH of metal ion uptake was determined by static batch experiment. Briefly, 0.1 g of the dry chelated AXAD-4-8HQ resin was suspended into 10 ml of mluti-elements solutions containing 100 ng/ml of Co, Ni and Cu in 0.2 M ammonium acetate solution. The pH of the metal ions solution was adjusted prior to equilibration over a range (pH 2-10) with nitric acid (0.1 M), acetic acid (0.1M) or ammonia (0.1 M). The solutions were then centrifuged, and the residual metal concentration of the supernatant was measured versus the original concentration using ICP-MS. All experiments were performed in triplicate (AlSuhaimi *et al.*, 2017; Islam *et al.*, 2010).

2.7 Effect of contact time

The potential of this parameter was investigated for the sorption of metal ions; Co, Ni and Cu as a function of time in batch mode experiment. Briefly, the synthesized AXAD-4-8HQ resin (0.1gm) was agitated with 100 ml of solution containing (100 ng/ml) of the tested metal ions and left to equilibrate for different time intervals (2, 5, 10, 15, 30, 45, 60, 80 and 120 min). The concentration of metal ions in the supernatant solution was determined by ICP-MS.

2.8 SPE Manifold and procedure

The dynamic SPE experiments conducted using a 12-way standard SPE manifold (Ato Science, China) operated with a vacuum pump (AP-9950; Ato Science, China). About 0.5g of the synthesized resin packed into SPE cartridges (bond straight barrel; Agilent Technologies) to make discs of 5 mm height sandwiched between a pair of porous Teflon filters. The SPE protocol performed according to the following sequences. Initially, the SPE cartridges were conditioned by passing 5 ml of buffer solution at 1 ml/min flow rate and then 25 ml of samples were loaded at 0.5 ml/min flow rate. After that, the cartridges were flushed with 5 ml of water (at 0.5 ml/min) to remove any residual metals and matrices. Finally, the sequestered (chelated) metal ions were eluted with 2.5 ml of 1.5 M HNO_3 at a flow rate of 2 ml/min. The eluted metals were collected into 10 ml PTFE sample tubes and diluted with 5 ml Millipore water for ICP-MS analyses. This protocol has been used for all the standards and the real samples (Liu *et al.*, 2014; Zhao *et al.*, 2011)

3. Results and discussion

3.1 Chemical modification reaction

The attachment of 8-HQ chelating agent onto the surface of Amberlite XAD-4 was attained making use of a three-step chemical reaction as shown schematically in (Figure 1). In first step, 4-nitroaniline groups were covalently anchored onto Amberlite XAD-4 surface throughout the chemically activated one-electron reduction of the in-situ generated 4-nitrobenzenediazonium salt intermediate in the presence of hypophosphorous acid as a reducing catalyst. Meanwhile the second step involves the reduction of nitro groups into amines using sodium hydrosulfite ($Na_2S_2O_4$). In the final step, the 8-HQ moiety was coupled onto Amberlite XAD-4 via the classical diazo linkage (Abiman *et al.*, 2008; Fan *et al.*, 2007; Kempegowda and Malingappa, 2013; Scheuerman and Tumelty, 2000; Wildgoose *et al.*, 2005).

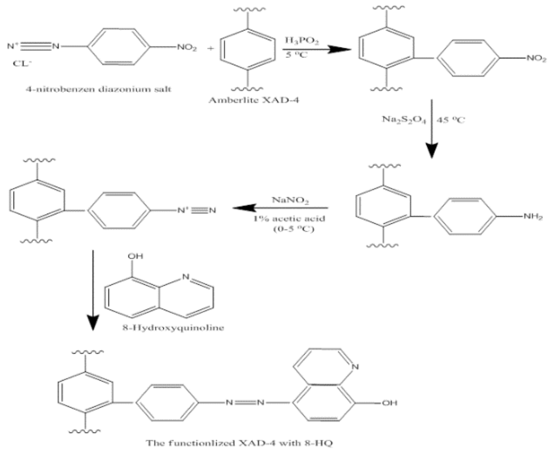

Figure 1. Reaction sequence of XAD-4 functionalization with 8-HQ

3.2 Characterization of AXAD4-8HQ resin

3.2.1 ATR-IR characterization

The successfulness of AXAD4-8HQ resin synthesis has been confirmed by ATR-IR analysis. The IR spectrum of AXAD4-8HQ is compared with that of that of a plain Amberlite XAD-4 (Figure 2). Obviously, few bands in the regions 1560-1345 cm^{-1} and 1250-500 cm^{-1} which are due to the plan resin, can be seen in both spectra. The linkage of 8-HQ moiety however can be recognized from many IR bands. These include, the appearance of the distinctive band at 3448.98 cm^{-1} in IR spectrum of the AXAD4-8HQ resin which belong to phenolic hydroxyl group (O-H), and the band at 2927.11 cm^{-1} that comes from C-H (stretching). The existence of C=N connection is clearly identified from the band around 1604.53 cm^{1}.

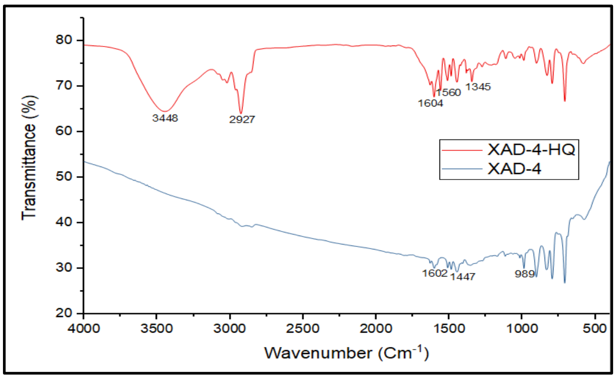

Figure 2. The IR spectrum of Amberlite XAD-4 and AXAD4-8HQ resin

The fingerprint peak at 1345.99 cm^{-1} confirmed the presence of C-N and that observed at 1560.39 cm^{-1} confirms the existence of -N=N-. This result indicates that the 8-HQ moiety has been successfully immobilized onto Amberlite XAD-4 surface through diazotized N=N coupling (Cheira, 2015; Nezhati *et al.*, 2010; Saxena and Meena, 2014).

3.2.2 TGA characterization

The TGA experiments were conducted for plain AXAD-4 and AXAD-4-8HQ resin at a heating rate of 10 ℃/min from ambient temperature to 900 ℃ in flow of N_2. The TGA curves for the bare AXAD-4 and AXAD-4-8HQ resin are represented in (Figure 3). The thermogram of plain AXAD-4 polymer, exhibited clear mass degradation over the temperature range 320 - 895 ℃ (100%). On the other hand, the TGA of chelating resin; AXAD-4-8HQ, displayed two step weight losses up to 645 ℃. The resin has lost about 12% of its original weight at 220-330 ℃ as a result of displacement of 8-HQ moieties out of the polymer. The weight loss after 330 ℃ (88%) could be associated to the dissociation of polymeric matrix (Gladis and Rao, 2002; Pacurariu *et al.*, 2013).

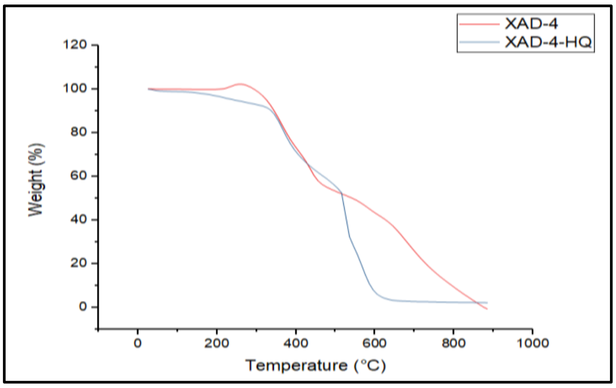

Figure 3. TGA Thermogram of AXAD-4 and AXAD-4-8HQ resin

3.2.3 XPS characterization

The chemical bonding of 8HQ moiety onto the AXAD4 surface has been ascertained using X-ray photoelectron spectroscopic (XPS) technique. XPS analysis is reliable approach to confirm the successfulness of modification of AXAD-4 with 8-HQ. The survey spectra of AXAD-4 and AXAD4-8HQ resin is shown in (Figure 4). It was clear from (Figure 4) that the XPS spectrum of AXAD4-8HQ showed peaks for N1s (two components peaks of pyridinic N at 398.08 eV and 400.08 eV corresponds to (N=N), which arose from the present of 8-HQ ligands and its linkage on the AXAD-4 surface. The clear existence of N (from the 8-HQ) from the spectrum strongly indicates that the 8-HQ molecule is covalently bonded to the AXAD-4 surface (Kosa *et al.*, 2012).

Table 1. Comparison of sorption capacity of the synthesised chelator with other 8-HQ-amberlite resins for Co, Ni, Cu metal ions.

Adsorbent	Metal ions (mM/g)			Refs.
	Co	Ni	Cu	
Amberlite XAD-7	-	0.011	0.018	Lee *et al.* (1988)
Amberlite XAD-2000*	0.115	0.132	0.148	Duran *et al.* (2007)
Amberlite XAD-2010*	0.161	0.187	0.136	Gundogdu *et al.* (2007)
Amberlite IR-120*	-	-	0.038	Sadia *et al.* (2016)
Amberlite XAD-4	0.366	0.265	0.328	Current work

* *the unit was converted from (mg/g) to (mM/g) by division on atomic weight for metal.*

Table 2. Trace metals contents of real water samples with the proposed method (mean conc. ±RSD (ng ml^{-1})) Sample volume 25 ml, eluent 1.5 M HNO_3

Sample	Metals	Added (ng/ml)	Found + RSD (ng/ml)	Recovery (%)
1	Co	0	1.21±0.48	96.4%
		5	6.03±1.66	
	Ni	0	0.97±1.60	97.82%
		5	5.86±1.20	
	Cu	0	2.04±0.83	105.41%
		5	7.31±1.31	
2	Co	0	1.24±1.37	96.62%
		5	6.07±1.29	
	Ni	0	1.12±0.98	97.81%
		5	6.01±1.76	
	Cu	0	1.97±0.56	103.05%
		5	7.12±1.97	
3	Co	0	1.15±0.9/	98.81%
		5	6.09±1.28	
	Ni	0	0.95±1.16	99.20%
		5	5.91±1.86	
	Cu	0	2.27±0.88	97.81%
		5	7.16±1.08	
4	Co	0	1.17±0.94	98.04%
		5	6.07±1.18	
	Ni	0	1.03±1.65	99.61%
		5	6.01±1.10	
	Cu	0	2.15±0.47	94.41%
		5	6.87±1.167	
5	Co	0	1.32±0.83	99.81%
		5	6.31±1.83	
	Ni	0	1.04±1.92	99.61%
		5	6.02±0.18	
	Cu	0	2.19±1.50	115.40%
		5	7.96±1.38	

3.3 Chelator sorption capacity

The sorption capacity of a resin is a key factor to estimate the required mass of sorbent resin to achieve quantitative extraction/preconcentration of the elements from a given sample matrix. The calculated sorption capacity (SC) values in mmol/g unit for Co, Ni and Cu were shown in 3 replicates at pH 6 and compared with sorption capacity for unmodified AXAD-4 under the same condition as seen in (Figure 5). It is clear from (Figure 5), the sorption capacity for AXAD4-8HQ resin was improved by more than (95.90% for Co), (87.13% for Ni) and (99.28% for Cu) in comparison with the unmodified AXAD-4 for the investigated ions (Vassileva and Furuta, 2003).

The comparison of sorption capacity values of the XAD4-8HQ chelating resin with other amberlite resins functionalised with 8-HQ chelating agent (Table 1) revealed that the XAD4-8HQ chelator exhibits higher sorption values (at least twice) for the investigated metal ions. This finding could be ascribed for the high surface area of XAD-4 and the efficiency of the chemical functionalisation used in this work.

3.4 The effect of solution pH

The pH of solution plays a significant role in SPE studies because most metal chelating ligands are conjugate bases of weak acids with a very strong tendency for (H) ions. The removal percentage of the studied metals plotted versus pH as presented in (Figure 6). The maximum sorption for Co and Ni were 96.42% and 97.06% at pH 8 meanwhile Cu ion reached its optimal removal percentage (85.76%) at pH

6. The effect of pH on the sorption of metal ions by immobilized 8-HQ chelator may be influenced by the behavior the chelating agent in the acidic media and basic media, i.e., at low pH values, the nitrogen of heterocyclic ring of 8-HQ is protonated whilst the phenolic OH group dissociates in the alkaline environment. Accordingly, the ligand tends to chelate with the metal ions under slightly alkaline conditions because the chance for the formation of more stable complexes is better. Hence, pH 8 is an adequate for the extraction of Co, Ni by this chelator, meanwhile pH 6 is optimal to form stable complex with Cu. These pH values were chosen as optimal in the further experiments (Islam *et al.*, 2010).

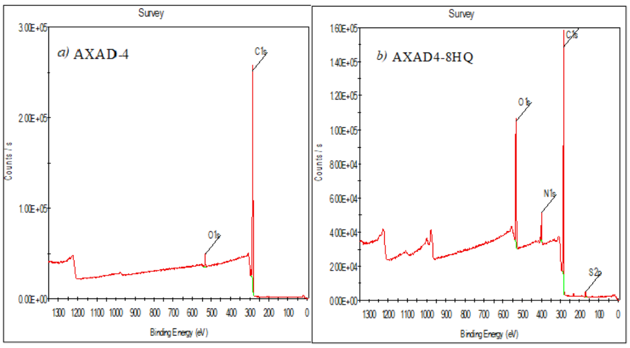

Figure 4. XPS spectra of a) AXAD-4 and b) AXAD4-8HQ resin

3.5 The effect of contact time

The effect of contact time is a significant parameter for the quantitative retention of analytes by SPE chelator. The removed percentage of the investigated metal ions as a function of time is shown in (Figure 7). The data represented in (Figure 7) illustrate that the chelating resin uptake 50% of Co and Cu after 10 minutes, however only 27% of Ni is removed during this time. However, an equilibration time of 60 minutes was effective for the resin to absorb about 85% of Cu and Co, and almost 80% of Ni (Xie *et al.*, 2008).

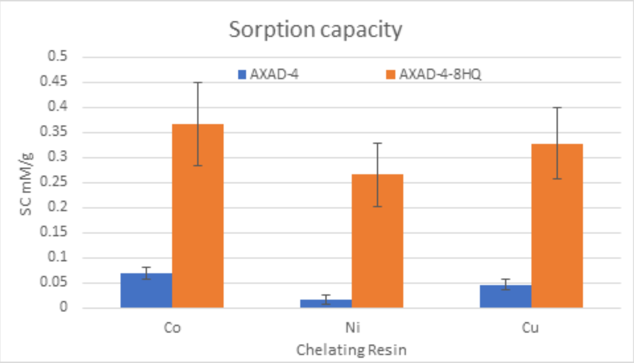

Figure 5. Sorption capacity for XAD-4 and AXAD4-8HQ resin

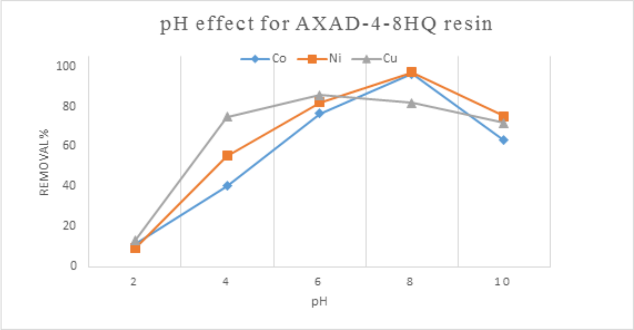

Figure 6. Effect of contact time on the removal of Co, Ni and Cu from Amberlite XAD-4-8HQ resin

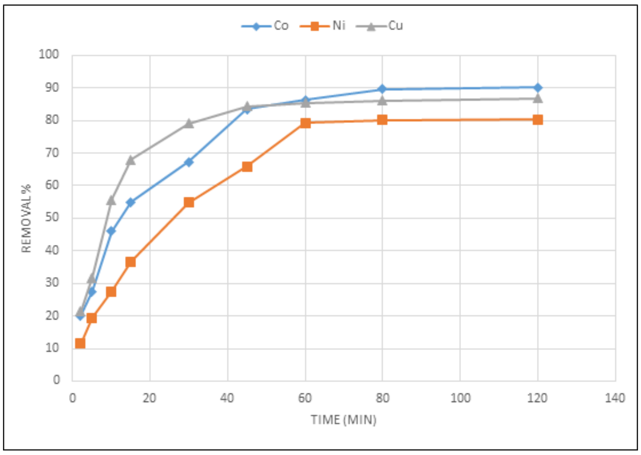

Figure 7. Effect of pH on the removal of Co, Ni and Cu from Amberlite XAD-4-8HQ resin

3.6 Stability and reusability of chelator

Stability and reusability of SPE materials are viable characteristics to gauge the sustainability and economic efficiency of sorbents. In this article, the chelator stability was evaluated using our previous methods (AlSuhaimi, 2019: AlSuhaimi et al., 2019). Briefly, the chelator was treated with acidic and alkaline solutions of different concentrations and its sorption capacity determined for the tested metal ions. The results have shown that the chelator can withstand for concentration of nitric acid up to 3 M HNO_3 without exhibiting any significant diminution in the value of sorption capacity (i.e., the maximum reduction is below 2.7%). However, the treatment of chelating resin with more concatenated acid (≥4 M HNO_3), results in a reduction in sorption by about 8% of the original value. Also, a reddish coloration was observed in solution, which could be ascribed to the detachment of the chelating moieties along with the linkage molecules from the XAD beads. Similarly, the material was soaked in alkaline solution pH12 (the pH value adjusted using ammonium solution) and its sorption capacity was tested. Yet, no significant change in sorption capacity being observed. The reusability of the chelating resin has been evaluated by determining its sorption capacity for the investigated metal ions after 50 loading and elution cycles. It was found that there is no substantial change in sorption capacity and hence, it can be reused several times and it is appropriate for dynamic SPE processing. Furthermore, the chelating resin show no significant variation in sorption capacity upon storage in the desiccator for more than 8 months in the laboratory.

3.7 Method Application: The Analysis of Groundwater Real Samples

The SPE method using the prepared metal chelator has been used for the preparation of groundwater samples prior to the analysis of the selected elements with ICP-MS. The groundwater samples were collected from 5 narrow mouth wells of depth ranged from 130 to 170 m within Swary valley (upper catchment AlWadi AlMubarak), AlMadina Almonawarah province. The samples (1 L) were acidified, filtered in field and transported to laboratory in iceboxes (see map in Figure 8).

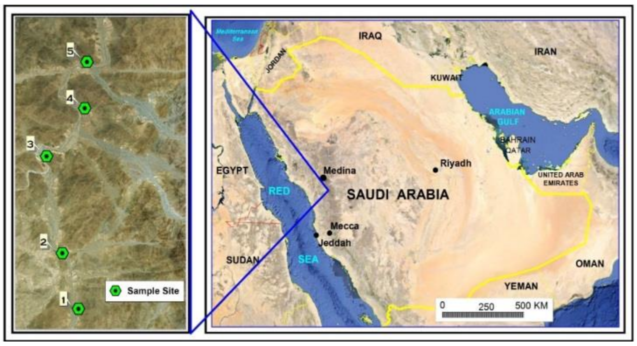

Figure 8. Sampling sites from Swary Valey, AlMadinah AlMunawarah

Prior to the ICP-MS analysis 25 ml of groundwater samples were prepared using SPE protocol described in section 2.8. The concentration of the analyzed metals; Co, Ni and Cu, in real samples, along with the recovery for the spiked samples are presented in (Table 2). The recoveries as estimated from the addition of concentrations of spikes to water samples were in the range (96.4%-99.8%, 97.8%-99.6% and 94.4%-115.4%) for Co, Ni and Cu respectively. Thus, the proposed method has proved to be an efficient sample treatment procedure during the simultaneous analysis of trace metals in groundwater real samples.

4. Conclusion

The developed chemical modification reported in this article enabled the synthesis of AXAD-4-8HQ metal chelator by aryl radical addition of aniline to the XAD-4 surface followed by diazotization step to couple 8-HQ moieties. ATR-IR, TGA and XPS analysis confirmed the success of resin synthesis. The most important parameters influencing SPE process e.g., the effect of pH and contact time of metals with sorbent have been investigated. It was found that resin could extracts about 96.42 and 97.06% of Co for Ni at pH 8, and 85.76% for Cu at pH 6. Contact time experiments showed that the equilibration time of 60 min was found to be effective for maximum sorption of Co, Ni and Cu. The chelator exhibited relatively higher sorption capacity in comparison with 8-HQ immobilized onto other amberlite substrates using classical nitration/diazotization chemical modifications. Noticeably, although the 60 minutes equilibration time seems to be relatively long, the resin work well as SPE material in dynamic mode using the standard SPE manifold in the examined concentration range. This also has been established by the application of the new metal chelator as an efficient SPE material for sample preparation of trace metals from groundwater real samples of high to moderate salinity.

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