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Removal of Nitrite Ions from Aqueous Solutions by Ethylenediamine Polysiloxane Immobilized Ligand System

Suha T. Alkahlout[1]
Asmah A. Abu Shaweesh[1]
Nizam M. El-Ashgar[1,*]

[1]Department of Chemistry, Faculty of Science, Islamic University of Gaza, Gaza Strip, Palestine

*** Corresponding author**
e-mail address: nashgar@iugaza.edu.ps

Abstract

The functionalized porous solid ethylenediamine polysiloxane immobilized ligand system P-NN (where P represents [Si-O]n polysiloxane network and NN represents ethylenediamnie group) was prepared by hydrolytic polycondensation of 3-aminopropyl-2-aminoethyltrimethoxysilane with tetraethylorthosilcate (TEOS) in the presence of CTAB surfactant. CTAB was used to enhance the porosity of the material and therefore increases the adsorption capacity of the immobilized ligand system. The functionalized ligand system was investigated as adsorbent for nitrite ions from aqueous solutions. Both batch and column methods were carried out and the effect of various parameters was studied that include contact time, pH, nitrite concentration and temperature in order to investigate the optimum conditions for the nitrite ions removal. The optimum nitrite adsorption was established in acidic medium, at 75^{o}C, and at contact time equals 24 h. The nitrite removal was about 65-100% at 5-50 ppm of initial nitrite concentration. The use of this adsorbent is proved to be repeatable and recyclable. The adsorbent can be considered as a promising material for nitrite removal from different water and waste water and aqueous extracts containing nitrite ions.

Keywords:
Silica based solid supports,
Immobilized polysiloxanes,
sol-gel,
Template synthesis,
Nitrite removal.

1. Introduction:

Nitrite (NO_2^-) is an inorganic ion that naturally occurs .It is a part of the nitrogen cycle (Cammack *et al.,* 1999). It is formed in the body *via* the oxidation of nitric oxide (NO) or through the reduction of nitrate (NO_3^-). Commensal bacteria in the oral cavity and gastrointestinal tract contribute to nitrite formation *via* a one-electron reduction of nitrate. Reduction of nitrite to NO occurs in blood and tissues and proceeds through several enzymatic and non-enzymatic pathways. The acidic reduction of nitrite leads to the generation of NO and other nitrogen oxides. Oxidation of nitrite occurs in the red blood cells and produce both nitrate and methaemoglobin (Lundberg, Weitzberg, & Gladwin, 2008). On the other hands; nitrite is used as food additives. For example it is normally added to crude meatsin order to enhance the flavor and the color. It is also act as inhibitor to the growth of food spoilage bacteria under anaerobic conditions (Cammack *et al., et al.,* 1999). The other most common sources of nitrite are overflowing septic tanks, livestock, domestic wastes effluents and herbicides that are used in industrial agriculture (Okafor & Ogbonna, 2003). The wastes of the production of explosives, decomposition of decaying organic matters buried in the ground and the plantation of leguminosae crops which fix atmospheric nitrogen in the form of nitrate (Zyoud, Nassar, El-Hamouz, & Hilal, 2015). Exposure to nitrates and nitrites at levels above health-based risk values has been reported to have adverse health effects on infants and children which well known as blue baby syndrome (methemoglobinemia) (Öztürk & Bektaş, 2004; Mizuta, Matsumoto, Hatate, Nishihara, & Nakanishi, 2004; Okafor & Ogbonna, 2003; Ayyasamy *et al.,* 2009; Mishra & Patel, 2009; Grommen, Van Hauteghem, Van Wambeke, & Verstraete, 2002). There are several methods used in removing nitrite from aqueous medium, such as cyanobacteria, activated carbon prepared from Olive Stones (Zyoud *et al.,* 2015), coconut coir pith (Namasivayam & Sangeetha, 2005), activated carbon from other sources, immobilized cells of Dunaliella salina (Thakur, & Kumar, 1999) or sulfamic acid (Granger & Sigman, 2009). Some of these approaches suffer from limitations especially the low ability to remove quantities at trace levels. Recently, immobilization of reactive groups on the surface of inorganic solid supports, especially silica gel and polysiloxanes, are gaining high importance due to their excellent thermal, mechanical and chemical stability (El-Nahhal & El-Ashgar, 2007; El-Nahhal, El-Shetary, Salib, El-Ashgar, & El-Hashash, 2001; El-Nahhal *et al.,* 2003; El-Ashgar, 2008; Saadeh *et al.,* 2005; El-Ashgar *et al.,* 2006; El-Ashgar, El-Nahhal, Chehimi, Babonneau, & Livage, 2012; El-Ashgar, El-Nahhal, Chehimi, Babonneau, & Livage, 2009). Polysiloxanes functionalized by organic ligands have been widely exploited for extraction and preconcentartion of chemical species such as trace metal ions and inorganic moieties from different media by batch and dynamic methods (Dioum & Hamoudi, 2014; Ebrahimi-Gatkash, Younesi, Shahbazi, & Heidari, 2015; El-Ashgar, 2009; El-Nahhal, El-Ashgar, Abu-Shawish, El-Aziz Ahmed, & Babonneau, 2015; El-Ashgar, Silmi, El-Nahhal, Chehimi, & Babonneau, 2015; Ahmed, 2016). There is consequently interest in developing functionalized polysiloxanes with suitable silane agents which have high potential for chemical and physical sorption (Dioum, & Hamoudi, 2014; Ebrahimi-Gatkash *et al.,* 2015; El-Ashgar, 2009; El-Nahhal, *et al.,* 2015; El-Ashgar *et al.,* 2015; Ahmed, 2016). These immobilized ligand systems could be synthesized either directly by the low temperature sol-gel process or by chemical modification of the pre-prepared polysiloxanes (Dioum, & Hamoudi, 2014; Ebrahimi-Gatkash *et al.,* 2015; El-Ashgar, 2009; El-Nahhal *et al.,* 2015; El-Ashgar *et al.,* 2015; Ahmed, 2016). A new synthetic approach of inorganic-organic hybrid mesoporous materials in the presence of CTAB and silica under acidic conditions has resulted in stable materials after removal of the surfactant species through acid-solvent extraction (Dioum & Hamoudi, 2014; Ebrahimi-Gatkash *et al.,* 2015; El-Ashgar, 2009; El-Nahhal *et al.,* 2015; El-Ashgar *et al.,* 2015; Ahmed, 2016). In this work a functionalized porous solid ethylenediamine polysiloxane immobilized ligand system (P-NN) has been prepared by hydrolytic polycondensation of 3-aminopropyl-2-aminoethyltrimethoxysilane with tetraethylorthosilcate (TEOS) in the presence of CTAB surfactant. CTAB surfactant was used to modify morphology and porosity of the polysiloxane adsorbents. The functionalized porous solid ethylenediamine polysiloxane immobilized ligand system; P-NN was investigated for removing of nitrite ions from aqueous solution.

2. Experimental:

2.1. Chemicals and techniques:

Tetraethylorthosilicate (TEOS), 3-Aminopropyl-2-aminoethyltrimethoxysilane, cetyltrimethylammoniumbromide (CTAB) surfactant were purchased from (MERCK) and used as received. Phosphoric acid H_3PO_4, diethylether and absolute ethanol was purchased from SIGMA Aldrich Company and used as received. Nitrite ion solution of the appropriate concentration was prepared by dissolving sodium nitrite (analar grade) in distilled water. Different pH values in the range (3.5 –8) were controlled using acetic acid/sodium hydroxide buffer solution. Elemental analysis for carbon, hydrogen, and nitrogen were carried out, using an Elemental Analyzer EA 1110-CHNS CE Instrument. Thermogravemetric analysis TGA was carried out using Mettler Toledo SW 7.01 analyzer in the range of 25-600°C under nitrogen. The infrared spectra of the materials were recorded on a Perkin-Elmer FTIR, spectrometer using KBr disk in the range of 4000 to 400 cm^{-1}.

2.2. Preparation of polysiloxane-immobilized diethylenetriamine ligand system (P-NN):

Polysiloxane-Immobilized ethylenediamine (P-NN) was prepared as previously reported (El-Ashgar *et al.,* 2012) by adding 3-Aminopropyl-2-

aminoethyltrimethoxysilane (11.12 g, 0.05 mol) to a stirred solution of tetraethylorthosilicate (20.83 g, 0.10 mol) in 25 mL ethanol and phosphoric acid (4.95 mL, 0.42 M). CTAB (3.644g, 0.01 mol) that dissolved in ethanol was added to the solution mixture while stirring. Gelation occurred within 12 hours. The product was left to stand for 12 hours then dried in vacuum oven at 80°C for 12 hours. The solid material was crushed, sieved, to a particle size (125-150) μm. Cetyltrimethylammonium bromide (CTAB) was removed by refluxing with hot ethanol. The material was then washed successively with 50 mL portions of 0.025 M NaOH, water, methanol and diethylether. The solid material was dried in a vacuum oven at 80°C for 12 hours.

2.3. Acidification of the functionalized polysiloxane:

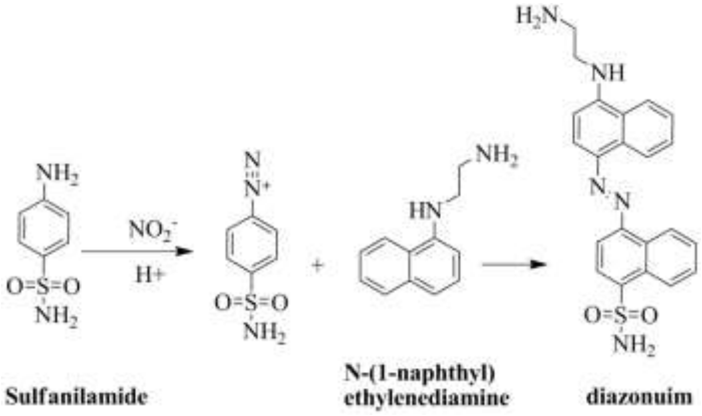
The functionalized polysiloxane was acidified by soaking (5.0 g) of the material in dilute HCl solution (1.0 M, 100 mL) for 48 hours. The material then was filtered and washed with the same concentration of the acid and dried in oven at 90°C for 12 hours.

2.4. Preparation of nitrite detection reagent:

Phosphoric acid (50 mL, 85%) was dissolved in 200 mL distilled water followed by 5.0 g of sulfanilamide, then 0.5 g of N-(1-naphthyl)ethylenediamine was added to the mixture with stirring. The solution mixture was then completed to 500 mL by distilled water.

2.5. Nitrite determination experiment:

Nitrite adsorption onto functionalized siloxane was studied by both batch and column experiments. Experiments were conducted in a set of 100 mL polyethylene cups. A fresh sodium nitrite stock solution (1000 ppm) was prepared daily in deionized water. Because of ion instability, the samples were analyzed immediately after collection (Michalski, 2009). Sample of 1.0 ml was withdrawn using a micropipette then 1.0 ml of nitrite detection reagent was mixed until pink color was appeared (1 minute). All samples were determined at λ_{max} = 543 nm using a UV-Vis spectrophotometer Scheme 1.



Scheme 1 *Detection of nitrite*

2.6. Nitrite removal experiments:

2.6.1. Batch method:

The functionalized diamine polysiloxane-immobilized ligand system, P-NN (50 mg) was shaken with aqueous solution of nitrite ion (25 mL, 5 ppm) using 100 mL polyethylene cups. Determination of the nitrite ion concentration was carried out by allowing the insoluble complex to settle down and 1.0 ml of the supernatant was withdrawn using a micropipette then 1.0 ml of nitrite reagent was mixed for 1.0 min until pink color appeared. The nitrite ion removal was calculated as mg of NO_2^-/g ligand according to equation:

$$q = \frac{(C_{o} - C_{f})V}{m}$$

where q (mg g^{-1}) is the adsorption capacity of the adsorbent at equilibrium, C_o and C_f (mg L^{-1}) are the initial and final concentrations of the adsorbate in solution, V (L) is the volume of the solution and m (g) is the mass of the adsorbent. Each study was performed at least in a triplicate. Nitrite adsorption was examined under various factors including time, concentration of nitrite, pH, competitive ions and temperature.

2.6.2. Column method:

A glass column (500 mm long, 10 mm diameter) was washed sequentially with 0.1 M nitric acid, water and acetone. It was then oven-dried and packed with a bed (0.75 g, 60-80 mesh) of the diamine immobilized ligand system, P-NN. The packed material was activated for each run by washing with (50 mL, 0.1M) of HCl. Nitrite solution (50 mL, 5ppm) was passed through the column with a flow rate of 1.5 mL min^{-1}. The nitrite adsorption capacity of the ligand was calculated as mg NO_2^-/g of the ligand system.

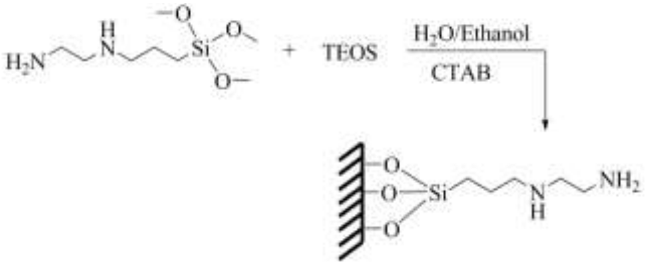
2.7. Recycling efficiency of the functionalized polysiloxane (P-NN):

The loaded functionalized polysiloxane immobilized ligand system (P-NN), was collected from the adsorption experiments and washed with 0.1 M NaOH for nitrite desorption followed by washing with distilled water and then dried for 12 hours. The recycled material was then activated by acidification with 1 M HCl for 12 hours then filtered and dried in oven for 24 hours. The dried material was re-examined for nitrite adsorption capacity.

3. Results and discussion:

3.1. Synthesis:

The functionalized polysiloxane-mesoporous immobilized diamine ligand system, P-NN was prepared as previously reported (El-Ashgar *et al.*, 2012) in a one step reaction by hydrolytic polycondensation of 3-Aminopropyl-2-aminoethyltrimethoxysilane with tetraethylorthosilicate, in 1:2 molar ratio in the presence of CTAB as surfactant Scheme 2. The elemental analyses results of the prepared polysiloxane are given in Table 1. It is found that percentages of C and N are slightly lower than expected due to the formation of small oligomers which leached during the washing process (El-Ashgar *et al.*, 2012). The equal ratios of both expected and found results confirm that complete functionalized monomer of ligand leached.



Scheme 2 *Sythhesis of ethylendiamine polysiloxane immoblizid ligand system, P-NN*

Table 1 *Elemental analysis for polysiloxane-immobilized etylenediamine ligand system (P-NN)*

Element	C%	H%	N%	C/N	mmol N/g
Expected	21.80	5.40	10.10	2.15	7.2
Found	19.45	5.6	9.13	2.13	6.5

3.2. FTIR for diaminepolysiloxane:

FTIR spectrum for the diaminepolysiloxane immobilized ligand system (P-NN) is given in Figure 1. The spectrum shows three regions of absorption at 3600-3100 cm^{-1} due to ν(OH), ν(NH) or ν(NH_2), 1660-1540 cm^{-1} due to δ(OH), δ(NH_2) or δ (NH) and 1200-900 cm^{-1} due to ν(Si-O) respectively. The strong band at 1640 cm^{-1} is due to δ(NH_2/NH) vibrations. This confirms that the ethylenediamine functional group is chemically bonded to the polysiloxane surface.

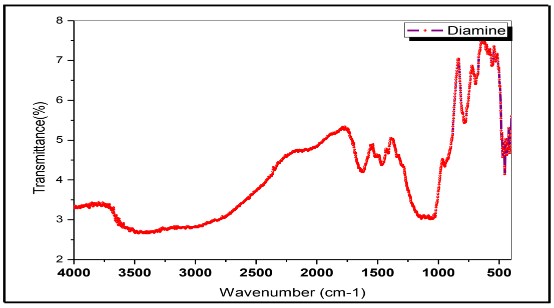


Figure 1 *FTIR spectrum of ethylendiamine polysiloxane immoblizid ligand system, P-NN*

3.3. Thermogravimetric Analysis:

Thermogravimetric analysis (TGA) and the derivative thermogravimetry (DTG) were examined for P-NN under nitrogen at temperature range of 25-600ºC with 10 ºC/min. The weight loss of the polysiloxane was studied as a function of change in temperature Figure 2. Four DTG peaks (maxima) were observed. This could be explained by a four–stage degradation process for the P-NN. The first peak at ~99.5ºC is attributed to the loss of adsorbed water (dehydration) and alcohol from the pore system (Dvornic & Lenz, 1990; Vansant, Van Der Voort, & Vrancken, 1995; Klonkowski, Koehler, & Schlaepfer, 1993). The second peak at ~180ºC is due to the loss of surface the entrapped water and ethanol from the pore matrix. The third stage at ~350ºC is due to cleavage and degradation of the organofunctional group bonds which attached directly to the silicon atoms producing gases, e.g. CO_2 and formaldehyde (H_2CO) which takes place as a product of the thermal decomposition (Kłonkowski, Koehler, Widernik, & Grobelna, 1996; Kłonkowski *et al.*, 2001; Jovanovic, Govedarica, Dvornic, & Popovic, 1998). The DTG peak 525ºC is attributed to dehydroxylation of surface silanol groups, forming siloxane bonds (Kłonkowski *et al.*, 1996; Kłonkowski *et al.*, 2001; Jovanovic *et al.*, 1998).

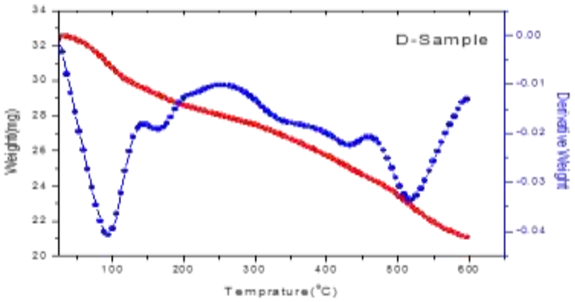
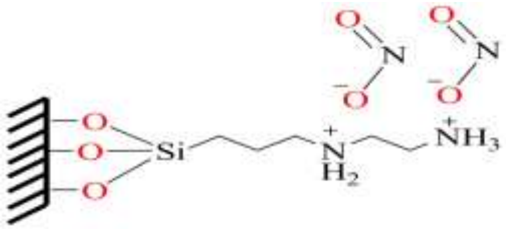


Figure 2 *TGA of ethylendiamine polysiloxane immoblizid ligand system, P-NN*

3.4. Nitrite removal capacity of P-NN:

3.4.1. Batch method:

The nitrite removal capacity by P-NN was determined by shaking the acidified functionalized ligand system with nitrite ions solutions for 48 hours. The adsorption of nitrite onto the P-NN is due to electrostatic attraction between the anionic nitrite and the protonated nitrogen atoms Scheme 3.



Scheme 3 *Adsorption of nitrite ions by the protonated P-NN via electrostatic attraction*

3.4.2. Effect of contact time:

The nitrite removal capacity was determined by shaking the functionalized ligand system P-NN with nitrite ion solution (5 ppm). Measurements of nitrite removal capacity (%) of P-NN were carried out at different time intervals (1-72) h, the results are given in Figure 3. It is shown that the removal of nitrite increases as a function of shaking time and reaches equilibrium nearly after 24 hours where maximum removal is obtained. After 24 hours it is found that at 5 ppm concentration, nitrite is completely adsorbed and become constant. So the optimum time of adsorption is considered 24 hours contact time.

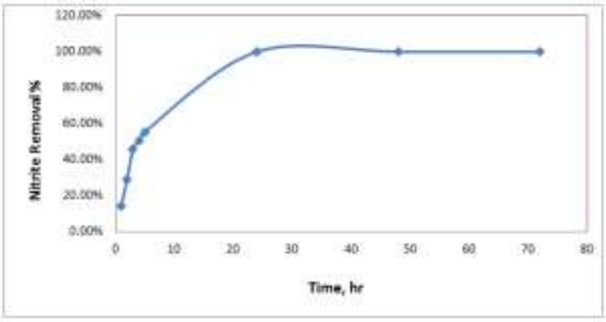


Figure 3 *Effect of contact time on the % of nitrite removal (50 mg of P-NN, 5 ppm nitrite and RT)*

3.4.3. Effect of initial concentration of nitrite:

Measurement of the percentage of nitrite removal capacity of P-NN was carried out at different nitrite initial concentrations (5-50) ppm; the results are given in Figure 4. It is found that the percentage of nitrite removal decreases by increasing concentration and seem to be constant at concentrations higher than 10 ppm. This can be explained by saturation of the polysiloxane material with the adsorbed nitrite. In addition some nitrite ions detached from the solid support after neutralization by counter ions present in the solution because of degradation of polysiloxane matrix.

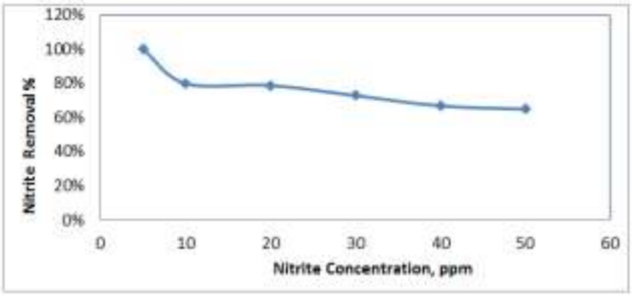


Figure 4 *Effect of initial concentration of nitrite on % of nitrite removal capacity (50 mg of P-NN, RT and 24 h contact time)*

3.4.4. Effect of *p*H:

The effect of the *p*H on the percentage of removal effeciency of nirite ions by P-NN is shown in Figure 5. The results showed a decrease of % nitrite ions removal with increasing *p*H and reaches its minmum (0 %) at *p*H 8. High % removal effeciency occurs at low *p*H values (*p*H = 3.5) due to protonation of amine groups. In *p*H >7 there is no any uptake of nitrite as the amine groups become deprotonated and the nitrite ions repelled away.

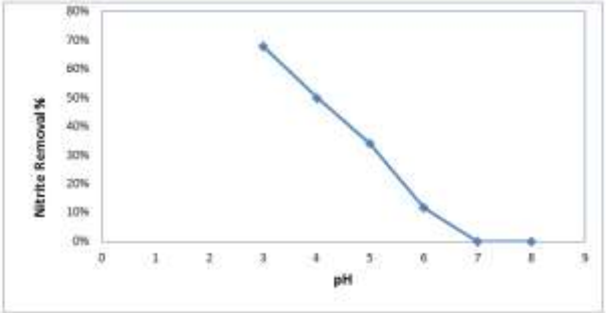


Figure 5 *Effect of pH on % of nitrite removal capacity (50 mg of P-NN, 5 ppm nitrite, RT and 24 hr contact time)*

3.4.5. Effect of temperature:

The effect of temperature on removal effeciency of nitite ions by P-NN is shown Figure 6. The results show an increase of nitrite ions removal with increasing tempearture and reaches its maximum at 75 ^{0}C, were nitrite is completely adsorbed. This is attributed to high diffusion of nitrite ions by increasing temperature.

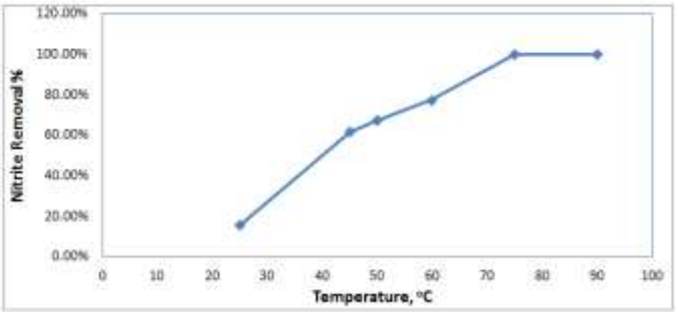


Figure 6 *Effect of temperature pH on % of nitrite removal capacity (50 mg of P-NN, 5 ppm nitrite and 24 hr contact time)*

3.4.6. Recycling of the P-NN material:

The solid material P-NN was retained by desorption of nitrite using sodium hydroxide solution in order to investigate the recycling efficiency for re-adsorption of nitrite ions. After recycling of P-NN by washing with 0.1 M NaOH; nitrite was desorbed. Then the solid material was washed with distilled water and dried for 12 hours. The recycled material then activated by acidification with 1 M HCl for 12 hours then filtered and dried in oven for 24 hours. The dried material was re-examined for 5 ppm nitrite ions at room temperature for 24 hours. The nitrite ion was determined and the removal efficiency was found 90-95 %.

3.4.7. Column method:

After passing 5 ppm nitrite solution (50 mL) through the column with a flow rate of 1.5 mL min^{-1}. The nitrite ions were completely adsorbed. The column was recycled and re-examined another time and found repeatable.

3.4.8. Competitive ions:

In the presence of different interference anions which include (NO^-_3 , SO_4^{2-} and PO_4^{3-}), the polysiloxane ligand system; P-NN was examined for adsorption of nitrite removal efficiency at 5 ppm concentration of each anion. It was found that removal efficiency of nitrite ions was 74%. The lower of efficiency than the solution containing only nitrite ions is attributed to competition with other anions present.

Conclusion:

Solid porous 3-aminopropyl-2-aminoethylpolysiloxane ligand system; P-NN was prepared and used as nitrite adsorbent after acidification. The optimum conditions were investigated and found efficient in acidic medium, 24 hours contact time and temperature of 75^{0}C. The nitrite removal was about 65-100% for concentrations of 5-50 ppm. This adsorbent has been found repeatable and recyclable so it promised for good nitrite removal that can be used as solid supports filters in waste water manipulations.

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إزالة أيونات النتريت من المحاليل المائية باستخدام مجموعة الإيثلين ثنائي الأمين المثبتة على أنظمة البولي سايلوكسان

تم تحضير مجموعة فعالة تتمثل في الاثيلين ثنائي الأمين المثبتة على أنظمة البولي سايلوكسان المسامية الصلبة P-NN حيث تعبر P عن شبكة البولي سايلوكسان وتعبر –NN عن مجموعة الإيثلين ثنائي الامين، وذلك باستخدام عملية التحلل المائي والتكثيف المتعدد لكل من 3- أمينوبروبيل-2-امينوإيثيل ثلاثي ايثوكسي سيلان ورباعي ايثوكسي سيلان في وجود مادة CTAB النشطة سطحيا. وقد تم استخدام مادة CTAB لتحسين مسامية المادة ومن ثم زيادة القدرة الإمتزازية لنظام التثبيت الحامل للمجموعة الفعالة. وقد تم اختبار المجموعة الوظيفية المثبتة على نظام البولي سايلوكسان في عملية امتزاز ايونات النتريت من المحاليل المائية. وتم اجراء كل من طريقة الدفعة وطريقة عمود الفصل واختبار مجموعة من العوامل المؤثرة على درجة الامتزاز تمثلت في زمن الاتصال مع العينة، الرقم الهيدروجيني (pH)، تركيز أيون النتريت ودرجة الحرارة وذلك للتحقق من الظروف المثالية لإزالة أيونات النتريت. وقد وجد أن أفضل الظروف للامتزاز هي الوسط الحمضي ودرجة حرارة 75°م، وزمن اتصال مقداره 24 ساعة. كما وجد أن المادة المازة المحضرة يمكن تكرار استخدامها وإعادة تدويرها. لذلك تعتبر المادة المازة المحضرة مادة واعدة يمكن استخدامها في إزالة أيونات النتريت من المحاليل المائية المختلفة، وكذلك المياه العادمة الملوثة بالنتريت.

كلمات مفتاحية:
مواد سيليكا داعمة،
مثبتات البولي سايلوكسان،
الصل- جل،
التركيب القالبي،
إزالة النتريت.