Synthesis, characterization, and application of lignin azo oxine biosorbent for detection and determination of iron in pharmaceuticals samples

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ABSTRACT

Novel chelating biosorbent (lignin azo oxine, Lig-N=N-OxB) was synthesized from lignin of orange tree. The Lig-N=N-OxB was applied to detect and estimate the iron content in the pharmaceutical compounds. The biosorbent was characterized by scanning electron microscope, infrared spectrum, X-ray diffraction, and thermal analysis (TGA). The FTIR spectrum of Lig-N=N-OxB demonstrated the presence of several active groups in its material matrix. XRD showed that Lig-N=N-OxB is amorphous structure. The Lig-N=N-OxB are good thermal stability up to 1000 ^{0}C and also at pH 1-14. The different parameters (pH, time, concentration and temperature) and also the models of physicochemical for explaining of the sorption process of iron from aqueous solution onto Lig-N=N-OxB. The Lig-N=N-OxB had an important application for determination of iron in drug compounds, owing to the recovery percentages 100% with lower detection limit 0.3 µg/L and preconcentration factor 125.

KEY WORDS: Biosorbents, Orange tree, Chromatography, Batch, Separation.

1. INTRODUCTION

Iron has wide applications in many pharmaceutical samples; it is the main micronutrient in the human body as well as for aerobic life (Popovic, 2019). It plays important physiological roles in many biological systems including enzyme catalysis, electron transfer and also oxygen carrying in hemoglobin which contributes to the prevention of pernicious anemia and production the cell of red-blood (Isidori, 2018; Xiaoyun Chen, 2019). The high level of iron is creating health risk, thalassemia, hemochromatosis, chronic liver disease (Conway, 2013).

The accuracy of determination for traces of iron ions is very important for analytical chemists (Ebrahimi, 2019). Direct determination of iron ions in different medical purposes is to some extent a problem because of the high concentration of interfering matrix components (Czech, 2020; Zoltowska-Aksamitowska, 2018). The preconcentration and separation processes are necessary for the elimination of interfering elements prior to detection of iron (Zhai, 2020; Ahsan, 2018).

Wood of orange biosorbent is composed of many chemical components e.g., lignin and cellulose with functional groups that are able to adsorb the heavy elements (Yu, 2020). Lignin is one the most abundant biological material on the planet, where it serves as a binding agent for cellulose and hemicellulose. It contains active functional groups on the surface e.g., phenolic, hydroxyl, carboxylic, ketones, and ether (Klapiszewski, 2017).

The mechanism used for the preconcentration of trace compounds through the lignin column on the reaction between the functional groups of lignin and these compounds. The lignin is capable of binding the ionic species by creating chelating complexes or new chemical bonds with the adsorbate (Tang, 2020). Very simple preparation procedures of biosorbents have minimized the usage of the chemicals, consequently reducing the hazardous on the environment, and also the reducing of the biosorbent synthesis costs (Santos, 2017). Although the excellent properties of biosorbents for the preconcentration of iron (Moawed, 2019), the leaching of lignin is a problem that necessitates the treated of a biosorbent to prevent the loss of its active components through leaching (Moawed, 2018). The aim of the work is to use lignin (LigOB) extracted from orange biosorbent (OrB) for preparation new chelating Lig-N=N-OxB) as new stable biosorbent to treat the leaching of orange biosorbent components.

2. EXPERIMENTAL

Apparatus: The structure of Lig-N=N-OxB was investigated using XRD patterns using an X-ray diffractometer (D8-Brucker Model) equipped with Cu Ka radiation (? = 1.54 Å). The surface morphology of the Lig-N=N-OxB was examined using scanning electron microscopy analysis (SEM, JEOL model JSM-6510LV, USA). FTIR spectrum recorded using JASCO-410 spectrometer (JASCO, Easton, MD). The ultraviolet and visible spectra detected using JASCO Spectrophotometer (V 630, Japan) was employed for absorbance measurements of the iron. The TGA, DSC and DTA were estimated by DSC-TGA device model (SDTQ 600, USA) under N_2 atmosphere with a heating rate of 10°C min^{-1} (29-1000°C).

Reagents and materials:

Lignin of orange biosorbent (LigOB): orange stem was cut into small pieces, washed with water to remove dust. The pieces were dried overnight in oven at 105°C, followed by grinded in a food–processing blender. A 100 g of orange powder was soaked in 250 mL of H_2SO_4 (1:1) for 24 h, followed by washing with distilled water till neutral pH, filtrate and, then dried at 105°C.

Lignin azo oxine (Lig-N=N-OxB): 10 g of LigOB placed in a 0.1 mol/L NaOH solution in an ice-bath, then coupled by adding cold solution of diazonium salt of meta nitro aniline, and then the mixture was left for 2 h in the fridge. The product was soaked in 1 mol/L ascorbic acid in order to make reduction for nitro group to amino group then placed in a 0.1 mol/L HCl solution, then diazotized with 50 mL of $NaNO_2$ (0.5 mol/L), For the coupling step, a 50 mL of (1%) solution of 8-Hydroxyquinoline-5-sulfonic acid was added dropwise to the diazotized resin, then the mixture was left for 2 h in the fridge, and washed with distilledwater then air-dried.

Vitamins drugs stock solutions: A capsule of Feroglobin B12 (Cu: 0.9 mg; Fe: 24 mg; Zn: 10 mg; Vitabiotics Egypt for Pharmaceutical Industries, Alexandria, Egypt), capsule of Ferro Sanol Duodenal (Fe: 100 mg; Mina Pharma, Schwarz-10th of Ramadan city- Egypt)and capsule of Vitamix plus (Cu: 2 mg: Fe: 9 mg; Mn: 5 mg; Mo: 30 μg; El Salam City – Cairo – Egypt) were heated in 25 mL concentrated nitric acid and gently evaporated several times till dryness, then the solid residue was dissolved in distilled water to 25 mLin a measuring flask containing 1mL of concentrated nitric acid.

Recommended procedures:

Batch experiment: A 25 mL of iron solutions were shacked for 60 min with 100 mg of Lig-N=N-OxB. The sorption percentages of iron and capacity of biosorbent was calculated using thefollowing equations:

$$\text{Sorption level, } \% = \frac{(C_o - C)}{C_o} \times 100 \qquad (1)$$

$$\text{Capacity} = \frac{C_o EV}{M} \qquad (2)$$

In the continuous experiments: 5.0 g portion of biosorbent was packed into a column (54 cm long and 1.9 cm in diameter). A 25 mL of iron solution passed in the column (L = 100 mm) at 1-2 mL/min and the effluent was collected and were analyzed spectrophotometrically.

3. RESULTS AND DISCUSSION

Characterization of Lig-N=N-OxB: Infrared spectrum of lignin of orange (LigOB) and lignin derivative (Lig-N=N-OxB) was shown in figure 1. LigOB spectrum have a broadband at 3749–3290 cm^{-1} and several sharp peaks at 2924, 2855, 1729, 1631, 1162–1031 cm^{-1} which assigned to OH, CH (Aromatic), CH (Aliphatic),C=O, C=C and C-O-C groups. These bands were shifted in Lig-N=N-OxB spectrum to 3671–2969, 2924, 2856, 1710, 1618, 1207-1038 cm^{-1} and additional Three new sharp peaks at 1528, 1350 and 1284 cm^{-1} for N=N, C-N and SO$_3$H groups.
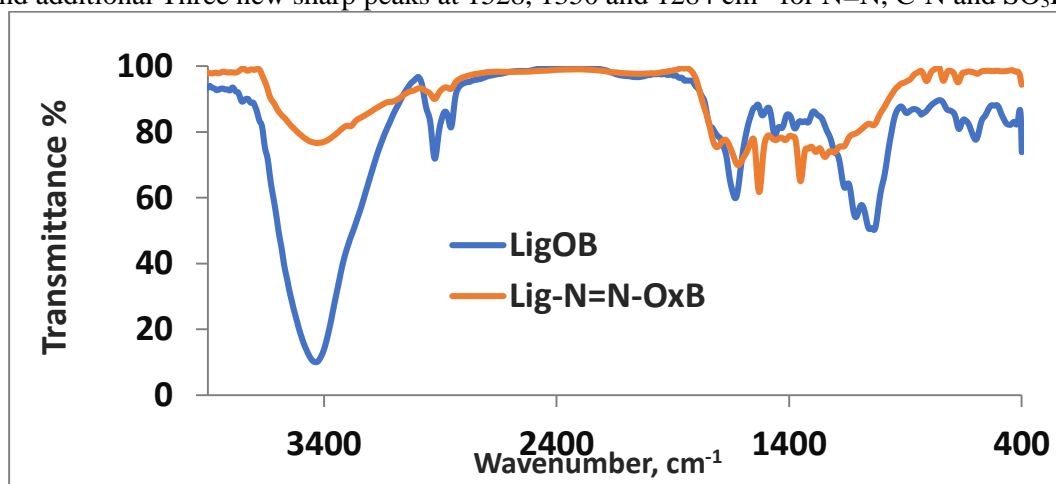
**Fig.1. FTIR spectra for LigOB and Lig–N=N-OxB**

The pH$_{ZPC}$ values of LigOB and Lig-N=N-OxB are the pH values at which the biosorbents surfaces charges equal to zero. At pH < pH$_{ZPC}$, the surfaces of the biosorbents are positively charged, and at pH greater than pH$_{ZPC}$, they become negatively charged. The estimated pH$_{ZPC}$ values of Lig-OB and Lig-N=N-OxB were 2.4 and 5.0 respectively (Fig.2). The different values of pH$_{ZPC}$ Lig-OB and Lig-N=N-OxB are due to the differentof surfaces functional groups.
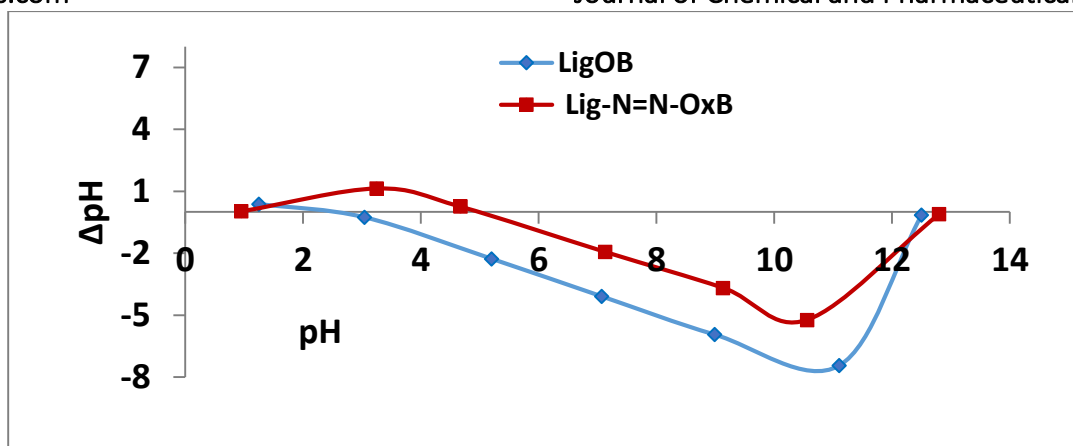
Fig.2. pHzpc curves for LigOB and Lig-N=N-OxB

The UV spectrum of LigOB using Nujol mulls procedure contains many absorption bands at ranges of 200, 210, 212, 214, and 218 nm, the Higher energy bands are assigned to (s-s* and p-p*) transitions. The lower energy bandsare assigned to the n-p* transition. These bands were appeared at 201-203, 205-209 and 221 nm for Lig-N=N-OxB due to formation of new bonds.

The surfaces morphology of LigOB and Lig-N=N-OxB were investigated using scanning electron microscopy (SEM) with different magnifications. The SEM images at 1,000x magnification (Fig.3A) illustrate, LigOB surface was rough and amorphous while at a higher magnification of the LigOB image (5,000x, Fig.3B), it shows that gaps have appeared. The surface of LigOB was completely changed after coupling with 8-hydroxyquinoline-5-sulfonic acid, the gaps between the particles were increased and also the surfaces convert to nearly smooth shape (Figs 3C, 3D). The surfaces areas of LigOB and Lig-N=N-OxB were calculating using iodine number procedure. The iodine values of LigOB, and Lig-N=N-OxB were 2.28 and 1.69 mmol/g,respectively.
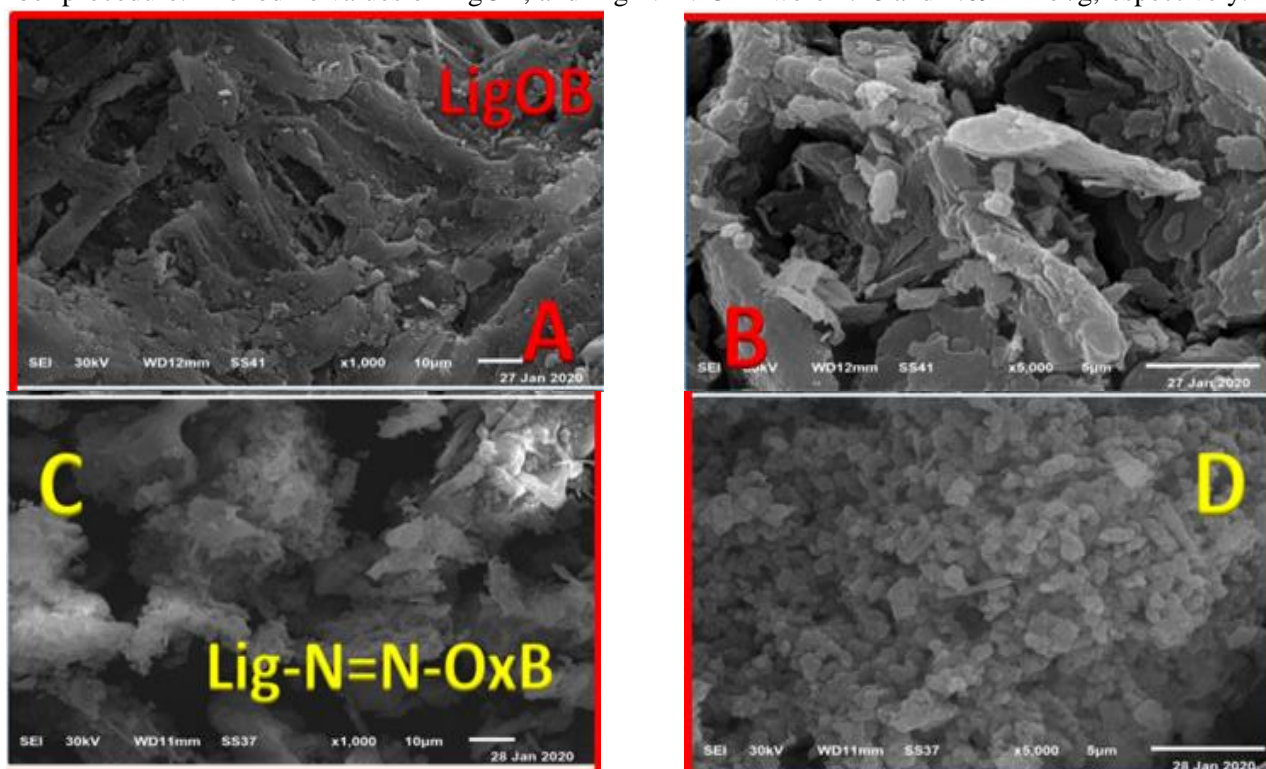
Fig.3. Surface morphology for LigOB and Lig-N=N-OxB

The surface area of biosorbent was calculated using the following equation, $(S = \frac{IN \times N \times A}{M})$, where S isthe area covered by adsorbed iodine molecules at the maximum mono-layer surface (m^2/g), N is the Avogadro number (6.02×10^{23}), A is the iodine surface area (0.2096×10^{-18} m^2) and M is the iodine molar mass (126.9 g/mol). The calculated specific surface areas were 1133.5, and 840.2 m^2/g. The maximum amounts of methylene blueexchanged onto one gram of LigOB, and Lig-N=N-OxB is called methylene blue values or cation exchanging capacities. The methylene blue values of LigOB and Lig-N=N-OxB were 15 and 14 mg/g.

The basic and acidic functional groups of LigOB, and Lig-N=N-OxB were determined through Boehm technique. The total acidic sites (-COOH, -CO and –OH) of tested sorbents were 4.9, and 3.3 mmol/g while the number of basic sites were 0.2 and 0.3 mmol/g. The obtained results show that the amounts of acidic sites were decreased in Lig-N=N-OxB while the basic sites were increased after coupling processes. These results show agreement with FTIR spectra. Thermal properties of LigOB, and Lig-N=N-OxB were evaluated using TGA, DTA and DSC analysis (Figure.4 and Figure.5).

TGA curves of tested sorbents show a smooth stepwise with two steps of thermal decomposition. The first step of the decomposition was at ranges 29-103, and 29-115°C with weight loss percentages were 21.2, and 8.5%, respectively (Fig.4). The weight loss in this step was usually due to the evaporation of adsorbed water molecules, the weight loss for the LigOB (21.2%) was higher than Lig=N=N-OxB (8.5%). The weight loss was 39.0, and 45.7% of the second step at ranges 104-1000, and 116-1000°C. The DTA curves of biosorbent showed that one endothermic peak has appeared in this step at 54-58^{0}C. The results obtained of DSC were similar with DTA data, the endothermic points of DSCcurves at the first step were at 54-58 °C. The other endothermic points were at 150-155°C for LigOB, and Lig-N=N-OxB.
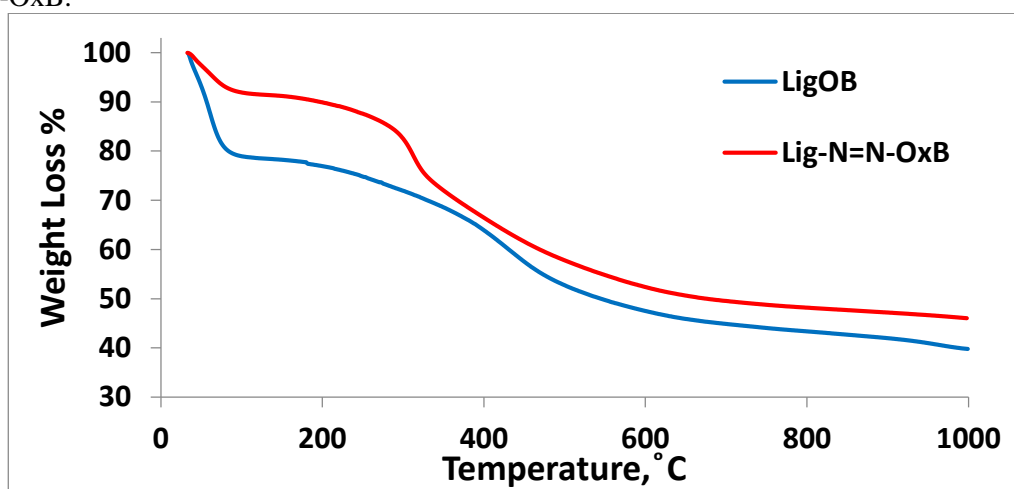

Fig.4. TGA curves for LigOB and Lig-N=N-OxB

Figure.5, shows the XRD patterns of both LigOB and Lig-N=N-OxB. A broad diffraction peaks are observed at 2^0, 23.11° and 22.49° for LigOBand Lig-N=N-OxB, respectively. Which clear that the LigOB kept its amorphous character. The peak intensity of Lig-N=N-OxB increased compared tothat of LigOB. Which indicate the successful preparation of Lig-N=N-OxB.
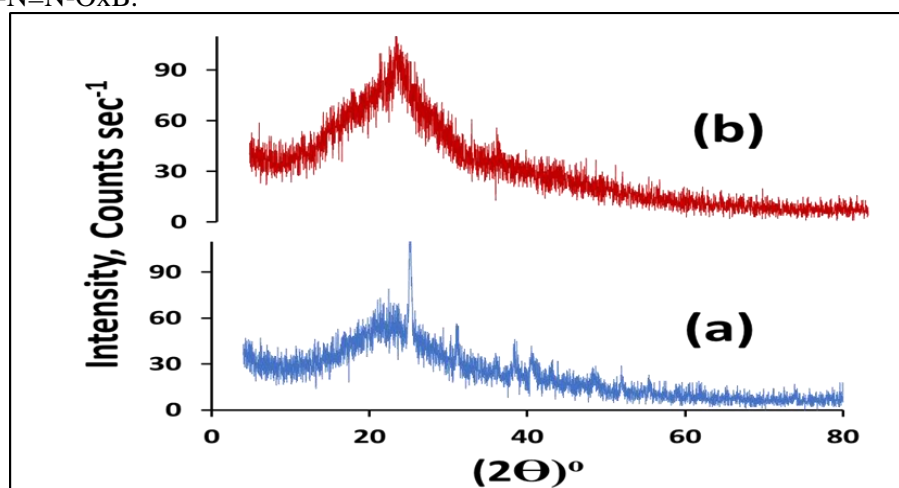

Fig.5. XRD curves for (a) LigOB and (b) Lig-N=N-OxB

Optimum condition for sorption of iron (III) onto Lig-N=N-OxB: The sorption percentageof iron against the pH values (1-6) was tested. It is noted that the maximum sorption percentages of Fe (III) ion were at pH values 2-6. Based on the behavior of Fe (III) ion extracted, it is speculated that the sorption process mainly depends cation chelation or ion exchange processes. The times required for sorption of iron onto Lig-N=N-OxB were 1-5 minutes. It indicates that the rates of sorption of the iron ions onto this biosorbent is very rapid. It is concluded that the rapid sorption time of iron onto biosorbents depends on the nature of the reaction between iron ions with specific functional groups of biosorbent.

The effects of temperature (20–60°C) on the extraction of Fe(III) ions using Lig-N=N-OxB was studied. The sorption percentages of Fe(III) ions was plotted against temperature. The obtained results revealed that the sorption of Fe(III) ions were slight effecting with increasing of temperature. The kinetic parameters for sorption iron (III) ions using Lig-N=N-OxB was estimated by pseudo first-order and pseudo second-ordermodels. The average values of R^2 obtained for pseudo second-order sorption model (0.998) is higher than that obtained for pseudo first-order kinetic first order kinetic (0.41).

Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) was evaluated. The enthalpy (ΔH) was -9.05 kJ/mol, the positive value of ΔH reveal to the extraction process of Fe(III) ions using Lig-N=N-OxB is exothermic. ΔG was -20.1 kJ mol-1; these values attributed to the sorption process are spontaneous. Finally, the entropy (ΔS) of sorption Fe(III) ions onto Lig-N=N-OxB was 37.3 J/mol.

The effect of Na^+, K^+, NH_4^+, Mn^{2+}, Cu^{2+}, Ni^{2+}, pb^{2+}, Co^{2+} and Ca^{2+} (40 µg/mL) on iron adsorption (10 µg/mL) onto Lig-N=N-OxB was studied (Fig. S1). The obtained data reveal that the Na^+, K^+, NH^{4+}, Pb^{2+}, Ca^{2+}, Co^{2+} and Ni^{2+} ions didn't interfere using Lig-N=N-OxB but Mn^{2+} and Cu^{2+}were slightly interfered (14-17%). A masking agent e.g., phosphate, citrate and tartaric acid and pH controlling were used to eliminate the interfering ions.

The plots of Fe(III) ions concentrations with Lig-N=N-OxB capacities have good linear relationship with R^2 values are 0.997 (Fig.6). It is obvious that the increase Fe(III) ions concentrations followed by a subsequent increase in biosorbent capacities. The maximum capacity of Lig-N=N-OxB was 0.25 mmol/g, this value is greater than other sorbents (Moawed, 2017; Moawed, 2017; Al-Makhadmeh, 2016; Abou El-Reash, 2020). The equilibrium data for adsorption iron (III) ions using LigOB, and Lig-N=N-OxB were analyzed by Freundlich and Langmuir models. The average values of R^2 obtained from Freundlich model (0.90) is higher thanthat obtained from Langmuir model (0.48), suggesting for multilayer sorption over heterogeneous surfaces. The effect of flow rate (0.3-5 mL/min) on the extraction of Fe(III) using Lig-N=N-OxB column was examined to get the appropriate time of analysis.

It was found that the extraction percentages iron (III) ions from thiocyanate medium were 100% at 0.3 to 5 mL/min. The effect of various eluting agents like $SC(NH_2)_2$, $H_2C_2O_4$, HCl, KCl, and HCl/KCl on the stripping Fe(III) ions from Lig-N=N-OxB columnhave been studied, It was observed that Fe (III) ions were completely eluted from Lig-N=N-OxB column with oxalic acid. The stripping of Fe(III) ions from Lig-N=N-OxBcolumn was different eluent concentrations (0.05-0.5 M $H_2C_2O_4$).

It clear that Fe(III) ions are completely eluted from Lig-N=N-OxB column by all concentrations of $H_2C_2O_4$ within the first 4-30 mL. The elution of 0.25 mg of Fe (III) from the Lig-N=N-OxB column by using 0.05 M $H_2C_2O_4$ was also tested at various flowrates (1-5 mL/min). The chromatograms indicate that iron was completely eluted within the first 4-32 mL (Fig.6). The results show that the best chromatogram observed when flow rate is 1 mL/min.
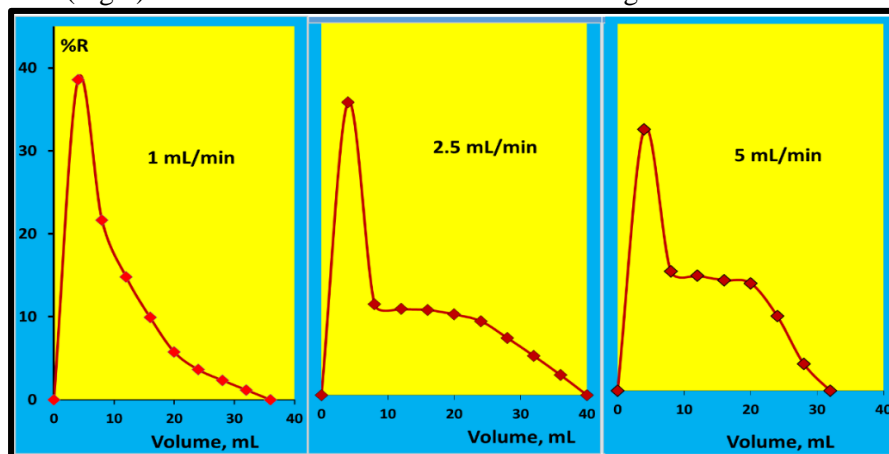
Fig.6. Effect of flow rates on the stripping of Fe(III) from Lig-N=N-OxB column

To determine the breakthrough capacity of Lig-N=N-OxB for Fe(III) ions, column is saturated with Fe(III) under optimum conditions.The saturation of the column is reached after passing 1050 mL of 8 mg/L of Fe(III) is estimated to be 0.15 mmol/g (8.4 mg/g). the breakthrough capacity is less than the total capacity determined from the batch method, As the first one is determined under dynamic flow of metal ion solution where the contact time is short unlike the batch capacity where enough contact time betweenthe metal ion and the sorbent allows high mass transport to the solid phase.

The effect of preconcentration factor (ratio of sample volume to that of the eluent) on the uptake percentage was studied. 1000 mL of Fe (III) ions were passed through the Lig-N=N-OxB column at 1 mL/min. A 0.05 mol L-1 oxalic acid was adequate for the complete elution of Fe (III) ions at elution volume of 8 mL. The estimate preconcentration factor is 125. These results show that Fe(III) ions can be effectively concentrated when present at tracelevels using Lig-N=N-OxB column.

Application of Lig-N=N-OxB biosorbent: The accuracy and precision for using Lig-N=N-OxB column in the determination of Fe in pharmaceutical samples are the most important criteria for judging the performance of an analytical method. Table 1 shows the results of recovery experiments using a dynamic method for extraction and recovery of Fe from vitamins drug samples (Vitamix blus capsule and Ferro Sanol Duodenal capsule). The average values of recovery percentages and relative standard deviation (n=5) of Fewere 99.7% and 0.76%. The obtained values for the recovery of Fe are satisfactory and reflect the accuracy and precision of the proposed method.

Table.1. Determination of Fe(III) in Pharmaceutical sample using dynamic technique

Pharmaceutical Samples	Added μg	Found μg	Recovery %	RSD %
Vitamix Plus Capsule	80	79.84	99.8	0.27
Ferro Sanol Duodenal	100	99.4	99.4	1.26

The recovery of different amounts of iron (100–400 μg) in vitamins drug (Vitamix plus Capsule, Feroglobin B12 Capsule and Ferro Sanol Duodenal capsule) was tested using Lig-N=N-OxB column (Table.2). The sorption of Fe (III) was in ranges 95–100%. The average values of RSD% were 0.8-3.9 % (n=5). These results showed the suitability ofLig-N=N-OxB column for determination of iron in pharmaceutical samples.

Table.2. Recovery percentages of iron from Pharmaceutical samples

Added, μg	Ferro Sanol Duodenal capsule		Vitamix plus capsule		Feroglobin B12 capsule	
	Found, μg	%	Found, μg	%	Found, μg	%
100	100	100	100	100	100	100
200	200	100	200	100	200	100
300	300	100	288	96	297	99
400	400	100	380	95	384	96

4. CONCLUSION

The chelating resin developed in this study by reaction of diazotization using the biopolymer lignin and the complexing agent 8-hydroxyquinolinee-5-sulfonic acid (Lig-N=N-OxB) resulted in an efficient analytical performance in the extraction and determination of Fe(III) in pharmaceutical samples. Lig-N=N-OxB was shown to be chemically stable in all the analyses carried out in this study. The maximum extraction percentages of Fe(III) ions occurred at pH ranges 2–6. The sorption mechanism of iron ions onto Lig-N=N-OxB may proceed via the cation chelation or ion exchange processesThe kinetic and thermodynamic parameters for the extraction of the Fe(III) ions onto Lig-N=N-OxB were estimated. The ΔG (-ve value) indicated that the nature of iron sorption was spontaneous. This study could conclude that Lig-N=N-OxB has the ability to recovery and determine iron in pharmaceutical samples with a lower RSD of 0.76%. The lower detection limit was 0.3 μg/L and preconcentration factor 125.

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