

FULL PAPER

Separation of Some Metal Ions Using β -Naphthol Modified Polyurethane Foam

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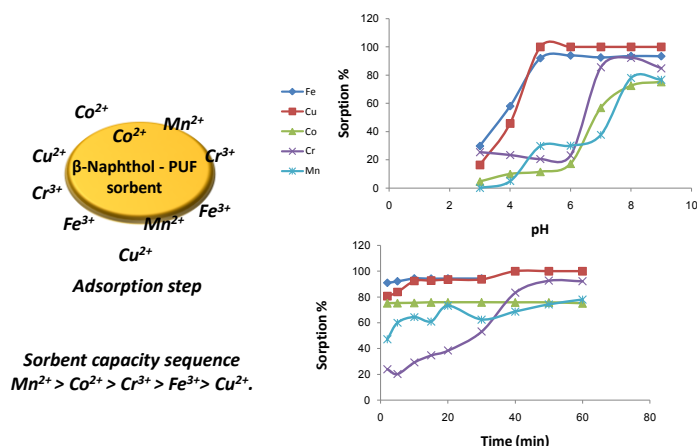
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ABSTRACT: Polyurethane foam was chemically functionalized with β -naphthol to adsorb metal ions (Fe^{3+} , Cu^{2+} , Cr^{3+} , Co^{2+} and Mn^{2+}), applying the off-line solid phase extraction procedure. The concentrations of the metals have been determined using the flame atomic absorption spectroscopy (FAAS). Various factors including, the pH of the sample solution and the time of extraction were examined. The interference effects of the additional ions in the solution were studied, metal ions of Na^+ , K^+ , Mg^{2+} and Ca^{2+} and anions, CO_3^{2-} and SO_4^{2-} . The new sorbent was examined for separation of Cu, Mn, Cr, Co and Fe ions. The adsorption of metal ions onto β -Nap-PUF was tested using the Morris-Weber equation. The straight line of the plot qt (adsorbed amounts at time t) vs t in all cases, with low R^2 (0.767) in case of Mn, indicates the intra particle transport phenomena. The Lagergren equation was applied for mass action phenomenon. The plots of $\log(1-F)$ Vs t for Mn, Cr, and Cu were straight with high R^2 0.99, 0.98, and 0.81 respectively, indicates that mass action phenomenon are controlling the mechanism following first order process. The capacity sequence of the sorbent was in the order $\text{Mn}^{2+} > \text{Co}^{2+} > \text{Cr}^{3+} > \text{Fe}^{3+} > \text{Cu}^{2+}$.

KEYWORDS: Preconcentration; Solid phase Extraction; β -Naphthol; Modified Polyurethane Foam.

GRAPHICAL ABSTRACT:

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1. Introduction

The ability to separate the trace elements in various types of samples is important in many areas of science including

environmental, food, geochemical, forensic, and pharmaceutical. The amount of certain elements can indicate the level of contamination in a region, the nutritional value of a food and the quality of a

manufactured product, among other things [1].

Various methods of separation and preconcentration have been used, such as solid-phase extraction (SPE), liquid–liquid extraction (LLE), and cloud-point extraction (CPE) or co-precipitation. SPE has the advantages of high preconcentration factor, low cost, ease of automation, and usually does not require organic solvents [2, 3].

Solid-phase extraction (SPE) is an effective sample preparation method for removal of interfering compound and enrichment of analyte. The analytes are transferred to solid sorbent where they are retained during the sampling process and then recovered by elution. The principal goals of SPE are trace analytes enrichment and sample clean-up. SPE has been used in many areas, including environmental, pharmaceutical, clinical, food, and industrial chemistry. Over time, various SPE formats and sorbents have been developed to facilitate the process of different sample types and to extend the scope of the method [4].

Solid phase extraction is not limited to the use of solid particles to extract the solutes from liquid sample. Air or other gaseous samples can also be passed through a packed tube to extract organic vapours or other substance present in the sample [5]. There are three objectives for applying SPE procedures. The first goal is the analyte concentration in order to be able to measure the quantity of a compound at higher concentration than in the sample. This will ensure the largest response from the detection system and will minimize error in precision caused by background noise. The second aim of SPE is sample clean up. Since concentration of the analyte is pointless if we cannot measure the analyte in a final concentrated solution. The extracted sample contains interfering compounds. Among these components,

some contaminates that mask the analyte during analysis. The third target is sample matrix removal and solvent exchange. Many analytical instruments (GC or LC, NMR and IR) require the sample to be analyzed in a specific environment. In such case, we need to remove the sample matrix and convert it into a form compatible with the instrument to be used [6,7].

Polyurethane foam (PUF) is an efficient sorbent material [2]. The absorption properties of PUFs have been studied, and the interesting about this material and its derivatives has increased, and they have been used as a solid sorbent for a wide variety of compounds in different media and for different purposes [8]. Unloaded and loaded PUF have been used in extraction methods for the determination of inorganic and organic species using different analytical techniques [2]. The PUF is an excellent sorbent material due to high available surface area, [9], resistant to pH changes, low cost and good stability in organic solvents [10]. Moreover, PUFs can be used in batch techniques, column techniques in off – line or flow injection preconcentration system with low resistance to passage of fluids as commonly occur when using other sorbents [11].

2. Experimental

Apparatus: The absorption measurements were made with Analytic jena, novAA350 atomic absorption spectrometer. The pH measurements were made by a JENWAY 3150 pH-Meter.

Reagents: All the reagents were of analytical reagent grade. Deionized water was used throughout. The metals solutions were prepared from a standard solutions (1000mg/l) from Merck (Germany). Appropriate dilutions were made, whenever necessary, with deionized water. The

sorbent has been prepared according to the method described by Moawad *et al.* [12]

General Procedures

Preconcentration of Cu^{2+} , Mn^{2+} , Fe^{3+} , Co^{2+} , or Cr^{3+} was performed by a batch technique at 25 °C. β -Nap-PUF (0.2 g) was mixed with the metal ion solution ($1\mu\text{g mL}^{-1}$, 25 mL) in a shaker adjusted to the desired shaking speed. After a fixed time and removing the foam from the solution the amount of the remaining metal was determined using flame atomic absorption spectroscopy (FAAS). The percentage sorption of metal ion was calculated using the equation [13, 14, 15]:

$$\text{Sorption \%} = \left(\frac{C_o - C}{C_o} \right) \times 100$$

Where C_o and C are the initial and remaining concentrations (mg L^{-1}) of the metal ion respectively.

3. Results and Discussion

Sorption of Metal Ions as a Function of pH

The pH effect on the uptake metal ions was investigated by batch procedure. An aliquot of varying pH values containing each metal ion separately (Cu^{2+} , Mn^{2+} , Fe^{3+} , Co^{2+} , or Cr^{3+}) was stirred with 0.2 g PUF for 1.0 h. The results obtained are shown in Figure 1.

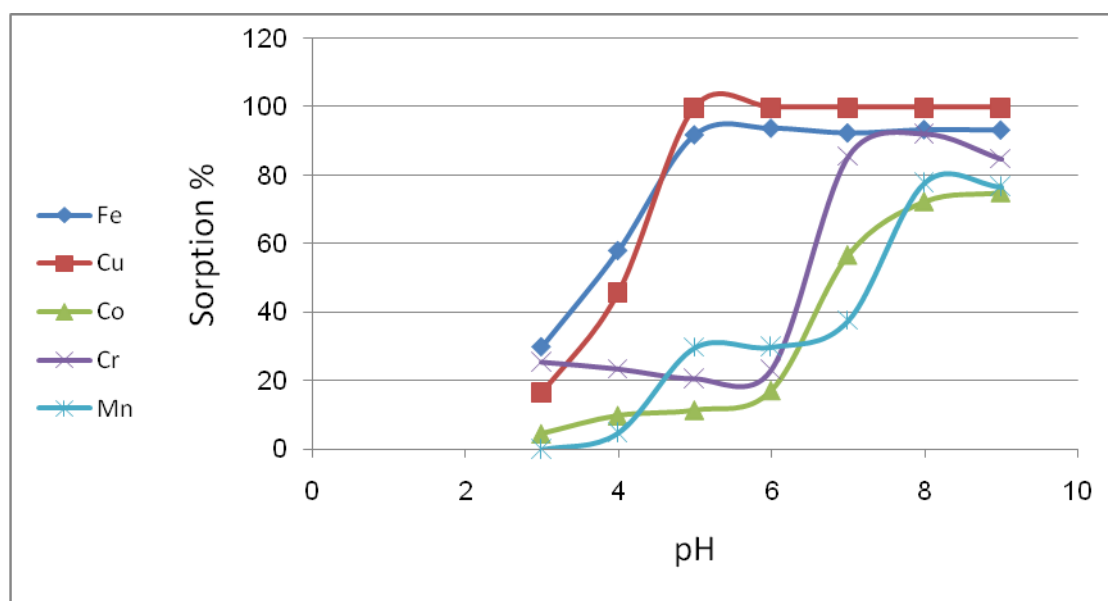


Fig. 1. Effect of pH on the extraction of Fe^{3+} , Cu^{2+} , Co^{2+} , Cr^{3+} and Mn^{2+} with β -Nap-PUF sorbent.

It was found that the uptake increased by increasing the pH till reaching a limiting value then leveling off within certain range of pH which is usually followed by a decrease. By increasing the pH in the range 5–7, the sorption of metal ions increased regularly for the all elements. The obtained results confirm approximately similar sorption mechanism for all metal ions. However, Cu^{2+} was found to be more

extracted than Fe^{3+} , Cr^{3+} , Co^{2+} or Mn^{2+} . This is may be due to the greater stability of copper complexes with the reacted foams. With exception of the trivalent metals, Fe^{3+} and Cr^{3+} , the order of adsorption percent of divalent metals are in agreement with Irving-Williams series, ($\text{Mn(II)} < \text{Co(II)} < \text{Cu(II)}$) which refers to the stability of the complexes formed by the divalent metal ions. Maximum adsorption by β -Nap-PUF

was observed in the pH ranges 5–9 for Fe^{3+} and Cu^{2+} , 8–9 for Mn^{2+} and Co^{2+} and 8 for Cr^{3+} . At low pH ($\text{pH} < 5$), the chelating groups ($-\text{N}=\text{N}$ and $-\text{OH}$) in the sorbent become protonated and might behave as weak anion exchanger which reduce the tendency of the sorbent towards the positively charged metal ions.

The increase in metal ion removal as increased pH can be explained on the basis of a decrease in competition between H^+ and positively charged metal ion at the surface sites which results in a lower electrostatic repulsion of the adsorbing

metal ion and consecutively increased metal ion removal [5]. The decrease in percentage sorption higher than pH 8 for Mn^{2+} and Cr^{3+} ions may be attributed to the possible precipitation of metal hydroxides [11]. The values of the separation factors (α) for the metal ions are summarized in Table 1. The selectivity sequence extracted from sorption percent at different pH is $\text{Cu}^{2+} > \text{Fe}^{3+} > \text{Cr}^{3+} > \text{Mn}^{2+} > \text{Co}^{2+}$ in the pH range 5-6, and $\text{Cu}^{2+} > \text{Fe}^{3+} \approx \text{Cr}^{3+} > \text{Mn}^{2+} \approx \text{Co}^{2+}$ in the pH range 7-9. These result show that control of the pH can be used to enhance the selectivity for separation of these metal ions by use of β -Nap-PUF.

Table 1. Effect of pH on separation factor (α) and selectivity for adsorption of metal ions by β -Nap-PUF sorbent.

pH	Separation factor (α) based on pH									
	Fe/Cu	Fe/Cr	Fe/Mn	Fe/Co	Cu/Cr	Cu/Mn	Cu/Co	Cr/Mn	Cr/Co	Mn/Co
4	1.3	2.5	11.9	5.8	2.0	9.4	4.6	4.8	2.3	0.5
6	1.1	4.3	3.3	5.8	4.1	3.1	5.4	0.8	1.3	1.8
8	0.9	1.0	1.2	1.3	1.1	1.3	1.4	1.2	1.3	1.1

Sorption Kinetics

The adsorption process depends on the effective collisions between the solid-phase (β -Nap-PUF) and the metal ions, which is enhanced with the shaking of the solution. Even with the efficient shaking, certain time is required to achieve maximum transfer of metal ions from liquid to the solid-phase. The influence of shaking time on the percentage of sorption is recognized of significant importance to determine the possible discrimination order of β -Nap-PUF behavior towards Fe^{3+} , Cu^{2+} , Mn^{2+} , Cr^{3+} and Co^{2+} . Variation of sorption against shaking time has showed dramatic profile.

It is evident from the results represented in Figure 2, that the equilibrium between Co^{2+} ions and the phase is faster than Fe^{3+} , Cu^{2+} ,

Cr^{3+} and Mn^{2+} ions, respectively. An equilibration time of about 2 min was sufficient to achieve 75% sorption of Co^{2+} but about only 24% and 47% from Cr^{3+} and Mn^{2+} , respectively. The optimum recovery for Fe^{3+} and Cu^{2+} was at 40 min., 2 min. for Co^{2+} , 50 min. for Cr^{3+} and 20 and 50 min. for Mn^{2+} . These results show that the rate of adsorption of these metal ions during separation with β -Nap-PUF is relatively fast and efficient compared with some other sorbents.

The PUF material is highly porous with the spherical and symmetrical macropores and micropores. The macropores are relatively large compared with the molecular size of the solute and readily accessible to the solute. Sorption into the macropores is rapid

and characteristic of film diffusion. In contrast, the micropores are similar in size to the solute molecule. Diffusion in such pores would be severely hindered due to

steric interaction, so that the subsequent slow approach to equilibrium would be characteristic of an intra-particle diffusion process.

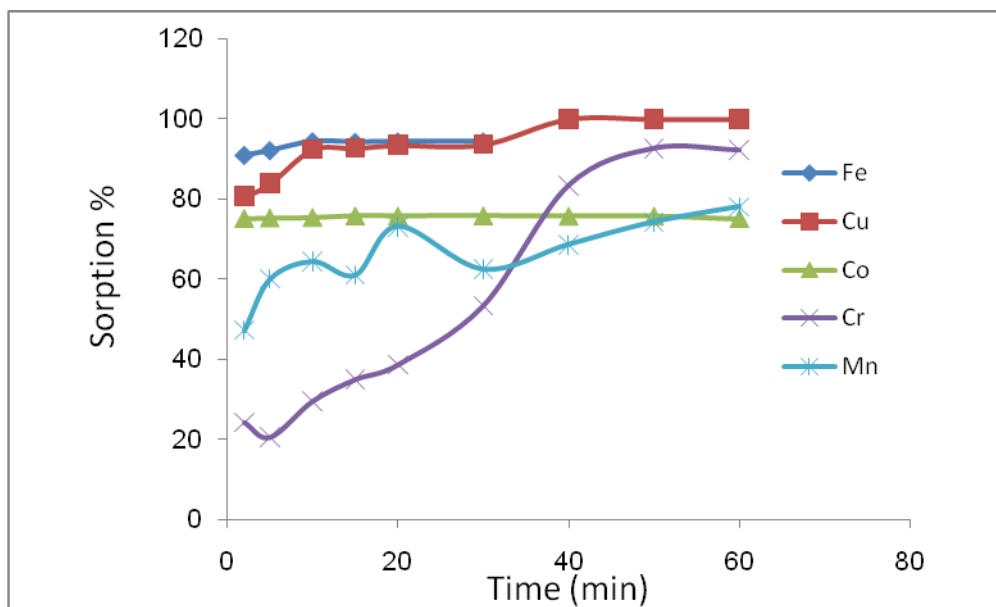


Fig. 2. Rate of sorption of Fe^{3+} , Cu^{2+} , Co^{2+} , Cr^{3+} , and Mn^{2+} with β -Nap-PUF sorbent.

The mass transfer or heat transfer processes usually control the rate of adsorption at the solid surface rather than by intrinsic adsorption kinetics. Variation of a slow activated rate process with concentration is not linear, which is expected from diffusion theory. The interpretation of adsorption data of adsorbate offers many difficulties and can be solved by applying the well known diffusion equations on the diffusion process and mass action phenomenon.

The rate of the adsorption process will be controlled by the slowest step, which would be either diffusion or intra particle diffusion.

The surface adsorption is usually a fast reaction because solute particles have a very little chance to diffuse into the adsorption particles, sorption may be attributed to film diffusion, and the process of adsorption occurs at the macropores of the adsorbent, while time dependent sorption process may be film diffusion or intra particle diffusion.

The adsorption of metal ions onto β -Nap-PUF was tested by using the Morris-Weber [15] equation in the form:

$$q_t = k_i (t)^{1/2}$$

where q_t is the amount of ion adsorbed at time t and k_i is the adsorption rate. The straight line of the plot q_t Vs t in all cases, with low R^2 (0.767) in case of Mn, indicates the intra particle transport phenomena.

In the diffusion process, the slope of the curve depends upon the particle size, film thickness and distribution co-efficient of solute, whereas in mass action, the rate depends upon temperature and concentration of the solute in solution.

The Lagergren equation [15] was applied for mass action phenomenon and which is given below:

$$\log (1 - q_t/q_e) = \frac{-k_1 t}{2.303}$$

or

$$\ln(1 - F) = -k_1 t$$

where q_e and q_t are the adsorbed amounts at equilibrium and at time t respectively, k_1 is the rate constant of the sorption process, and

$F = q_t/q_e$. The plots of $\log(1-F)$ Vs t for Mn, Cr, and Cu were straight with high R^2 0.99, 0.98, and 0.81 respectively, indicates that mass action phenomenon are controlling the mechanism following first order process.

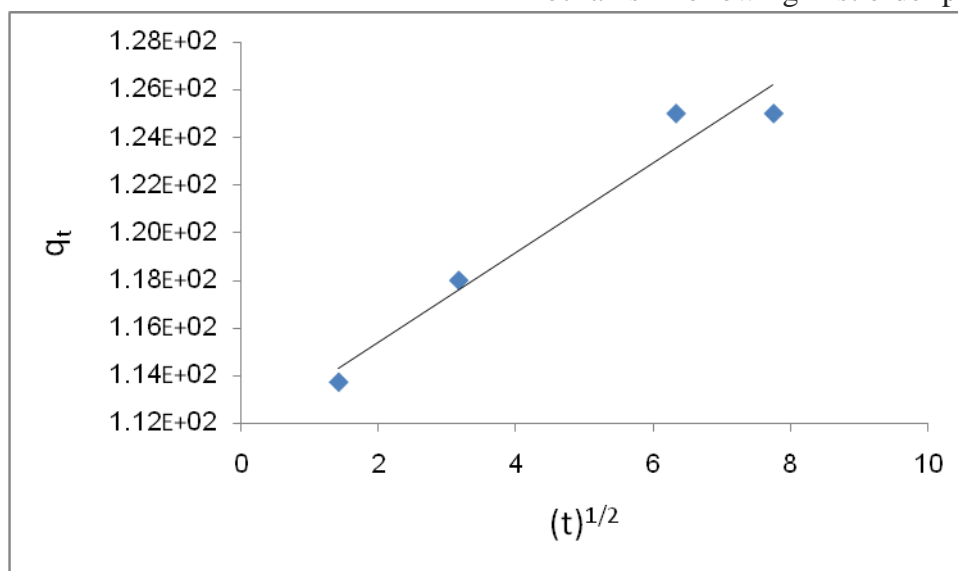


Fig. 3. Morris-Weber plot of Fe^{3+} with β -Nap-PUF sorbent.

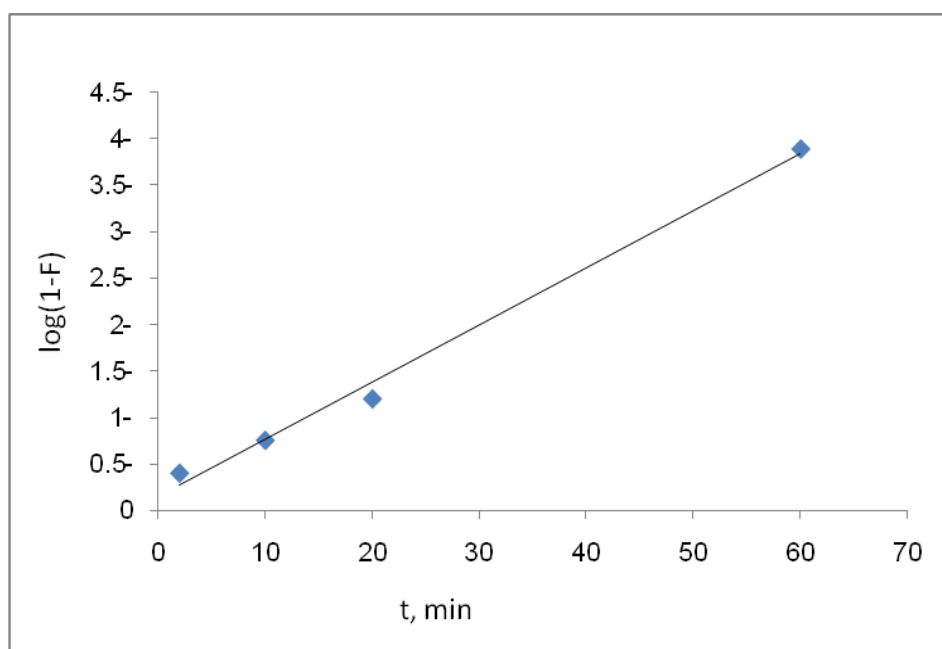


Fig. 5. Lagergren plotting for Mn^{2+} with β -Nap-PUF sorbent.

Moawed *et.al.* [15] have studied the sorption kinetics of β -Nap-PUF toward

Ni^{2+} , Cu^{2+} , Ag^+ , and Hg^{2+} . Their kinetic data were treated in accordance with a mass

action process, which assumes that the metal ions adsorbed on the foam in accordance with a first-order reaction (time-dependence), The results show that the rate constant for adsorption depends mainly on

the reaction between the metal ion and the chelating groups of β -Nap-PUF.

Table 2. Effect of shaking time on separation factor (α) and selectivity for adsorption of metals by β -Nap-PUF.

Shaking Time (min).	Separation factor (α) based on shaking time									
	Fe/Cu	Fe/Cr	Fe/Mn	Fe/Co	Cu/Cr	Cu/Mn	Cu/Co	Cr/Mn	Cr/Co	Mn/Co
2	1.1	3.8	1.9	1.2	3.3	1.7	1.1	0.5	0.3	0.6
10	1.0	3.2	1.5	1.3	3.1	1.4	1.2	0.5	0.4	0.9
20	1.0	2.5	1.3	1.2	2.4	1.3	1.2	0.5	0.5	1.0
40	1.0	1.2	1.5	1.3	1.2	1.5	1.3	1.2	1.1	0.9
60	1.0	1.1	1.3	1.3	1.1	1.3	1.3	1.2	1.2	1.0

Capacity of Sorbents

The sorption capacity is defined as the maximal amount of metal ion adsorbed per unit mass of sorbent. Adsorption capacity is an important factor to evaluate the sorbent, as it determines how much solid phase is required for a given solution. The pre-concentration and determination of the analyte is possible if the total load of the analyte is less than the sorption capacity.

An aliquot of 25 ml solutions containing excess concentration of metal ion were adjusted to the optimum pH and shaken for 1.0 h with 0.2 g modified PUF sorbents at room temperature. The total sorption capacity Q ($\mu\text{g g}^{-1}$) per gram of PUF was calculated from the following equation [16, 17]:

$$Q = \frac{(C_0 - C) \times V}{m}$$

where V the sample volume in liter, C_0 and C are the initial and remaining concentrations (mg.L^{-1}) of the metal ion respectively, and m is the weight of PUF in grams. The calculated capacities for three replicate measurements for each metal ion

at saturation of the PUF sorbents are listed in Table 3.

Experimental values of the capacity allow us to discuss the dependence of the chromatographic efficiency on both the properties of the stationary phase and the solutes to be separated and the experimental conditions.

The capacities shown in Table 3 were calculated in $\mu\text{g/g}$. This is useful for the analytical purposes but to explain the obvious difference in the capacity it is required to discuss the distribution of metal chelates on the sorbent surface, therefore the capacity has been calculated in $\mu\text{mol/g}$.

From the data listed in the above table we see the capacity for Mn^{2+} is more than other metal ions. The capacity sequence was in the order $\text{Mn}^{2+} > \text{Co}^{2+} > \text{Cr}^{3+} > \text{Fe}^{3+} > \text{Cu}^{2+}$. The variation in sorption capacities of the various metal ions probably arises due to the difference in their sizes, degree of hydration and binding constants with the chelating matrix [5].

Table 3. Total capacity of Cu^{2+} , Mn^{2+} , Co^{2+} , Fe^{3+} , and Cr^{3+} with β -Nap-PUF sorbent.

Capacity (Mean \pm S.D)					
Metal ion	Fe^{3+}	Cu^{2+}	Co^{2+}	Cr^{3+}	Mn^{2+}
$\mu\text{g g}^{-1}$	3696 ± 0.3	2120 ± 0.12	4250 ± 0.035	2290 ± 0.12	5640 ± 0.517
$\mu\text{mol g}^{-1}$	66	33.38	72.03	44.0	102.55

Precision of Method

In order to determine the precision of the applied procedure and its validity for applications in the analysis of real samples, the reproducibility test was examined.

Similar ten samples of 25 ml volume and concentration of 1 mg L^{-1} each element were stirred with 0.2 g foam sorbent for 1.0 h. The obtained data are in Figure 6.

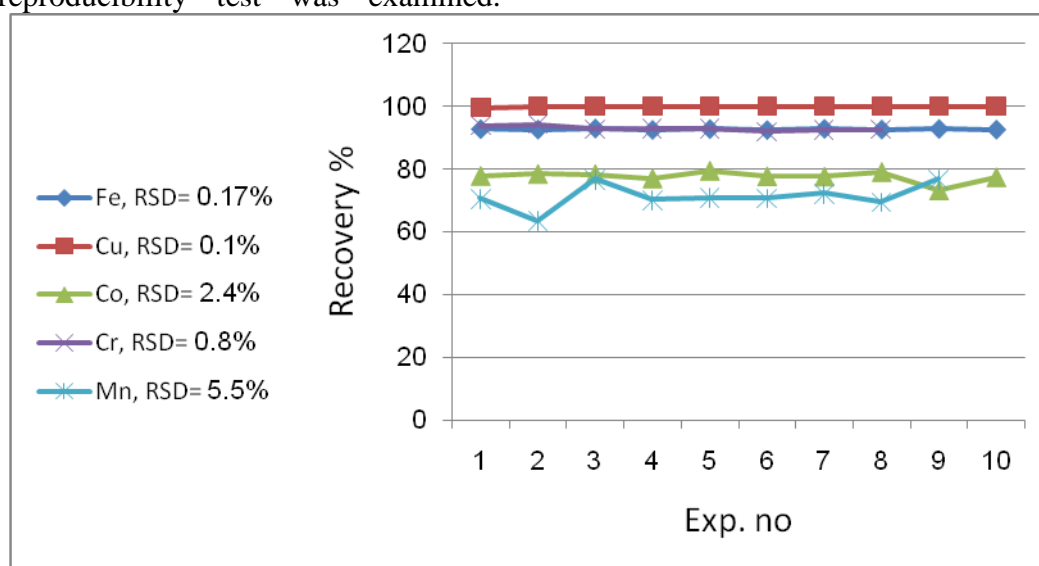


Fig. 6. Precision of the sorption capacity of β -Nap-PUF with Cu^{2+} , Mn^{2+} , Cr^{3+} , Co^{2+} and Fe^{3+} .

The relative error, expressed as RSD% doesn't exceed 5.5 % which confirm the possibility of using this method for determination of these metal ions in natural samples.

Interference Effect

Foreign ions in the sample solution can interfere with the solid phase extraction of metal complexes in a trace analysis because the ions may compete with analyte ions in the process of complex formation. The influence of presence of some anions and cations with different sizes, different charges and different abilities to form metal

complexes with β -Nap-PUF has been examined in order to know more about the sorbent behavior. Various salts and metal ions (sodium, potassium, magnesium, calcium, sulphate, and carbonate ions) are added individually to 25ml of solutions containing 1 mg L^{-1} Cu^{2+} , Mn^{2+} , Cr^{3+} , Co^{2+} and Fe^{3+} in different ratios (1:1), (1:10), (1:100) and (1:1000) and the general procedure was applied. In case of iron, there are no effect of interfering ions in the ratios (1:1, 1:10, 1:100), the exceptions are (1:10, 1:100) for Mg^{2+} ion. In the ratio (1:1000) all ions interfered with Fe ion, except K^+ and SO_4^{2-} ions.

All ions are interfere with the sorption of Cu ion into the β -Nap-PUF. In the case of Co^{2+} there was no significant change in presence of all ions in all cases at (1:1, 1:10, 1:100, 1:1000) ratios except (1:100, 1:000) for Mg^{2+} and CO_3^{2-} and (1:1000) for Ca^{2+} ions.

In the case of Cr^{3+} there was no significant change in presence of all ions in all cases at (1:1, 1:10, 1:100, 1:1000) ratios except in case of K^+ ion in all ratios and in ratio(1:10) for Mg^{2+} and Ca^{2+} . The great effect was coming from CO_3^{2-} ions (1:10,1:100, 1:1000).

Na^+ , K^+ , SO_4^{2-} ions do not effect adsorption of Mn^{2+} ion except (1:1000). Mg^{2+} and Ca^{2+} cause interference in all ratios except (1:1) for Mg^{2+} .

Conclusion

Development of the solid phase extraction sorbent and method are convenient, simple, and low coast. Different factors including, the pH of the sample solution and the shaking time were examined to optimize the conditions for the separation of these metal ions in aqueous solutions. The interference effects of the additional ions in the solution have been studied, metal ions of Mg^{2+} , Ca^{2+} , Na^+ , and K^+ , and anions, CO_3^{2-} , and SO_4^{2-} . Cu was affected by all the ions. Adsorption of the metal ions onto β -Nap-PUF was tested using the Morris-Weber equation. The straight line of the plot qt vs t in all cases, with low R^2 (0.767) in case of Mn, indicates the intra particle transport phenomena. The Lagergren equation was applied for mass action phenomenon. The plots of $\log(1-F)$ Vs. t for Mn, Cr, and Cu were straight with high R^2 0.99, 0.98, and 0.81 respectively, indicates that the mass action phenomenon can control the mechanism following the first order process. The capacity of the sorbent was also studied. The capacity sequence was

found to be in the order $\text{Mn}^{2+} > \text{Co}^{2+} > \text{Cr}^{3+} > \text{Fe}^{3+} > \text{Cu}^{2+}$.

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