A novel core@shell magnetic molecular imprinted nanoparticles for selective determination of folic acid in different food samples

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ABSTRACT

In this work, magnetic molecularly imprinted polymers (MMIPs) were synthesized and tested for the determination of folic acid (FA) in different food samples. The MMIPs were polymerized at the surface of $Fe_3O_4@SiO_2$ magnetic nanoparticles (MNPs) using acrylonitrile (functional monomer), ethylene glycol dimethacrylate (EGDMA) as cross-linking agent and azobiisobutyronitrile (AIBN) as an radical initiator. The morphological, topological and chemical characteristics of the MMIPs were investigated by field emission scanning electron microscopy (FESEM), high resolution transmission electron microscopy (HRTEM) and Fourier transform infrared (FTIR) techniques. The physico-chemical characterization, such as adsorption capacities and selectivity of MMIPs was investigated and compared with the respective MNIPs. The adsorption experimental data demonstrate that maximum adsorption capacity of MMIP at equilibrium was $8 \ mg \ g^{-1}$ and than the adsorption process of FA over MMIPs follows Freundlich adsorption isotherm model and pseudo-first-order reaction kinetic. For evaluation of this new proposed material, the recovery studies were carried out in spiked samples at different concentration levels and the obtained values were in the range of 95–104% for orange and for spinach the recoveries were between 99.5 and 102.5%. The relative standard deviations (RSD) for the recoveries were <0.5% for both samples. These results demonstrate that this novel MMIP material can be efficiently used for the selective extraction of folic acid from different food complex matrices.

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1. Introduction

Folic-acid (or folate) supplementation offers substantial and well-defined health benefits [1]. Numerous chronic diseases like gigantocytic anemia, leucopoenia, mentality devolution, psychosis; heart attack, malformation and neural tube defects during pregnancy are related due to the deficiency of folic acid (FA) [2]. Folic acid is found naturally in a wide variety of foods, including vegetables, fruits, poultry and meat [3]. It is necessary to monitor the quantity of FA in various food samples for their safety reasons. However, analysis of FA is not an easy task because of its presence in extremely lower concentration in biological systems, due to its lower stability under acidic conditions and its sensitiveness against light and high temperature [4]. Numerous methods have been used for the determination of FA including, spectro-photometry [5], flow injection chemiluminescence [6,7] fluorimetric [8], high-performance liquid chromatography (HPLC) [9,10], LC–MS [11,12], electrochemical [13,14] and capillary electrophoresis [15]. On the other hand microbiological assay of FA has widely been used, but it is lengthy, time consuming, need extreme care and skill for its analysis [16].

Among the chromatographic techniques the LC-MS is believed to be the most efficient [17,18]. However, methods those based on chromatography, involve complexes pre-treatment, pre-concentration and extraction procedures [19]. Some of these methods used to determine folates in biological fluids and foods, using solid phase extraction (SPE) [20] for the pre-treatment of the samples, in which the adsorbent material is the unspecified organic functionalized silica C8 or C18.

In addition there is also exist a most cost-effective procedure for FA analysis, which is based on the enzyme protein-binding assay [21], but although the measurement is not influenced by the matrix effect, the corresponding kits have short self-life, due to the biological material used in the detection.

In this sense, aim at more easy, rapid and efficient pre-treatment of complex samples, our research group have proposed the development of magnetic nanoparticles coated with MIPs for different analytes than can be used to separate and concentrate chemicals conveniently using a simple external magnetic field from a Neodimium magnet. Therefore, a combination of molecular imprinting technology would provide a powerful analytical tool with all desirables characteristics, besides being more selective than traditional silica adsorbent materials [22,

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23]. Thus, continuing the dissemination of the results of our research group, in this article we report the successful synthesis, characterization and application of a novel magnetic material based on magnetic nanoparticles coated with MIP selective to folic acid molecule.

2. Materials and methods

2.1. Reagents

Folic acid, $FeCl_2 \cdot 4H_2O$ (98%), $FeCl_3 \cdot 6H_2O$ (97%), tetraethoxysilane (TEOS), acrylonitrile (≥99%), [3(methacryloyloxy)propyl]trimethoxysilane (MPS), methylacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA), 2,2′-azobisisobutyronitrile (AIBN), were provided by Sigma-Aldrich. NH_4OH, NaOH and H_2SO_4 were obtained from Synth-Brazil. Acetonitrile (ACN), ethanol, methanol (HPLC grade) and acetic acid (glacial, 100%), were purchased from Panreac Quimica. All the reagents used without prior purification and solutions were prepared in deionized water (18 MΩ at 25 °C) obtained from Milli-Q Direct-0.3 (Millipore) purification system.

2.2. Preparation of magnetic nanoparticles (Fe_3O_4) and $Fe_3O_4@SiO_2$

Magnetic nanoparticles were prepared by co-precipitation method as described by Lu et al. [24] A known amount of both $FeCl_2 \cdot 4H_2O$ and

Fig. 2. Transmission electron microscopy (TEM) of magnetic molecular imprinted polymer (MMIP) for folic acid at two different scales.

$FeCl_3 \cdot 6H_2O$ were dissolved in 80 mL of water with vigorous stirring in nitrogen atmosphere. NH_4OH (10 mL) drop wise was added in the system and the reaction was maintained at 80 °C for 30 min. The black
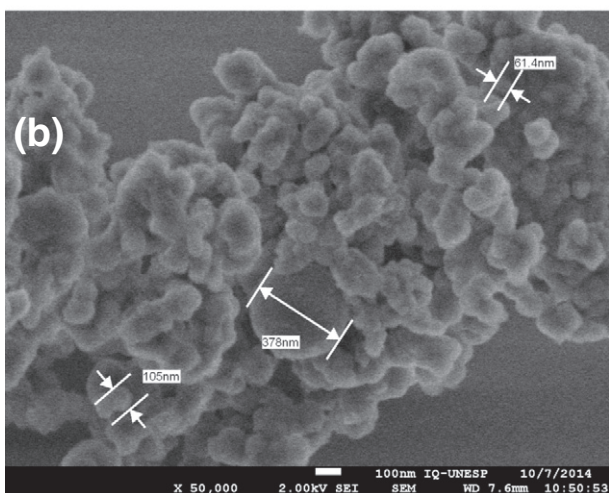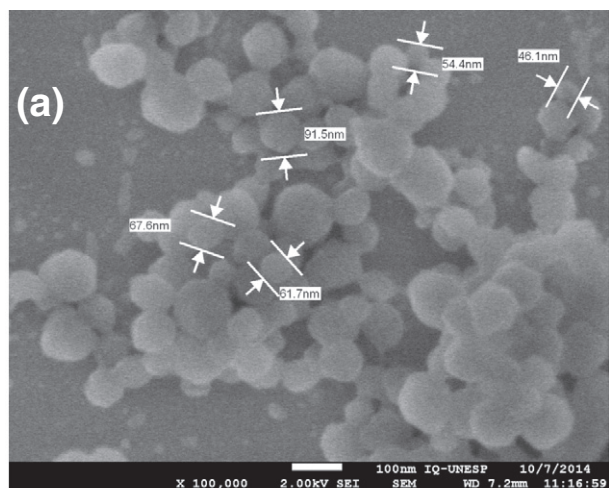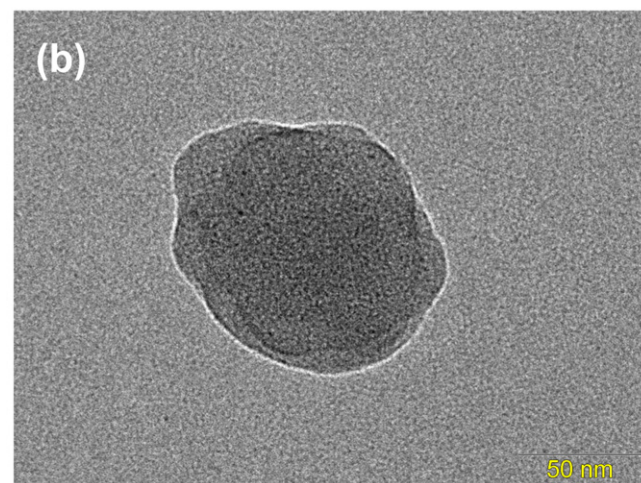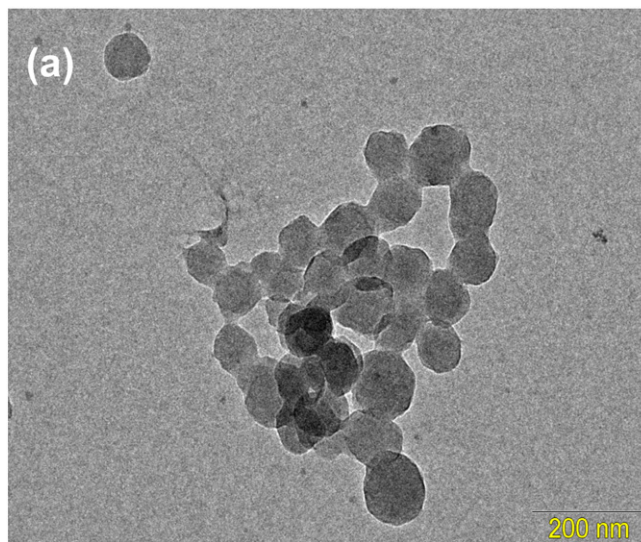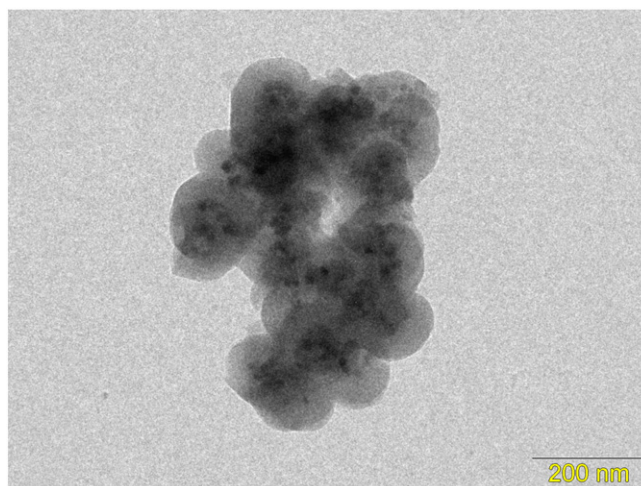

Fig. 1. Scanning electron microscopy images of MMIPs (a) and MNIPs, with their respective particles sizes.

Fig. 3. Transmission electron microscopy (TEM) of magnetic molecular non-imprinted polymer (MNIP).
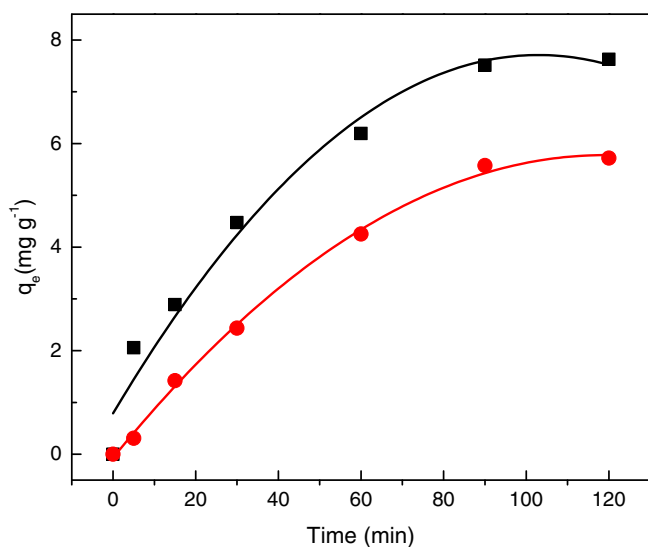
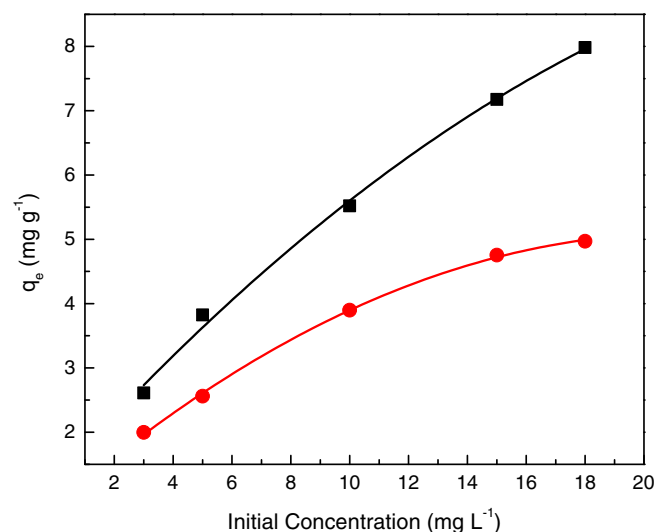**Fig. 4.** Binding capacity of folic acid vs time on to MMIPs (■) and MNIPs (•).

Fig. 5. Binding capacity of folic acid onto MMIPs (■) and MNIPs (•) at different initial concentrations (C_i).

precipitation of Fe_3O_4 nanoparticles was separated with a permanent magnet and washed thoroughly with deionized water to remove the unreacted chemicals, and then dried in the vacuum. 300 mg Fe_3O_4 nanoparticles were dispersed in 40 mL of ethanol (EtOH) and 4 mL of deionized water by ultra-sonication for 15 min and then followed by the addition of 5 mL of NH_4OH and 2 mL of tetraethoxysilane (TEOS). The mixture was left to react for 12 h at the room temperature. The products were collected by magnetic separation and was washed with deionized water three times and then dried in the vacuum. In the next step $Fe_3O_4@SiO_2$ nanoparticles were modified by 3-metacriloxipropiltrimetoxissilano (MPS) by taking 250 mg of the $Fe_3O_4@SiO_2$ nanoparticles was dispersed in 50 mL of anhydrous toluene containing 5 mL of 3-metacriloxipropiltrimetoxissilano (MPS) and the mixture was allowed to react for 12 h in dry nitrogen atmosphere. The obtained product was separated by an external magnet and dried in vacuum.

2.3. Preparation of MMIPs and MNIPs

MMIPs were prepared by polymerization of 0.2 mmol of folic acid (FA), 0.8 mmol of monomer (Acrylonitrile, Supplementary data) in ethanol (30 mL). The mixture was shaken in a water bath at 25 °C for 12 h, then 200 mg $Fe_3O_4@SiO_2$–C≡C were added into the reaction system and was shaken for more 3 h. Furthermore, 4.0 mmol of EGDMA and 0.05 mmol of AIBN were added into the system and the mixture was sonicated for 5 min in nitrogen atmosphere, and the reaction mixture was left at 60 °C under nitrogen gas protection for 24 h. After polymerization, the template molecule was leached out by Soxhlet extraction using methanol: acetic acid (9:1, v/v) as eluent, and the eluent was replaced every 12 h. The template (Folic acid) had been determined using HPLC in eluent at the interval of 12 h. After complete removal of template molecule the products (MMIPs) were dried at 40 °C under

vacuum. Similarly magnetic non-molecular imprinted polymers (MNIPs) were prepared under the same conditions as described above without analyte.

2.4. Folic acid solution and food samples

A stock solution of FA (pH 6.5) was prepared by dissolving 10 mg FA in 100 mL of deionized water with a few drops of 0.1 mol L^{-1} NaOH, the prepared solution stored in a dark flask and kept in a refrigerator to prevent degradation. All working solutions of FA were prepared daily by appropriate dilution and the pH was adjusted to 6.5 with the help of 0.1 mol L^{-1} NaOH.

The spinach, and orange were purchased from a local supermarket in Araraquara in the state of São Paulo - Brazil. The spinach samples were prepared as previously described [25]. A 50.0 g of real sample (spinach) was cut into small pieces using a razor blade, and was boiled with water under reflux for 50 min. The mixture was cooled and filtered through a membrane filter. A suitable aliquot of the filtrate was used to determine folic acid. The orange juice was obtained by squeezing fresh orange by manual orange juice extractor. The orange juice was first filtered using semi-analytical whatman paper, after this it was filtered using Millipore membrane of 0.45 mm and the filtrate was stored in refrigerator for using it in further analysis [26].

2.5. Binding and selective adsorption experiments

To evaluate the binding capacity of prepared MMIPs and MNIPs adsorption tests were carried out, by adding 10 mg of MMIPs and MNIPs in a separated 20 mL glass vial and adds 10.0 mL of 10 mg L^{-1} of the folic acid solutions. The mixture was shaken in a rotating shaker for 120 min and after being shaken the magnetic polymer suspensions were separated by magnetic bar and filtered with a 0.45 μm membrane for HPLC

Table 1
The rate constant and binding capacity for the sorption of ametryne.

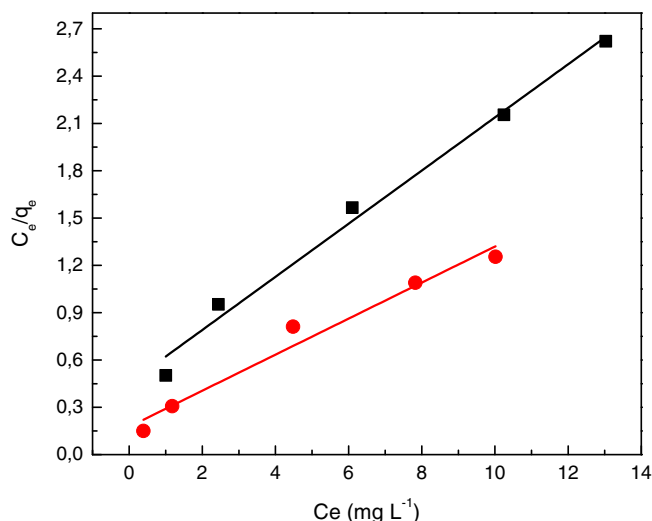|	Pseudo first order kinetic model			Pseudo second order kinetic model		
Sorbents	q_e (mg g^{-1})	R^2	k_1 (mg g^{-1} min^{-1})	q_e (mg g^{-1})	R^2	k_2 (mg g^{-1} min^{-1})
MIP	7.510	0.9936	0.0252	9.432	0.9756	0.00379
NIP	5.575	0.9902	0.0236	10.20	0.9506	0.00133

Fig. 6. Langmuir model fit for the adsorption of folic acid onto MMIPs (■) and MNIPs (•) material.

analysis. The binding capacity is calculated using by the Eqs. (1) and (2) [27,28].

$$Q_t = \frac{(C_o - C_e)\,V}{m} \tag{1}$$

$$Q_e = \frac{(C_t - C_e)\,V}{m} \tag{2}$$

Q_t (mg g^{-1}) is the experimental adsorption quantity at time t, Q_e (mg g^{-1}) equilibrium adsorption quantity, C_o (mg L^{-1}) is the initial concentration of FA, Ce (mg L^{-1}) is the equilibrium concentration, Ct is the final concentrations (mg L^{-1}), V (mL) is the volume of FA solution and m (g) is the weight of MMIPs and MNIPs. All the experiments were performed in triplicate.

2.6. Instruments and analytical methods of analysis

The chromatographic analyses were performed using a Shimadzu Model 20A liquid chromatograph, coupled to an SPD-20A UV/Vis detector, a SIL-20A autosampler and a DGU-20A5 degasser. The chromatography system was controlled by a microcomputer and the C18 column (250 mm × 4.6 m) was used in the analysis. The chromatographic conditions used were, mobile phase composed of a mixture of acetinitonitryle:water (90:10, v/v), flow rate of 1.0 mL min^{-1}, sample injection volume of 20 μL and wavelength of 280 nm for folic acid detection.

FTIR–VERTEX 70 spectrometer (BRUKER) with spectral range of 4000 to 370 cm^{-1} and a detector of DLaTGS was employed to examine the FTIR spectra of mag-MIPs and Mag-NIPs.

The size and surface morphology of nanoparticle samples were analyzed using field emission gun scanning electron microscope (FEG-SEM; JEOL model 7500F) (Germany) GmbH. TEM analysis were performed

using high resolution transmission electron microscope HR-TEM (Philips- model CM200 supertwin with resolution of 1.9 A.

3. Result and discussion

3.1. Morphologic characterization

The structures of MMIPs and MNIPS were well characterized by Field Emission Scanning electron microscopy (FESEM) and high-resolution transmission electron microscope (HRTEM). It could be seen from the Fig. 1 that the MMIPs were all spherical shape and the size of the particles was in the range of 50–100 nm (Fig. 1a). However, in Fig. 1b, corresponding to MNIP could be observed irregular spheres with a high degree of agglomeration and a roughness in the surface.

The TEM analysis further reveals that magnetic-nanoparticles were of spherical shape with approximately 100 nm in diameter, such suggest for the SEM images. It is evident in Fig. 2b than the core-shell structure of MMIPs was successfully constructed, since the double circle of microsphere indicates that in fact was obtained a core-shell particle of Fe$_3$O$_4$@MIP (MMIP), in wich can be clearly seen the SiO$_2$-MIP shell uniformly coating the Fe$_3$O$_4$ dark core, which for their small size was very helpful for more recognition sites and higher adsorption capacity of the template molecule, due to the high active area.

On the other hand, TEM images of MNIPs show aggregates of the nanoparticles (Fig. 3) from which it can be clearly distinguished a relatively large mesosphere of aggregates of fine particles with sizes c.a. 200 nm, which also confirms the SEM results.

3.2. Effect of contact time on the adsorption of folic acid onto MMIPs and MNIPs

The effect of contact time on the adsorption of FA was studied. As shown in Fig. 4 the adsorption increases with time, and was rapid in the initial 60 min and then continued slowly. The 90 min was taken as equilibrium time. Initially a large numbers of active sites are expected to be available on the surface of MMIPs and MNIPs. As the adsorption progresses the sites become saturated and rate of adsorption decreased and get covered and there is no free space is available to the adsorbate molecules. The initial rapid uptake of (upto 60 min) FA from solution was likely due to more exposed binding sites and the slow sorption phase likely resulted from more internal binding sites. Due to high surface area of MMIPs shows maximum adsorption than MNIPs for the FA.

3.3. Adsorption kinetics

In order to investigate the kinetics of adsorption of FA on MMIPs and MNIPs, the pseudo-first-order and pseudo-second-order equations [29] were applied. The pseudo-first-order expression is given by Eq. (3).

$$\log(q_e - q_t) = -\frac{k_1 t}{2.303} + \log q_e \tag{3}$$

Where q_e is the amount of adsorption of FA (mg g^{-1}) adsorbed at equilibrium and at time qt (minutes) respectively. k_1 is overall rate constant. Straight lines were obtained by plotting $\log(q_e - q_t)$ against t, as shown in Fig. S2. The values of rate constant k_1 were calculated from the slopes of straight lines of Fig. S2 and the values are reported in Table 1.

Table 2
Data obtained used the Langmuir and Freundlich isotherm models applied in our experimental results.

Langmuir isotherm equation				Freundlich isotherm equation		
Sorbents	q_e (mg g^{-1})*	R^2	K_1 (L mg^{-1})	R^2	1/n	K (mg g^{-1}) (L mg^{-1})$^{1/n}$
MIP	8.757	0.9639	0.646	0.9910	0.3357	3.557
NIP	5.938	0.9861	0.380	0.9886	0.3738	1.940

* q_e (mg g^{-1}) is calculated from Langmuir isotherm equation (Eq. 5).
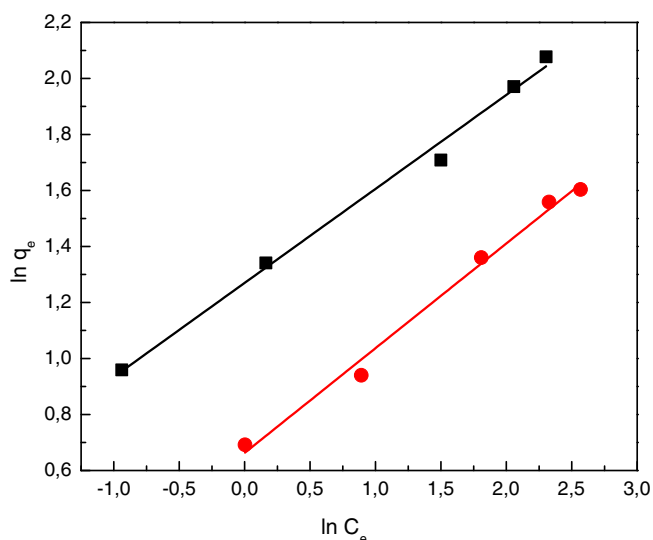
Fig. 7. Freundlidch model fit for the adsorption of folic acid onto MMIPs (■) and MNIPs (•) materials.

The pseudo-second order kinetics model in Eq. (4).

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e^2} + \frac{1}{q_e}\, t \tag{4}$$

where q_e is the maximum adsorption capacity $(mol\ g^{-1})$ for the pseudo-second-order adsorption, q_t the amount of the FA adsorbed at time t $(mol\ g^{-1})$, k_2 the equilibrium rate constant of pseudo-second-order adsorption $(mg\ g^{-1}\ min^{-1})$. The values of k_2 and q_e were calculated from the plot of t/q_t against t (Fig. S3). The calculated q_e values agree with experimental q_e values, and also, the correlation coefficients (R^2) for the pseudo-first-order kinetic plots at all the studied concentrations were above 0.9936 for MMIPs and 0.9902 for MNIPs (Table 1). These results imply that the adsorption system studied obeys to the pseudo-first-order-kinetic model.

3.4. Study of the folic acid onto MMIPs and MNIPs by adsorption isotherms

In order to study the effect of the FA adsorption in the MMIP and their corresponding MNIP, experiments were conducted at a fixed adsorbent dosage of 10 mg at different initial concentration (C_i). The results obtained from these experiments are given in Fig. 5 in which possible to observe that the adsorption increases as the FA concentration increases which mainly due to the availability of large number of site over the surface at certain level and after that the sorption capacity slightly decreases because the adsorption site become saturated with FA molecules. It's also obvious that quantity adsorbed by MMIP was more than the MNIP, which proposed that imprinted sites molded due to the reaction of imprinting and crosslinking. This also demonstrates

Table 3
Recovery results obtained for the analysis of folic acid collected from the supermarkets of the city of Araraquara-SP.

FA add (mg L^{-1})	Orange juice FA found	Recovery (%)	Spinach FA found	Recovery (%)
0	0.15 ± 0.05	–	0.09 ± 0.03	–
2	1.90 ± 0.03	95.0	2.05 ± 0.04	102.5
4	4.10 ± 0.11	102.5	4.07 ± 0.06	101.8
6	6.13 ± 0.17	102.2	6.10 ± 0.02	101.7
8	8.33 ± 0.20	104.1	7.96 ± 0.06	99.5
10	9.55 ± 0.36	95.6	10.1 ± 0.1	101.1
12	11.96 ± 0.41	99.7	12.1 ± 0.1	101.1

that initial FA concentration plays an important role in the adsorption process.

Since the determination of adsorption isotherm is important in designing the nature of adsorption system, two widely used isotherm models have been applied. The data were evaluated by applying the Langmuir (5) and Freundlich (6) isotherms.

For the Langmuir model was used the Eq. (5) follow:

$$\frac{C_e}{q_e} = \frac{1}{K_1 X_m} + \frac{C_e}{X_m} \tag{5}$$

where C_e is the equilibrium concentration of FA $(mg\ L^{-1})$, q_e is the amount $(mg\ g^{-1})$ of FA adsorbed; X_m $(mg\ g^{-1})$ is adsorption capacity (amount od adsorbate adsorbed per unit mass of the FA) and K_1 is Langmuir constants, representing the adsorption capacity $(mg\ g^{-1})$ respectively [30] [31].

Straight lines were obtained by plotting C_e/q_e against C_e as shown in Fig. 6 the linear plots indicate the applicability of Langmuir adsorption isotherm, consequently the formation of monolayer surface of the adsorbate on the surface of the adsorbent. Langmuir constant k_1 and X_m maximum adsorption capacity were calculated from the slopes and intercepts of plots and are given in Table 2.

The Freundlich isotherm is an empirical equation employed to describe the heterogeneous system. The linear form of Freundlich isotherm was also applied to the adsorption of FA.

$$\ln \frac{x}{m} = \ln K + \frac{1}{n}\ln C_e \tag{6}$$

where K $(mol\ g^{-1})$ and $1/n$ $(g\ L^{-1})$ are Freundlich constants, indicating the adsorption capacity and adsorption intensity respectively. x/m adsorption per gram of adsorbent which is obtained by dividing the amount of adsorbate (x) by the weight of the adsorbent (m). Straight lines were obtained by plotting $\ln x/m$ against $\ln C_e$ and K and $1/n$ were calculated from the slope and intercept of these lines (Fig. 7). The values of Freundlich constants are given in Table 2 For favorable adsorption, the value of $1/n$ is smaller than 1 and when the unfavorable adsorption takes place, the adsorption bond becomes weak and the value of $1/n$ is >1, so adsorption decreases. As shown in Table 2 that the value of $1/n$ for FA adsorption is less than unity, which shows high adsorption intensity. The correlation coefficient is more close to 1 for the Freundlich isotherm that indicates good agreement with experimental data and isotherm parameters, however it is important to emphasize that the MAC value obtained by the Langmuir isotherm $(8.757\ mg\ g^{-1})$ is very close that experimental value of Fig. 5 $(8.1\ mg\ g^{-1})$ indicating that this adjustment despite not being the best is also valid.

3.5. Application of the material

In order to applied the material to the samples, MMIPs was used as a adsorbent material used 10 mg of MMIP on a SPE system. For this, 100.0 mL of the filtrate of orange or spinach were spiked with 2–12 mg L^{-1} of FA solution and passed through the packed-bed column at 1 mL min^{-1} flow rate. After preconcentration step, the MMIPs retained on the column was eluted with 10 mL of CH$_3$OH at 0.5 mL min^{-1} flow rate followed by injection of eluent in the HPLC system. As it is observed that preconcentration procedure enhances the chromatographic peak of MMIPs and promotes a cleanup of the sample. The recovery values were obtained in the range of 95–104% for orange samples and for spinach sample good recovery were obtained in the range of 99.5–102.5. The recoveries obtained are shown in the Table 3. This excellent results can be attributed to than in the MMIP the imprinted sites are situated on the surface of imprinting materials and this property allows them have a higher sorption ability. In addition the magnetic property allows will perform the steps of pre-

concentration and extraction of the analyte from complex samples in a more simple way, since the inherent characteristics of the magnetic particle in separations will be used.

4. Conclusions

The MMIPs and MNIPs using Folic acid as template prepared under the same surface imprinting conditions which showed fast adsorption kinetics and selective recognition affinity in aqueous solution of folic acid. The surface molecularly imprinted magnetic microspheres possessed rapid dynamic adsorption, high adsorption ability and suitable repeatability. The percentage recovery for orange juice were obtained from 95.00 to 104.10 while for Spinach samples were obtained in the range of 99.50 to 102.50. The presented MMIPs extraction method had the characters of simplicity, rapidity and selectivity, while the application of this method provided a new promising alternative for simultaneous removal of folic acids in food matrices.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.reactfunctpolym.2016.07.011.

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