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This is the author's submitted version of the contribution published as:

Original

Removal of sulfanilamide by tailor-made magnetic metal-ceramic nanocomposite adsorbents / Sannino, Filomena; Pansini, Michele; Marocco, Antonello; Cinquegrana, Alessia; Esposito, Serena; Tammaro, Olimpia; Barrera, Gabriele; Tiberto, Paola; Allia, Paolo; Pirozzi, Domenico. - In: JOURNAL OF ENVIRONMENTAL MANAGEMENT. - ISSN 0301-4797. - 310:(2022), p. 114701. [10.1016/j.jenvman.2022.114701]

Availability:

This version is available at: 11696/75947 since: 2023-06-28T14:59:00Z

Publisher:

ACADEMIC PRESS LTD- ELSEVIER SCIENCE LTD

Published

DOI:10.1016/j.jenvman.2022.114701

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(Article begins on next page)

Journal of Environmental Management

Removal of sulfanilamide by tailor-made magnetic metal-ceramic nanocomposite adsorbents

--Manuscript Draft--

Manuscript Number:	JEMA-D-21-08739
Article Type:	Research Article
Keywords:	wastewater remediation antibiotic removal magnetic metal-ceramic nanocomposites thermal regeneration
Abstract:	<p>Three tailor-made magnetic metal-ceramic nanocomposites, obtained from zeolite A and a natural clinoptilolite, have been used as adsorbents to remove sulfanilamide (SA), a sulfonamide antibiotic of common use, from water. A patented process for the synthesis of nanocomposites has been suitably modified to maximize the efficiency of the sulfanilamide removal, as well as to extend the applicability of the materials.</p> <p>The role played by the main process parameters (kinetic, pH, initial concentration of SA) has been characterized. The SA removal was strongly affected by pH suggesting the adsorption mechanism to be based on an acid-base reactions.</p> <p>The adsorption kinetics were in all cases described by the pseudo second-order model. The adsorption isotherms data were satisfactorily described by the Langmuir and Freundlich model, suggesting that the monolayer adsorption of sulfanilamide on the magnetic nanocomposites results from a uniform surface energy.</p> <p>On the basis of the TG and DTA characterization of SA, an effective procedure for the thermal regeneration of the exhausted adsorbent was developed, ensuring an effective removal of the antibiotic and a proper recycle of the magnetic adsorbents.</p>

REMOVAL OF SULFANILAMIDE BY TAILOR-MADE MAGNETIC METAL-CERAMIC NANOCOMPOSITE ADSORBENTS

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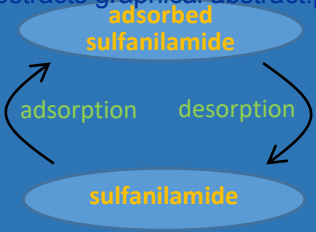
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Graphical Abstracts

- Cation exchange
- Thermal treatment under reducing atmosphere



**Tailor-made
magnetic
nanocomposite**



- Thermal treatment

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Highlights

- Three tailor-made magnetic metal-ceramic nanocomposites were obtained from zeolites
- The adsorption by magnetic adsorbents was affected by acid-base reactions
- A thermal regeneration treatment of the adsorbent was developed
- The magnetic adsorbents could be easily separated and regenerated

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Abstract

Three tailor-made magnetic metal-ceramic nanocomposites, obtained from zeolite A and a natural clinoptilolite, have been used as adsorbents to remove sulfanilamide (SA), a sulfonamide antibiotic of common use, from water.

A patented process for the synthesis of nanocomposites has been suitably modified to maximize the efficiency of the sulfanilamide removal, as well as to extend the applicability of the materials.

The role played by the main process parameters (kinetic, pH, initial concentration of SA) has been characterized. The SA removal was strongly affected by pH suggesting the adsorption mechanism to be based on an acid-base reactions.

The adsorption kinetics were in all cases described by the pseudo second-order model. The adsorption isotherms data were satisfactorily described by the Langmuir and Freundlich model, suggesting that the monolayer adsorption of sulfanilamide on the magnetic nanocomposites results from an uniform surface energy.

On the basis of the TG and DTA characterization of SA, an effective procedure for the thermal regeneration of the exhausted adsorbent was developed, ensuring an effective removal of the antibiotic and a proper recycle of the magnetic adsorbents.

Key words: magnetic metal ceramic nanocomposites, antibiotic removal, thermal regeneration

1. Introduction

Sulfonamides (sulfa drugs, SAs) are synthetic antibiotics able to inhibit both gram-positive and gram-negative bacteria. They are systematically used to treat/prevent bacterial infections (van Mil, 2011). In particular, sulfonamides antibiotics (SAs) are commonly used in human therapy, livestock production and aquaculture due to their low cost and good effect (Dibner and Richards, 2005; Neu and Gootz, 1996).

Unfortunately, the spread of sulfonamides has led to the increase of human allergies and drug-resistance bacteria. They can also deteriorate the quality of drinking water and may cause potential hazard (carcinogenicity, teratogenicity and mutagenicity) (Qin et al., 2020). Recently, antibiotics have been detected in natural waters at concentration levels going from ng/L to µg/L (Sabri et al., 2020; Zhou et al., 2019; Conde-Cid et al., 2021; Dekhi-Bemani et al., 2021). For this reason they have been declared as priority substances in water protection policies (Directive 2013/39/EU),

Several technologies have been developed to remove these contaminants such as coagulation, sedimentation, advanced oxidation processes, filtration, membrane technologies, and biological treatments (Ortiz et al., 2015; Kassinos et al., 2011; Pirozzi et al., 2020; Sannino et al., 2014; Sannino et al., 2015). However, most of these processes imply the transfer of the pollutants between different fluid phases, use of additional chemicals or high amounts of energy during the process and generate wastes and byproducts that have to be disposed in subsequent steps. Adsorption is considered an excellent method for treating wastewater containing low concentration of antibiotics on account of its high efficiency, intrinsic simplicity, antitoxic nature and low cost (Srivastava et al., 2009; De Gisi et al., 2016; Sannino et al., 2013a; Addorisio et al., 2011).

A point of weakness of the adsorption procedures, still limiting their full application, stems from the difficult separation of the exhausted adsorbent from water. This consideration suggested us to develop magnetic metal-ceramic nano-composites as adsorbents, that could be easily separated from the aqueous phase by the action of an external magnetic field.

In this view, tailor-made nano-composites have been produced starting from a zeolite precursor, to exploit the peculiar properties of zeolites, such as high cation exchange capacity, swelling, and wide availability. Zeolites have been already used to remove SAs from wastewater (Blasioli et al., 2014).

In order to obtain these magnetic nano-composite adsorbents, a patented process (Esposito et al., 2014, 2015; Marocco et al., 2012; Ronchetti et al., 2010; Esposito et al., 2018) has been suitably modified. According to it, commercial zeolites (precursors) have been exchanged with Fe²⁺ ions.



1 Subsequently, the heavy-metal cation-exchanged zeolites have been thermally treated at relatively
2 moderate temperatures (500-850 °C), under a reducing atmosphere.

3 During such thermal treatments, a nanocomposite formed by a dispersion of metallic Fe
4 nanoparticles in a mainly amorphous silica and alumina matrix was obtained, showing physico-
5 chemical properties markedly different from those of the parent zeolite. Yet, the nanocomposite
6 exhibited a residual porosity (Esposito et al., 2018), which is a remnant of the parent zeolite
7 structure, that may have an impact on its applications as adsorbent. The magnetic properties of the
8 nanocomposite were confirmed in a number of studies (Barrera et al., 2018, 2019, 2020).
9

10 The process has the characteristics of a scalable method, as it implies an ionic exchange and a
11 thermal treatment under gas flow. These nanocomposites have so far been tested in the separation of
12 DNA from crude cell lysate (Pansini et al., 2017) and from human blood (Esposito et al., 2020), the
13 removal of agrochemicals from water (Pansini et al., 2018; Marocco et al., 2020) and as moon dust
14 simulant (Freyria et al., 2019; Manzoli et al., 2021), showing a large potential for further
15 applications.
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17 In order to maximize the efficiency of the sulfanilamide removal from water, the zeolite A
18 and a natural clinoptilolite contained in a widespread rock (Sardinian Epiclastite) from Northern
19 Sardinia have been selected as starting materials. In particular, the choice of A zeolites has been
20 dictated by their high cation exchange capacity, due to their Si/Al ratio = 1.00. These zeolites have
21 been chosen also on the basis of their large availability with consequent low cost and on the basis of
22 the knowledge of their features.
23

24 Zeolite A and clinoptilolite have already been used used in several industrial applications
25 (Colella et al., 1998; Pansini and Colella, 1990; Albino et al., 1995; Colella and Pansini, 1988;
26 Cioffi et al., 1996, Pansini et al., 2010; de' Gennaro et al., 2008, Basile et al., 1992).
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28 Three different magnetic metal-ceramic nanocomposites have been produced. The aim of this
29 study is: i) to evaluate the ability of the magnetic nanocomposites in the removal of Sulfanilamide
30 antibiotic (SA) from waters by adsorption, investigating the role played by the main process
31 parameters (solid/liquid ratio, pH, time, initial concentration of SA); ii) to set up a proper
32 regeneration procedure of the exhausted adsorbent, ensuring a depletion of the antibiotic.
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34 2. Materials and methods

35 2.1. Materials

1 Reagent grade p-aminobenzenesulfonamide (Sulfanilamide, Scheme 1) (>99.0% purity) was
2 from Sigma-Aldrich Chemical Company. The solvents for analytical determinations were Carlo
3 Erba HPLC grade. Ultrapure water was used for all the experiments performed. Zeolite A
4 (framework code LTA (Sannino et al., 2012), $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}\cdot 27\text{H}_2\text{O}$) in its original Na form was
5 from Sigma-Aldrich Chemical Company.
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10 2.2. Preparation and characterization of materials

11 Magnetic adsorbents were prepared starting from the following raw materials:

- 12 1) Zeolite A (framework code LTA (Sannino et al., 2012), $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}\cdot 27\text{H}_2\text{O}$) in its original
13 Na form was from Sigma-Aldrich Chemical Company (the grain size distribution is reported in
14 Cappelletti et al., 2011).
- 15 2) A clinoptilolite bearing rock from Northern Sardinia (Italy) fully characterised in a previous
16 work (Manzoli et al., 2021).

17 Three different samples of magnetic metal-ceramic nanocomposites were prepared and
18 labeled, for the sake of uniformity with previous works, as follows: (Fe,H)A800C-0min,
19 (Fe,H)A600C-90min, and SMA_LacBen. These samples were produced by subjecting to Fe^{2+}
20 exchange procedures the relevant zeolites and by subjecting the Fe-exchanged zeolites to the proper
21 thermal treatment under a reducing atmosphere, according to refs. (Freyria et al., 2019; Breck,
22 1974). The chemical composition, quantitative phase determination, and the various
23 characterization (SEM, TEM, textural, magnetic) are reported in refs. (Pansini et al., 2018; Freyria
24 et al., 2019). In Table 1 the principal chemical-physical properties of the (Fe,H)A800C-0min,
25 (Fe,H)A600C-90min, and SMA_LacBen are reported.

26 Scanning electron microscopy (SEM) observations of samples (Fe,H)A800C-0min,
27 (Fe,H)A600C-90min, and SMA_LacBen were carried out on a FE-SEM Ultra Plus (Zeiss, GmbH)
28 microscope at 20 kV (Pansini et al., 2018).

29 SA was subjected to simultaneous differential thermal analysis (DTA) and thermogravimetric
30 analysis (TG) under inert atmosphere (N_2), using a Perkin-Elmer thermo-analyzer STA 6000, with
31 Al_2O_3 as reference material. The TG and DTA tests were performed keeping 9.45 mg of SA under
32 nitrogen atmosphere, varying the temperature from 30 to 1000 °C. A heating rate of 10 °C min^{-1}
33 was adopted.

34 2.3. Analytical determination

1 SA concentration in solution was analyzed with an Agilent 1200 Series HPLC apparatus
2 (Wilmington U.S.A.), equipped with a DAD array and a Chem Station Agilent Software. A
3 Macharey-Nagel Nucleosil 100-5 C18 column (stainless steel 250 × 4 mm) was utilized. The
4 mobile phase, a binary system of 80:20 acetonitrile: phosphate buffer (0.1% pH 2.70), was pumped
5 at 1 mL min⁻¹ flow in an isocratic mode. The detector was set at 224 nm and injection volume was
6 20 μL. The quantitative determination of the antibiotic was performed using a calibration curve
7 between 1.0–1163 μmol/L.
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10 11 12 13 14 2.4. Adsorption experiments 15 16

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18 100 mg of SA were dissolved in 500 mL of ultrapure water. The resulting 200 mg/L
19 (corresponding to 1163 μmol/L) solution was kept refrigerated and used to prepare all solutions
20 tested within this work. Batch experiments of SA removal from waters by adsorption on
21 (Fe,H)A800C–0 min, (Fe,H)A600C–90 min, and SMA_LacBen were performed. Aqueous
22 solutions of SA were contacted with magnetic nanocomposites in glass vials with Teflon caps at 25
23 °C; the vessels were continuously stirred in an orbital shaker at 150 rpm until steady state
24 conditions were approximated, which took about 24 h. Finally, the magnetic adsorbents were
25 separated from the liquid using an external magnet (VA03, UNIDISP s.r.l. Italy) and the liquid was
26 analysed to evaluate SA concentration, using HPLC analysis. The amount of SA adsorbed was
27 calculated as the difference between its initial and final concentration in solution. Blanks of SA in
28 ultrapure water were analysed in order to evaluate SA stability and sorption on vials. The following
29 experimental factors were evaluated:
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40 (a) Effect of pH: Magnetic nanocomposites samples, (Fe,H)A800C–0 min, (Fe,H)A600C–90
41 min and SMA_LacBen were contacted with 40.0 μmol/L SA solution at solid/liquid ratio (S/L) =
42 1/10,000 g/g for 24 h (this time was shown to be sufficient to attain a steady state). The pH of this
43 solution varied between 2.0 and 8.0, in steps of 0.5, by adding the proper amount of 0.01 or 0.10
44 mmol/L HCl or NaOH aqueous solution.
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49 (b) Adsorption kinetics: Kinetic studies were performed by contacting the SMA_LacBen
50 adsorbent with 40.0 and 126 μmol/L SA solution, at solid/liquid ratio S/L = 1/10,000 g/g at pH 4.0
51 As regard the (Fe,H)A800C–0 min sample, kinetic tests were carried out with 40.0 μmol/L SA
52 solution, at S/L = 1/10,000 g/g at pH 6.0. The suspensions were stirred for 10, 30, 60, 120, 240,
53 360, 900 and 1440 min and successively subjected to the separation procedure described.
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58 (c) Sorption isotherm: Magnetic adsorbents (Fe,H)A800C–0 min and SMA_LacBen were
59 contacted with solutions having SA concentration up to 1163 μmol/L at S/L = 1/10000 g/g, T = 25
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1 °C and pH = 6.0 or 4.0, respectively, for 24 h. The pH of each suspension was kept constant by
2 adding proper amounts of 0.01 or 0.10 mmol/L HCl or NaOH solution.
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5 3. Results and Discussion 6

7 8 9 3.1. Textural and morphological characterization of (Fe,H)A800C–0min, (Fe,H)A600C–90min 10 and SMA_LacBen 11

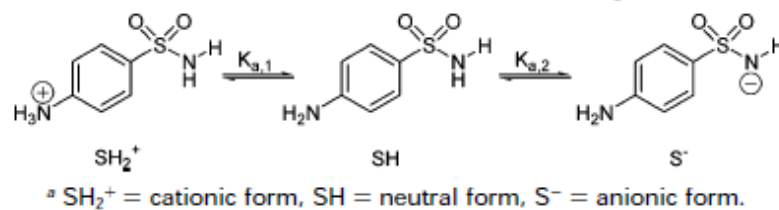
12 Table 1 reports the quantitative phase determinations, textural and main magnetic properties
13 of the magnetic adsorbents (Fe,H)A800C–0min, (Fe,H)A600C–90min and SMA_LacBen. The
14 magnetic adsorbents are formed by nanoparticles (5-30 nm) of ferromagnetic materials (Fe⁰ and
15 Fe₃O₄) dispersed in a prevailing amorphous ceramic phase. This phase originated from the
16 thermal collapse of the microporous zeolite structure. Such collapse is fully confirmed by the
17 textural data. Magnetic properties of the various adsorbents were demonstrated to be sufficient to
18 perform the separation of the solid adsorbent from the liquid (Esposito et al., 2020; Pansini et al.,
19 2018; Freyria et al., 2019) by using a commercial external magnet. The compositional,
20 morphologic, textural and magnetic features of the magnetic adsorbents were discussed in detail
21 elsewhere (Pansini et al., 2018; Freyria et al., 2019) (Figure 1).
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31 32 3.2. Effect of pH 33 34 35

36 The Figure 2 reports the amount of SA adsorbed on (Fe,H)A800C–0min, (Fe,H)A600C–
37 90min and SMA_LacBen magnetic adsorbents at S/L ratio = 1/10,000 after a contact of 24 h, as a
38 function of pH. Sulfanilamide uptake from water by the all the magnetic adsorbents tested strongly
39 depends on pH: actually a sharp maximum is recorded at pH 6.0, 7.0 and 4.0 for (Fe,H)A800C–
40 0min, (Fe,H)A600C–90min and SMA_LacBen, respectively, and small deviations from this value
41 result in a marked sulfanilamide sulphonamide adsorption decrease.
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47 This observation suggests that sulfanilamide uptake by the various adsorbents is an acid-base
48 reaction, similar to simazine uptake from water by zeolite H-Y or porous silica (Sannino et al.,
49 2012; Marocco et al., 2011; Sannino et al., 2013b; Esposito et al., 2013).
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52 The effect of medium pH on the antibiotic adsorption can be explained taking into account
53 that sulfanilamide, similarly to other sulfa drugs, undergo two acid-base processes (Boreen et al.,
54 2004; Fukahori et al., 2013), due to the protonation and the deprotonation of the amino and
55 sulfonamide groups as shown in the following scheme:
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The protonation state is therefore described by two values of pK (Braschi et al., 2013; Uhlemann et al, 2021):

$$\text{pK}_1 = 1.78$$

$$\text{pK}_2 = 10.6$$

As a consequence, in the range of pH 4.0-7.0 most of sulfanilamide molecules are in their neutral form. This suggests that the adsorption of sulfanilamide on all the adsorbents tested is based on hydrophobic interactions between neutral sulfanilamide and hydrophobic silica surfaces, as already found in previous works (Fukahori et al., 2013).

Such acid-base reaction occurs with slight different modalities over the surface of the three different magnetic adsorbents. As far as SMA_LacBen magnetic adsorbent is concerned, the acid-base reaction occurs between the acidic silanol groups (Si-O-H) of the adsorbent and the basic amine group of sulfanilamide. This reaction attains its maximum at pH = 4.0. At this pH the following two opposite trends exactly balance each other:

- 1) at pH < 4.0 the basic amine group of sulfanilamide turns out protonated to a too large extent and, thus, creates hydrogen bonds with the silanol groups of the magnetic adsorbent SMA_LacBen to a lower extent, which results in lower sulfanilamide adsorption;
- 2) at pH > 4.0 the concentration of hydroxonium ion is lower and, thus, is sufficient to bridge the silanol groups of SMA_LacBen with the basic amine group of sulfanilamide to a lower extent, which also results in lower sulfanilamide adsorption.

Adsorption of sulfanilamide on (Fe,H)A800C-0min, (Fe,H)A600C-90min magnetic adsorbents occurs through a similar mechanism. It must be evidenced that SMA_LacBen exhibits the highest SA adsorption ($9.8 \cdot 10^4 \mu\text{mol/kg}$) owing to the fact that this is the most acidic adsorbent. Actually, it was obtained starting from a natural rock bearing clinoptilolite of Si/Al ratio of 4.14 (Manzoli et al., 2021), whereas (Fe,H)A800C-0min, (Fe,H)A600C-90min magnetic adsorbents were obtained from zeolite A which has Si/Al = 1.00 (Baerlocher et al., 2001). Thus, the concentration of silanol groups over their surface turns out lower than the one of SMA_LacBen, which explains their lower sulfanilamide adsorption. The different of acidity between the various adsorbents explain both the lower uptake by (Fe,H)A800C-0min, (Fe,H)A600C-90min than SMA_LacBen and the fact that the maximum adsorption occurs at different pH values.

1 The maximum amount of adsorbed sulfanilamide increases according to the following order:
2 (Fe,H)A600C–90min ($6.00 \times 10^4 \mu\text{mol/kg}$), (Fe,H)A800C–0min ($7.00 \times 10^4 \mu\text{mol/kg}$), and
3 SMA_LacBen ($9.80 \times 10^4 \mu\text{mol/kg}$). Consequently, the subsequent experiments were performed
4 using the two magnetic adsorbents which exhibit the best results (Fe,H)A800C–0min and
5 SMA_LacBen) at the pH of maximum adsorption (6.0 and 4.0, respectively).
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10 3.3. Kinetic and equilibrium features of the adsorption process

11 The Figure 3a reports the sulfanilamide uptake by (Fe,H)A800C–0min and SMA_LacBen
12 magnetic adsorbents (S/L ratio = 1/10,000, pH 6.0 and 4.0, respectively) from an aqueous solution
13 exhibiting an initial sulfanilamide concentration of $40.0 \mu\text{mol/L}$, as a function of time. Both curves
14 show that the uptake is initially quite rapid, then gradually slows down and attains a steady state
15 after about 4 h.
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23 The Figure 3b reports sulfanilamide uptake from water by SMA_LacBen magnetic adsorbent
24 (S/L ratio = 1/10,000, pH 4.0) from sulfanilamide solutions of initial concentration of 40.0 and 126
25 $\mu\text{mol/L}$, as a function of time. Clearly, higher steady state values of sulfanilamide uptake are
26 attained as higher initial concentrations of sulfanilamide solution are adopted. The contact time of 4
27 h is sufficient to attain a steady state also for the solution of initial sulfanilamide concentration of
28 $126 \mu\text{mol/L}$. Consequently, the values of sulphonamide uptake or residual concentration in solution
29 recorded under such circumstances were considered as equilibrium values in further elaborations.
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36 The best model describing the adsorption kinetics reported in Fig. is the pseudo second-order
37 model, which can be expressed in a linear form according to Eq. (1) (Ozacar and Sengil, 2006):
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$$40 \frac{t}{q} = \frac{1}{k_2 * q_e^2} - \frac{t}{q_e}$$

41 where q_e and q are the amount of sulfanilamide adsorbed ($\mu\text{mol/kg}$) at equilibrium and at time
42 t , respectively, k_2 is the rate constant of adsorption ($\text{kg}/\mu\text{mol min}$) and t is the time (min). The
43 values of parameters calculated for two different concentrations of SA by using SMA_LacBen are
44 as follows. For $40 \mu\text{mol/L}$ of SA: $q_e=1.05 \cdot 10^5 \mu\text{mol/kg}$, $k_2 = 0.018 (\text{kg}/\mu\text{mol min})$, $r_2 = 0.99$; for 126
45 $\mu\text{mol/L}$ of SA: $q_e = 1.73 \cdot 10^5 \mu\text{mol/kg}$, $k_2 = 0.057 (\text{kg}/\mu\text{mol min})$, $r_2 = 0.99$. As regard
46 (Fe,H)A800C-0min the following kinetic parameters were evaluated for $40 \mu\text{mol/L}$ concentration of
47 SA: $q_e = 7.77 \cdot 10^4 \mu\text{mol/kg}$, $k_2 = 0.041 (\text{kg}/\mu\text{mol min})$, $r_2 = 0.99$.
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1 The equilibrium data, reported in the Figure 4, were satisfactorily described by the Langmuir
2 and isotherm model, while the the results (not reported) obtained with Freundlich model were
3 unsatisfactory, so indicating the monolayer adsorption of sulfanilamide on the magnetic
4 nanocomposites resulting from an uniform surface energy.
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7 The Langmuir isotherm was applied for adsorption equilibrium as shown below:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$$

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12 where C_e is the equilibrium concentration ($\mu\text{mol/L}$), and q_e is the amount of SA adsorbed per
13 kilogram at equilibrium ($\mu\text{mol/kg}$). Q_0 and b are Langmuir constants related to the adsorption
14 capacity ($\mu\text{mol/kg}$) and energy of adsorption ($\text{L}/\mu\text{mol}$), respectively. The linear plot of C_e/q_e versus
15 C_e showed that the adsorption obeyed a Langmuir isotherm model.
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21 Q_0 and b were determined from the slope and intercept of the plots to be $4.97 \cdot 10^5$ ($\mu\text{mol/kg}$)
22 and $5.62 \cdot 10^{-3}$ ($\text{L}/\mu\text{mol}$), for (Fe,H)A800C-0 min, and $1.02 \cdot 10^6$ ($\mu\text{mol/kg}$) and $2.41 \cdot 10^{-3}$ ($\text{L}/\mu\text{mol}$),
23 for SMA_LacBen, respectively. The results obtained in our investigation are very promising if
24 compared with other studies. Wan et al. (2020) reported the ability of magnetic-activated carbon
25 composites for sulfanilamide removal demonstrating a maximum adsorption capacity and kinetic
26 parameters lower than those estimated by us.
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33 34 35 3.4. Thermal analysis

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38 The sulfanilamide was also characterized as regards DTA analysis (Figure 5a) and TG
39 analysis (Figure 5b). The DTA curve exhibits an exothermic effect denoted by a sharp peak at about
40 180°C and an endothermic effect, which occurs in the temperature range $280\text{-}340^\circ\text{C}$ and attains its
41 maximum at about 320°C . The TG curve exhibits a small weight loss of about 5 % in the
42 temperature range room temperature- 280°C and then an evident weight loss of about 50 % in the
43 temperature range $280\text{-}340^\circ\text{C}$. For temperatures higher than this last value the weight of
44 sulfanilamide almost linearly decrease (with a small slope) thus attaining a final weight of about 18
45 % of the initial value at about 1000°C .
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53 The DTA and TG curve of sulfanilamide may be interpreted by considering that the
54 exothermic peak at about 180°C is due to a molecular rearrangement reaction. Such molecular
55 rearrangement reaction results in a final product of lower enthalpy and, thus, in the release of the
56 energy amount related to the same exothermic peak. The small weight loss in this temperature range
57 may be reasonably ascribed to sulfanilamide evaporation.
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1 The endothermic effect, occurring in the temperature range 280-340 °C and attaining its
2 maximum at about 320 °C, is related to the thermal decomposition of sulphonamide molecule. This
3 interpretation is confirmed by the TG curve, which records a mass reduction of more than 50 % in
4 this temperature range.
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7 The features of the DTA and TG curve suggested a simple thermal regeneration method of the
8 exhausted magnetic adsorbents. Actually, the magnetic adsorbents bearing adsorbed sulfanilamide
9 was incubated at 400 °C for 10 min under inert nitrogen atmosphere. Such a thermal treatment,
10 though not producing any structural variation in the magnetic adsorbent, yielded a full removal of
11 the antibiotic. In facts, once the thermal treatment was completed, the sulfanilamide uptake by the
12 regenerated magnetic adsorbent was about 99% of the uptake obtained using the fresh material.
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19 **4. Conclusions**

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23 Three tailor-made magnetic metal-ceramic nanocomposites, obtained from zeolite A and from
24 a natural clinoptilolite, have been developed by thermal treatments of heavy-metal cation-
25 exchanged zeolites at relatively moderate temperatures under a reducing atmosphere. The
26 nanocomposites have been successfully tested to remove sulfanilamide (SA), a sulfonamide
27 antibiotic of common use, from water.
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32 The adsorption behaviours of the nanocomposites has been characterized, showing that the
33 efficiency of the magnetic adsorbents strongly depends on pH. This indicates that the adsorption
34 mechanism is affected by acid-base reactions, being sulfanilamide subjected to two acid-base
35 processes, due to the protonation and the deprotonation of the amino and sulfonamide groups.
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40 The exhausted adsorbent has been subject to a regeneration procedure, developed on the basis
41 of DT and TGA analyses, allowing the complete removal of the sulfanilamide and the proper
42 recycle of the magnetic adsorbents.
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45 The results obtained are encouraging, demonstrating that sorption by magnetic metal-ceramic
46 nanocomposites obtained from zeolites is a technically and economically feasible method for sulfa
47 drugs removal.
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51 **Declaration of Competing Interest**

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54 The authors report no declarations of interest.
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LIST OF TABLES AND FIGURES

Table 1.
Chemical Physical properties of (Fe,H)A600C-90 min, (Fe,H)A800C-0 min and SMA_LacBen
From Pansini et al. (2018) and Manzoli et al. (2021)

	Magnetite	Wustite	Fe (wt %)	Amorphous phase				S_{BET} (m^2/g)	V_p (cm^3/g)	M_s (emu/g)
(Fe,H)A600C 90 min	7.1	0.2	4.8	87.1				28	0.15	12.3
(Fe,H)A800C 0 min	5.4		0.2	86.4				19	0.13	4.2
	Clinoptil.	K- feldspar	Quartz	Cristob	Muscov. / illite	Fe^0	Amorph. phase	S_{BET} (m^2/g)	V_p (cm^3/g)	M_s (emu/g)
SMA_LacBen	13.5	17.9	7.9	2.9	1.9	0.6	55.2	27.44	0.102	160

Captions for Figures

Scheme 1 - . p-aminobenzenesulfonamide (Sulfanilamide)

Figure 1 – SEM representative images of (Fe,H)A800C–0min (A, B, C), (Fe,H)A600C–90min (D, E ,F) and SMA_LacBen (G, H, I) magnetic adsorbents.

Figure 2 – Effect of pH on the adsorption of sulfanilamide on (Fe,H)A800C–0min, (Fe,H)A600C–90min and SMA_LacBen magnetic adsorbents. S/L ratio = 1/10000, contact time = 24 h

Figure 3 - Adsorption kinetics of sulfanilamide uptake:

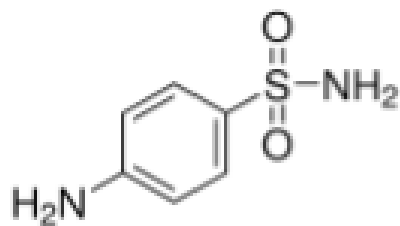
(a) in the presence of (Fe,H)A800C–0min and SMA_LacBen magnetic adsorbents (S/L ratio = 1/10,000, pH 4.0 and 6.0, initial sulfanilamide concentration = 40.0 $\mu\text{mol/L}$).

(b) in the presence of SMA_LacBen magnetic adsorbent (S/L ratio = 1/10,000, pH 4.0, initial sulfanilamide concentrations of 40.0 and 126 $\mu\text{mol/L}$).

Figure 4 – Adsorption isotherms of sulfanilamide

Figure 5 - DTA curve (a) and TG curve (b) of sulfanilamide

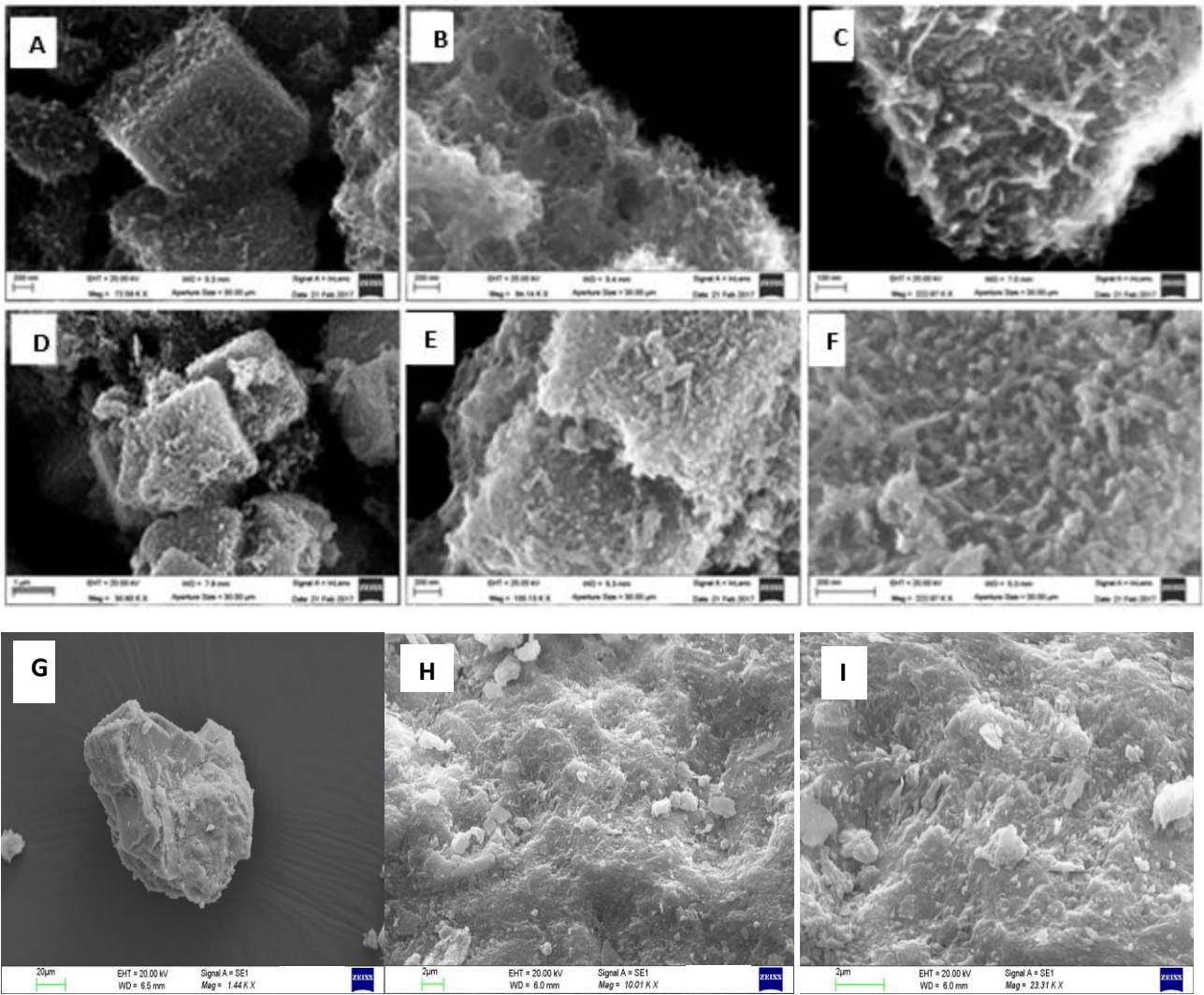
Scheme 1.



Scheme 1. *p*-aminobenzenesulfonamide (Sulfanilamide)

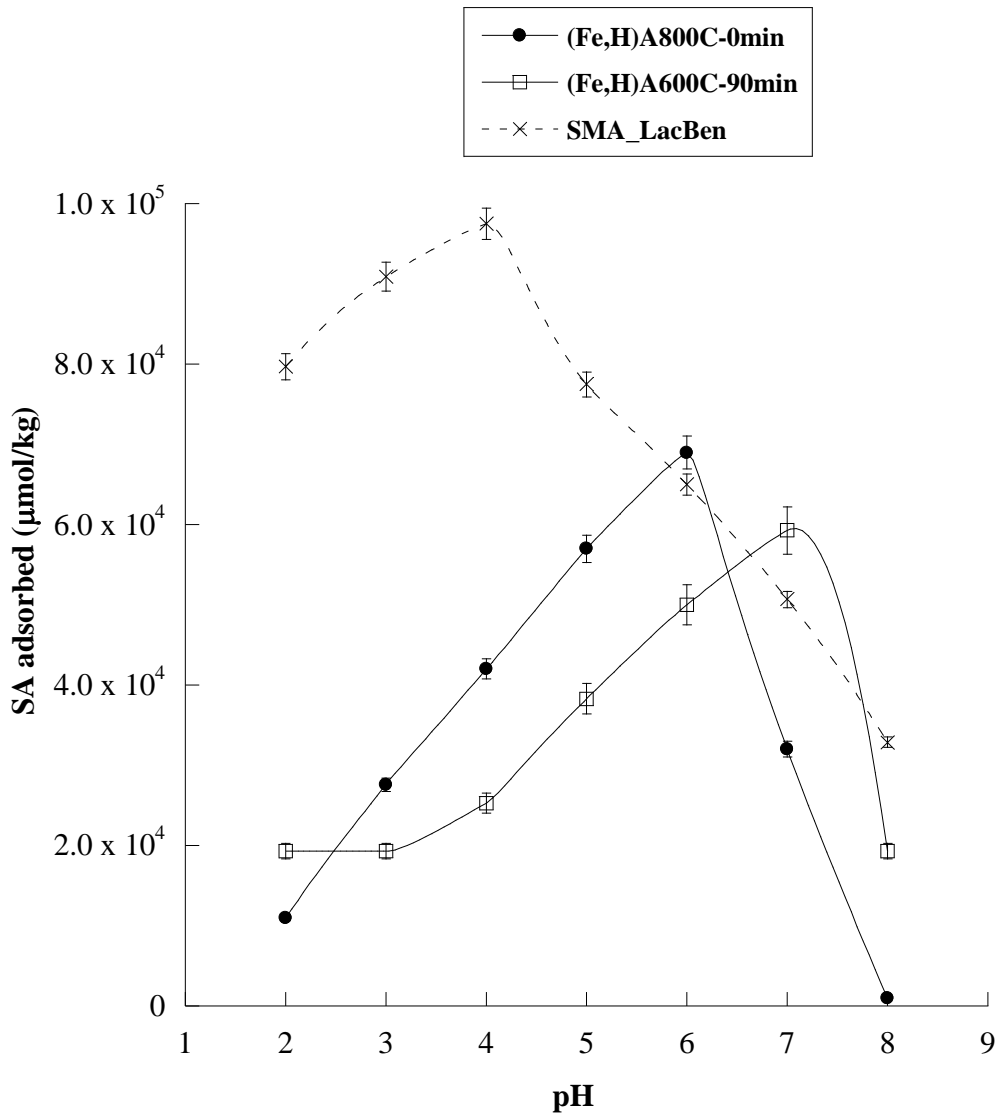
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Figure 1.



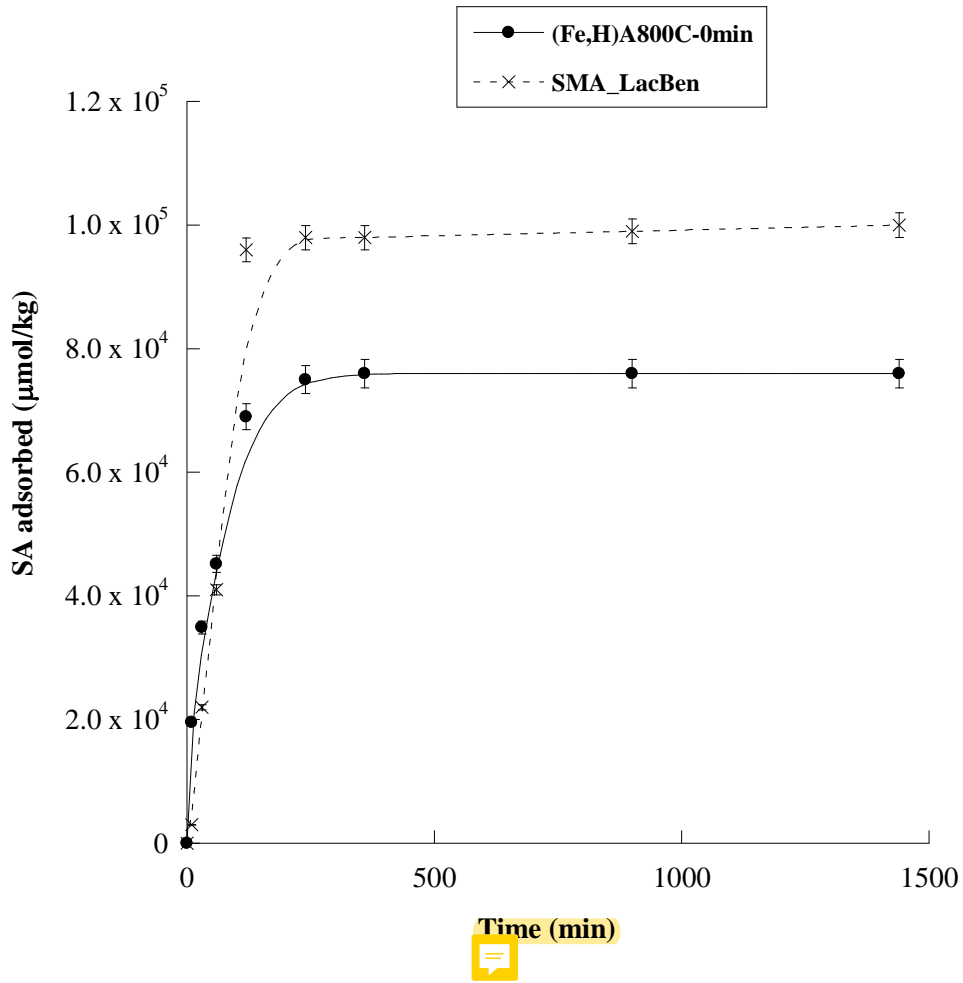
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Figure 2.



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Figure 3a.



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Figure 3b.

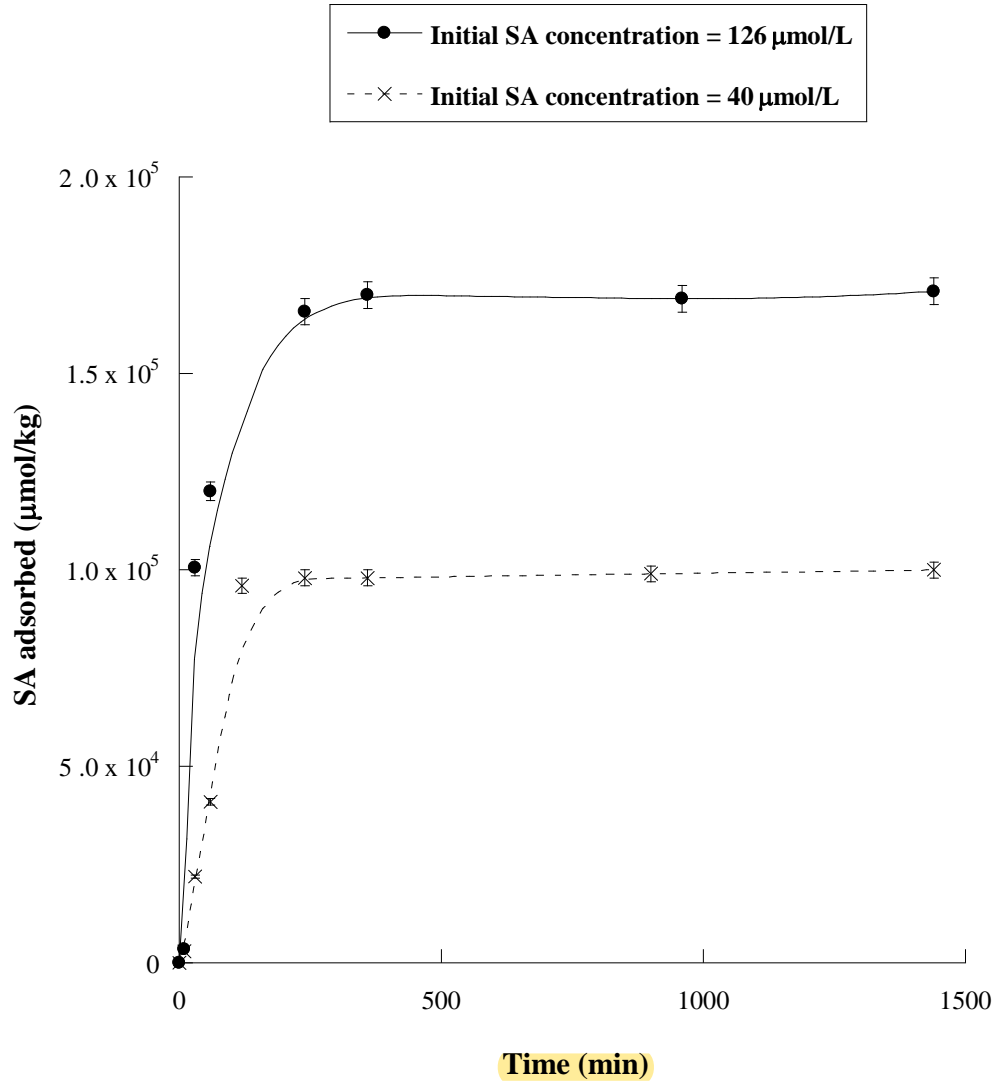
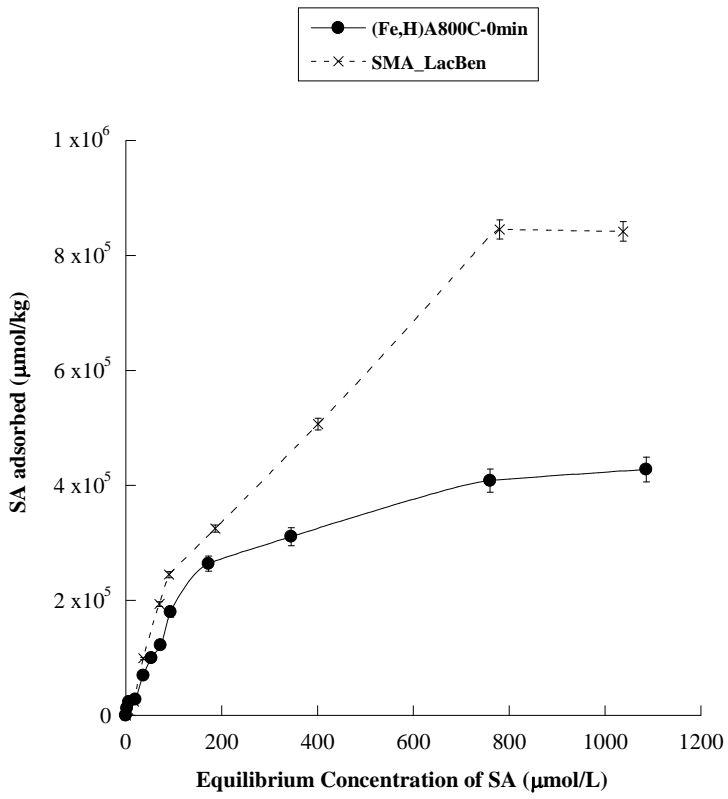


Figure 4.



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Figure 5a.

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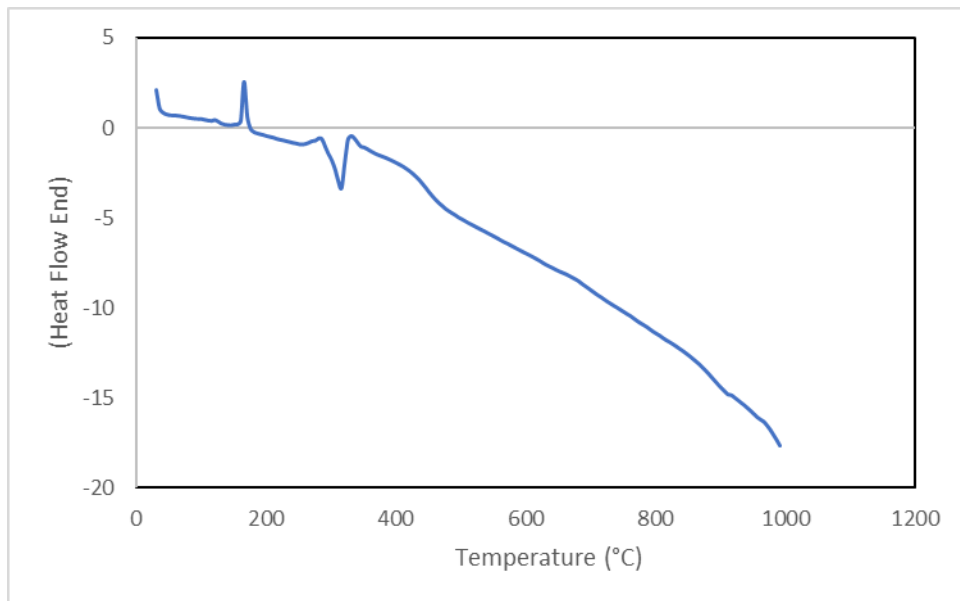


Figure 5b.

