

# Composite polyaniline-zeolite membrane material for wastewater ultrafiltration

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Both polyaniline and zeolites have been strongly studied for their use in techniques and technologies for water treatment. The composite polyaniline-zeolite membrane material prepared in this work is intended to be used for wastewater ultrafiltration having a complex composition: cations ( $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ) and phenolic derivatives (phenol, aminophenols or nitrophenols) commonly met on drugs and dyes manufacturing platforms or in textile and leather industries. The membrane material is obtained by polymerization of aniline on synthetic zeolite matrices. The polyaniline-zeolite material (PANI-Zeolite) was characterized in terms of morphology (SEM, HR-SEM), structure (EDAX, FTIR) and process performances - complex synthetic solutions ultrafiltration: cations ( $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ),  $10^{-4}$ - $10^{-6}$  M and phenolic derivatives (phenol, aminophenols and nitrophenols),  $10^{-4}$ - $10^{-6}$  M. The obtained results show that the developed composite polyaniline-zeolite membrane material is superior both to polyaniline and zeolite individually, retaining the potentially toxic chemical species (phenol or metal ions) from wastewater and producing benefic effects on the environment.

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**Keywords:** Organic inorganic composite, Adsorbent material, Phenol adsorption, Metal cations adsorption

## 1. Introduction

Industrial wastewater treatment on industrial sites that contain both organic substances and metal cations with major toxic potential, justify the extensive study of new types of adsorbent materials that correspond in terms of technico-economical requirements [1-3]. Among these materials, zeolites are microporous classic materials, aluminosilicate minerals commonly used as adsorbents [4-6]. On the other hand, polyaniline, a polymer widely available and used as adsorbent material, is becoming increasingly proposed as an alternative to inorganic adsorbent materials [7,8]. Although zeolites are known for ionic species retention within wastewaters and polyaniline for organic chemical species retention, their use in complex content wastewater treatment was not reported. This paper addresses to the synthesis of a zeolite-polyaniline composite (*PANI-Zeolite*) that responds to the need of simultaneous removal of ions and organic substances by wastewater ultrafiltration. The adsorbent zeolite-polyaniline material is obtained by polymerization of aniline acidic solution, made by oxidation of aniline hydrochloride with potassium persulphate, in the pores of the zeolite material. The micro-structured material, zeolite-polyaniline dioxide, was characterized in terms of morphology (SEM, HR-SEM), structure (EDAX, FTIR) and process performances for wastewater ultrafiltration (phenols adsorption, respectively lead, copper and zinc ion retention). The results show that the obtained composite material (*PANI-Zeolite*) is superior both to polyaniline and zeolite individually for phenol or metal ions retention,

showing both technical-economical and environment benefits.

## 2. Experimental

### 2.1 Materials

Zeolite MOLECULAR SIEVE 13X (SUPELCO Analytical), Polyaniline, emeraldine base, MW approx. 65,000 (Aldrich), quartz filters (Frisenette ApS QF.047), hydrochloric acid (Sigma Aldrich), lead nitrate, copper sulphate, zinc nitrate (Merck), potassium hydroxide, acetic acid and sodium acetate (Riedel -Dehaene), aniline, phenol, aminophenol and nitrophenol (Merck), potassium persulphate,  $\text{K}_2\text{S}_2\text{O}_8$  (Merck) and pure water obtained by Milipore method.

### 2.2. Methods

In a 500 ml autoclave of colloidal mill Retsch PM 100, it was introduced 50 g of quartz grinding machinery of 1 mm diameter, 40 g of Zeolite MOLECULAR SIEVE 13X and 50 ml of aniline. After 2 hours of homogenous mixing at 250 rpm, the autoclave was opened and then 150 ml of hydrochloric acid solution 37%, and 100 ml of 1 M potassium persulphate solution were added.

After 4 hours, a brown material is obtained and it is filtered in portions of 100 ml suspension on quartz filters, 47 mm in diameter, using a Sartorius funnel, then it is washed with distilled water four times and dried for 48

hours at 105°C in the vacuum oven. In parallel, there are obtained dynamic membranes by filtering a zeolite suspension on quartz filters (MZ) and, respectively, dynamic membranes by filtering a suspension of polyaniline on quartz filters (MP). The quartz filters together with the composite material *PANI-Zeolite* (MPZ) are introduced in one ultrafiltration module (Fig. 1).

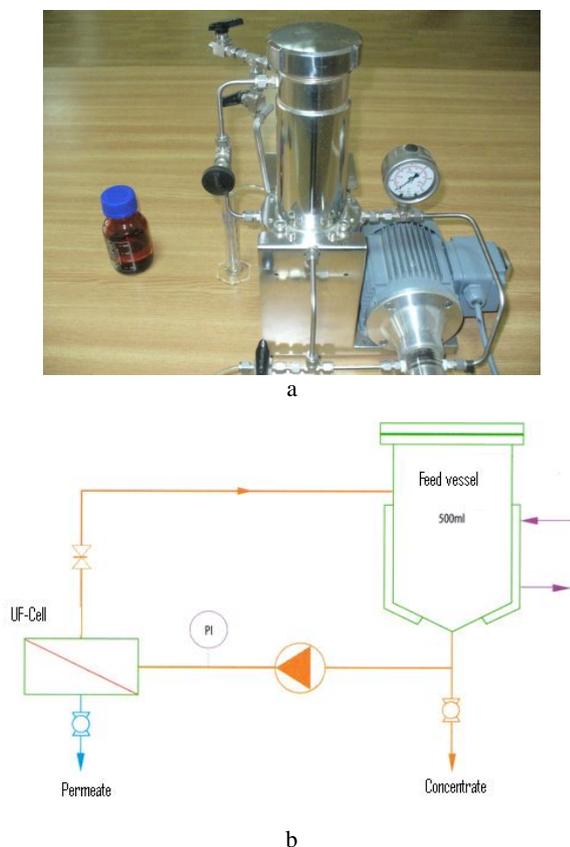


Fig. 1. KOCH ultrafiltration installation device LABCELL-CF1 a) general view, b) laboratory scheme.

The installation device allows testing of dynamic membranes on adsorbent material so that the ultrafiltration results represent an average of phenols retention obtained values [9].

Phenols retention ( $R_{ph}\%$ ) is determined using the relation (1):

$$R_{ph} (\%) = [1 - (C_{a_f} - C_{a_e}) / C_{a_f}] \times 100 \quad (1)$$

where:  $C_{a_f}$ - feeder phenol concentration  
 $C_{a_e}$ - effluent phenol concentration

$$C_f = A / \epsilon l \quad (2)$$

where:  $C_f$ - phenol concentration  
 $A$  - maximum absorbance of phenol  
 $\epsilon$  - phenol molar absorbance  
 $l$  - sample length

Phenol determination is accomplished by the spectrophotometric method [10], using a CAMSPEC spectrophotometer.

Retention of divalent ions  $M^{2+}$ , cations ( $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ),  $10^{-4}$ - $10^{-6}$  M ( $R_M^{2+}\%$ ) is determined using equation (3):

$$R_M^{2+} (\%) = [1 - (C_{M_f} - C_{M_e}) / C_{M_f}] \times 100 \quad (3)$$

where:  $C_{M_f}$ - feeder ion concentration  
 $C_{M_e}$ - effluent ion concentration

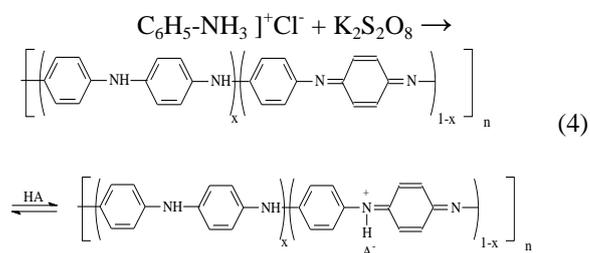
Metal ions determination is done by help of atomic absorption [11], using a Perkin Elmer AAS spectrometer.

Scanning electron microscopy (SEM) and EDAX analysis were performed with a FEI instrument (Hitachi S4500 FESEM).

### 3. Results and discussion

#### 3.1. Material synthesis

Chemical oxidation of aniline (4) was often carried out in aqueous solution, but also in polymer matrices [12-15].



In our case, the matrix consists of a commercial synthetic zeolite **MOL-SIEVE 13X** (Fig. 2 a, c), and aniline polymerization takes place after its adsorption by homogenization in the colloidal mill. The zeolite saturated with aniline is oxidized in potassium persulphate acidic solution, obtaining a composite material *PANI-Zeolite* (Fig. 2 b, d).

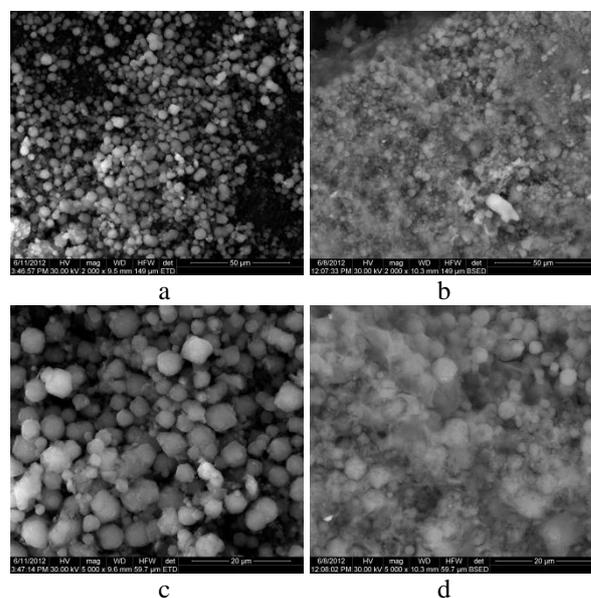
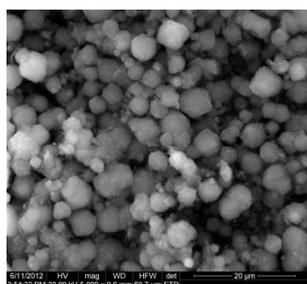


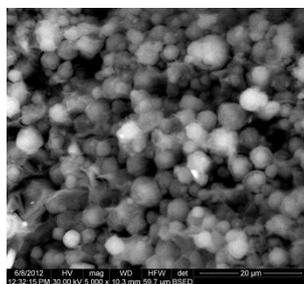
Fig. 2. Morphology of zeolite (a and c) and of zeolite-polyaniline composite material (b and d)

### 3.2. Scanning electron microscopy analysis

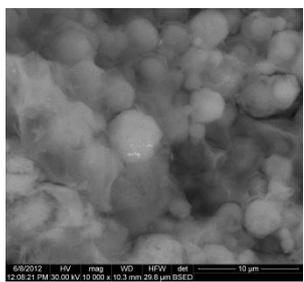
SEM analysis, performed with an FEI instrument (Hitachi S4500 FESEM) reveals a morphology dominated by the crystalline zeolite (Fig. 2 a, c), and by the appearance of fibers and threads of PANI (Fig. 2 b, d). Microcrystalline zeolite does not undergo any major changes in the process of ultrafiltration of aqueous solutions, while polyaniline threads changes insignificantly their size and shape after the process, Fig. 3 a and c compared with Fig. 3 c and d.



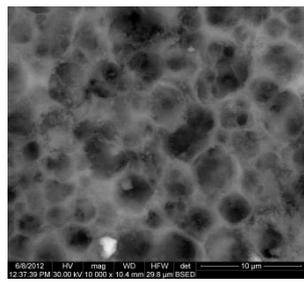
a



b



c



d

Fig. 3. The morphology of zeolite and of micro-composite material PANI Zeolite before (a, c) and after adsorption of aniline (b, d) at two resolutions  $\times 8,000$  (a, b) and  $\times 16,000$  (c, d).

### 3.3. Energy dispersive X-ray spectroscopy analysis

Map and EDAX spectrum (Fig. 4) shows the elemental distribution of the micro-composite material, **PANI-Zeolite** after the ultrafiltration of synthetic aqueous solutions.

The elemental distribution shows that the micro-structured material retains ions on the zeolite surface even after washing and preparation for analysis (Fig. 4 b).

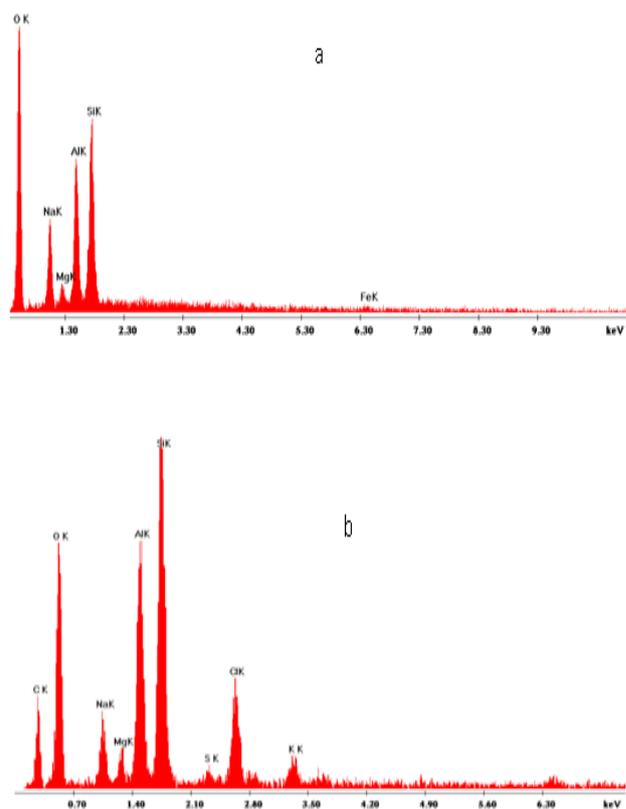


Fig. 4. EDAX image of zeolite material before (a) and after ultrafiltration (b).

### 3.4. Infrared spectroscopy

FT-IR spectra were obtained by help of a Bruker Tensor 27 instrument with diamond ATR (Fig. 5).

In order to characterize the obtained materials, the following have been analyzed by infrared spectroscopy: Polyaniline emeraldine base with MW approx. 65 000 (Aldrich), zeolite-polyaniline composite material obtained by chemical oxidation of aniline on the chosen zeolite. There are interesting differences that appear between polyaniline spectrum (Fig. 5a) and composite material zeolite-polyaniline spectrum (Fig. 5b). They suggest that polyaniline obtained in situ interacts chemically with the zeolite.

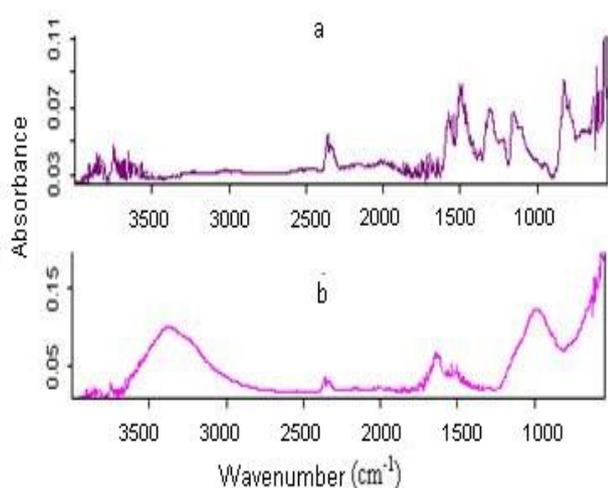


Fig. 5. FTIR spectra of PANI (a) and PANI-Zeolite composite (b).

Spectrum region between 3000-3600  $\text{cm}^{-1}$  shows the formation of hydrogen bonds and electrostatic interactions probably between imine groups of polyaniline and hydroxyl groups of the zeolite. Also, polyaniline obtained by polymerization in the presence of zeolite has shifted specific adsorption bands, thereby confirming the physical-chemical interaction polyaniline-zeolite.

Imine nitrogen atom from polyaniline (emeraldine-based Bronsted) is protonated by the hydroxyl groups of the dopant (acidic solution for oxidation), and this process is actually an acid-base equilibrium. FTIR spectra of polyaniline (emeraldine) shows two characteristic absorption bands at 1299  $\text{cm}^{-1}$  (assigned to the stretching vibration of C-N bond belonging to the signal of the secondary aromatic amine) and 832  $\text{cm}^{-1}$  (assigned to aromatic C-H bond). Polyaniline doping with the oxidation acid is confirmed by the presence in the FTIR spectrum of one absorption band due to the presence of non ionized HO groups in the remaining molecular architecture of inorganic material (3000-3600  $\text{cm}^{-1}$ ).

### 3.5. Retention tests

Retention of phenols and divalent metal cations from wastewater is an important aspect of labor toxicology and environmental protection both in the aromatic intermediates and dyes industries, and in the synthesis of drugs and pesticides ones.

Even though adsorption systems using polymeric and inorganic materials present satisfactory results, the use of organic-inorganic composite materials, as zeolite-polyaniline (PANI-Zeolite) present the advantage of physical retention on the inorganic material, and of physical-chemical retention on the organic polymeric material.

The experimental data (Table 1) obtained for the medium retention of phenols in synthetic waters made at three phenol concentrations:  $10^{-4}$  M,  $10^{-5}$  M,  $10^{-6}$  M

confirms an excellent retention for all the three materials studied. The results are even better for anilines with higher mass (toluidines versus aniline), and at the same molecular weight, the retention of asymmetric molecules (o-toluidine) is superior compared to the symmetric (p-toluidine) retention.

Table 1. Phenol retention on PANI-Zeolite composite material.

Feed concentration ( $10^{-4}$ - $10^{-6}$ M)	Medium Retention %		
	phenol	aminophenol	nitrophenol
Zeolite	97.16	98.97	98.88
PANI	97.80	99.54	99.12
PANI-Zeolite	98.15	99.78	99.23

The superior results of the medium retention of aminophenol than the other two compounds can be explained by its dual interaction with the material through which the ultrafiltration is realized, both with the hydroxyl and the amino groups. The better retention of nitrophenol compared to phenol is justified by the increase of the molecular weight and the molecule size.

The medium retention of the three cations studied, at the same concentrations, on membrane materials by ultrafiltration (Table 2), is significantly lower to organic substances.

Table 2. Cations retention on PANI-Zeolite composite material.

Feed concentration ( $10^{-4}$ - $10^{-6}$ M)	Medium Retention %		
	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>
Zeolite	67.22	58.75	68.88
PANI	47.80	79.02	93.12
PANI-Zeolite	72.59	87.48	99.55

The performed tests were carried out at pH= 4.8 (ensured by a sodium acetate/acetic acid buffer) in order to keep cations in solution and to avoid the formation of protonated amine groups in PANI. The medium retention of lead cations is higher on zeolite than on PANI, while the other two cations retention on PANI, exceeds that on the zeolite. This is explained by the interaction that occurs between these cations and the amino groups.

What appears as remarkable is the positive synergistic effect that occurs during the ultrafiltration on the composite material.

The pure water flows through the obtained membranes, based on three materials, increased with the increasing of operating pressure, being characteristic to micro and ultrafiltration (Fig. 6).

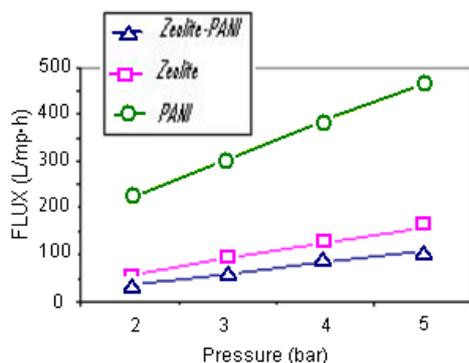


Fig. 6. Variation of pure water flows through membranes based on zeolite, PANI and PANI-Zeolite composite

The water flows containing phenols and metal ions through the membranes obtained, based on three materials, increased with the increasing of working pressure, but it was significantly lower than pure water flows, being characteristic to ultrafiltration (Fig. 7).

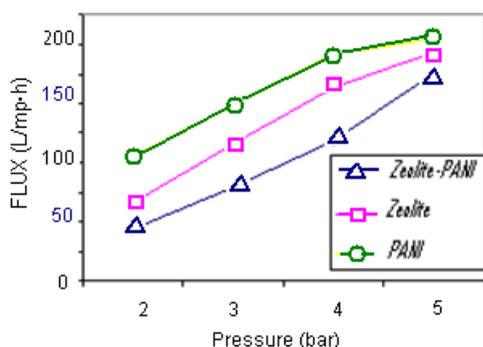


Fig. 7. Variation of water flows containing phenols and metal ions through membranes based on zeolite, PANI and PANI-Zeolite composite.

Analyzing the values of water flows and retention that can be processed by ultrafiltration (Tables 1, 2 and Figs. 6,7), there can be noticed that the new membrane material obtained, PANI-Zeolite, is the best for the treatment of waters containing simultaneously metal cations and phenols.

#### 4. Conclusions

The obtaining of new composite membrane materials, zeolite-polyaniline, allows a wide range of wastewaters that can be treated by ultrafiltration, including those with complex content of organic and inorganic chemical species.

The composite material, zeolite-polyaniline, has proven a superior performance in terms of retention of both phenols (phenol, aminophenol and nitrophenol) and cations ( $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ), in a wide range of concentrations  $10^{-4}$ - $10^{-6}$  M.

The water flows that can be treated are specific to ultrafiltration thus allowing the approach of the process to the usual working pressure (2-4 atm).

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#### References

- [1] V. Dulman, S. M. Cucu-Man, R. I. Olariu, R. Buhaceanu, M. Dumitras, I. Bunia, *Dyes and Pigments*, **95** (1), 79 (2012) ; DOI: 10.1016/j.dyepig.2012.03.024.
- [2] M. B. Yue, T. Xue, W. Q. Jiao, Y. M. Wang, M. Y. He, *Microporous and Mesoporous Materials* **159**, 50 (2012), DOI: 10.1016/j.micromeso.2012.04.027.
- [3] R. Vignola, R. Bagatin, A. D. F. D'Auris, C. Flego, M. Nalli, D. Ghisletti, R. Millini, R. Sisto, *Chemical Engineering Journal*, **178**, 204, (2011).
- [4] S. M. Auerbach, K. A. Carrado, P. K. Dutta, eds. *Handbook of zeolite science and technology*, CRC Press, 2003, p. 16. ISBN 0-8247-4020-3I.
- [5] B. A. Shah, H. D. Patel, A. V. Shah, *Environmental Progress & Sustainable Energy* **30**(4), 549 (2011).
- [6] C. R. Reyes, D. Appasamy, C. Roberts, *Dyna-Colombia*, **78**(170), 125 (2011).
- [7] G. Nechifor, S. I. Voicu, A. C. Nechifor, S. Garea, *Desalination*, **241**, 342 (2009).
- [8] F. Miculescu, I. Jepu, C. Porosnicu, C. P. Lungu, M. Miculescu, B. Burhala, *Digest Journal of Nanomaterials and Biostructures* **6**(1), 307 (2011).
- [9] S. I. Voicu, A. C. Nechifor, B. Serban, G. Nechifor, M. Miculescu, *J. Optoelectron. Adv. Mater.* **9**(11), 3423 (2007).
- [10] I. Diaconu, R. Girdea, C. Cristea, G. Nechifor, E. Ruse, E. E. Totu, *Romanian Biotechnological Letters*, **15**(6), 5702 (2010).
- [11] F. D. Balacianu, A. C. Nechifor, R. Bartos, S. I. Voicu, G. Nechifor, *Optoelectron. Adv. Mater. – Rapid Commun.* **3**(3), 219 (2009).
- [12] S. I. Voicu, F. Aldea, A. C. Nechifor, *Revista de Chimie* **61**(9), 817 (2010).
- [13] I. Diaconu, E. Ruse, E. E. Totu, G. Nechifor, *Revista de Chimie*, **61**(8), 718 (2010).
- [14] A. Cuciureanu, G. Batrinescu, N. N. Badea, D. A. Radu, G. Nechifor, *Materiale Plastice*, **47**(4), 416 (2010).
- [15] Z. A. Hu, X. L. Shang, Y. Y. Yang, C. Kong, H. Y. Wu, *Electrochimica Acta*, **51**(16), 3351 (2006). *Commun.* **4**(8), 1118 (2010).

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