

Fig5.1: Fixed frequency EIS studies for Pt/PSF in the presence of 0.11 M alginate acid and 0.11 M tannic acid

The capacitance response range for PSF was measured as 0.7 μ F to 1,2 μ F Farads. An initial fast decrease in capacitance was observed which slowed down at cut off time at 35mins for

tannic acid and for alginic acid the cut off time was 20min. This cut off time was interpreted as the time for the thin film membrane to become saturated (fouled) with analyte molecule under diffusion controlled. The average slope for the alginic acid at PSF was calculated to be 3.25×10^{-9} F/m and the standard deviation of the 3 slopes was 5.86×10^{-9} F/m. For the tannic acid the slope was 6.31×10^{-9} F/m and the STD was 1.80×10^{-9} F/m.

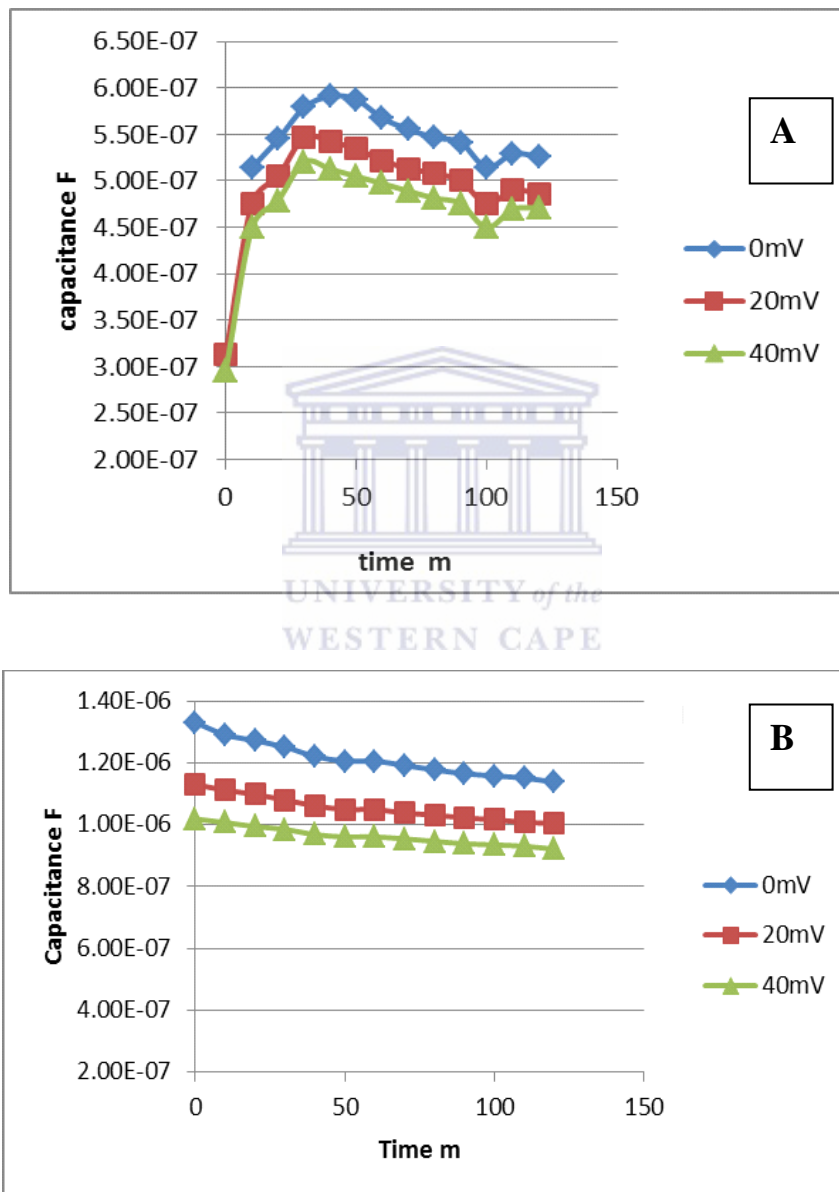
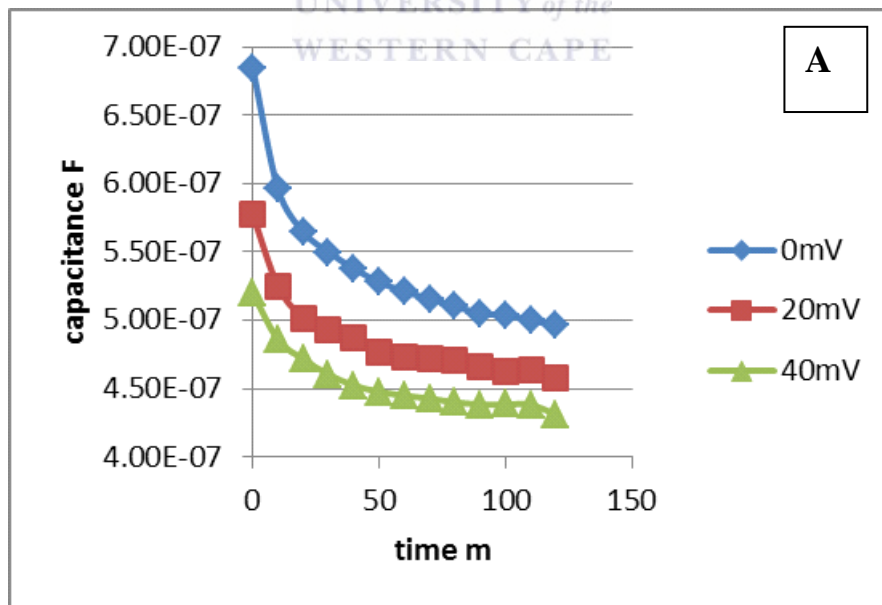


Fig5.2 Fixed frequency EIS studies for PSF/Co in the presence of alginic acid and tannic acid

The capacitance response range for PSF/Co thin film was observed to be in the range of 1 to 4 μ F for tannic acid and 0.3 – 0.6 μ F for alginic acid. The initial rate of decrease was slower. The cut off time for Pt/PSF/Co in the presence of alginic acid and tannic acid was 45min for both analytes. The average slope of the alginic acid was 1.80×10^{-9} F/m and the standard deviation of the three slopes was 4.32×10^{-9} F/m. The tannic acid slope was 2.07×10^{-8} F/m and the standard deviation was 1.93×10^{-8} F/m. The mechanism of interaction between PSF/Co and alginic acid resulted in an initial increase in capacitance which may be attributed to the approach of the alginic acid molecules to the PSF/Co. The higher surface area due to organised pore structures induced by cobalt nanoparticles as indicated by the SEM image, may be the reason behind the change in capacitance behaviour observed like a match between pore size and analyte molecule would allow for penetration of molecule into the PSF/Co porous network and result in a different adsorptive profile. The initial slope showed high sensitivity to alginic acid.



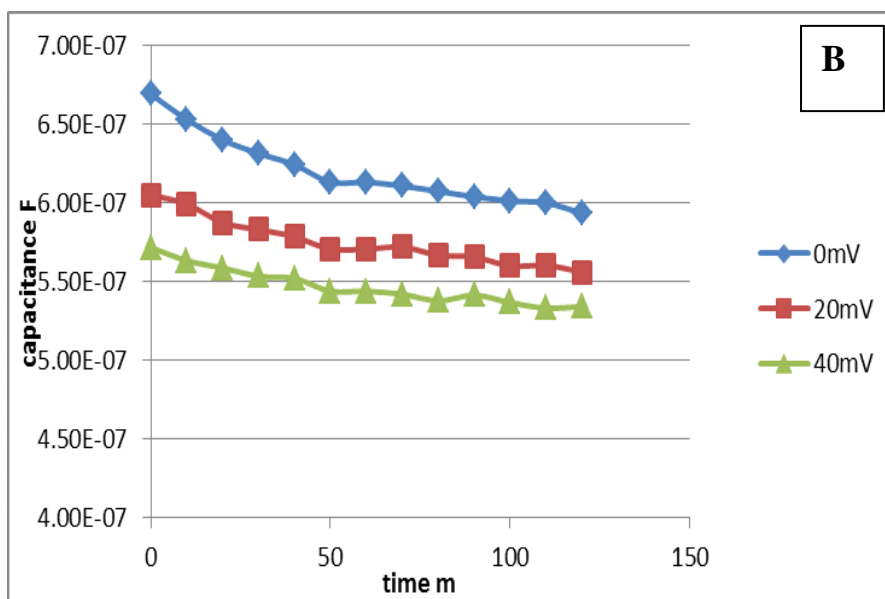


Fig5.3: Fixed frequency EIS studies for PSF/Ni in the presence of (A) alginic acid and (B) tannic acid

The capacitance response was observed in the range from 0.5 to 0.7 F/m for both the tannic acid and alginic acid. The slope of the alginic acid at the thin film was calculated to be 7.53×10^{-10} F/m and the standard deviation was 2.2×10^{-9} F/m. For tannic acid the average slope was 3.49×10^{-9} F/m and the standard deviation was 1.55×10^{-8} F/m. The decrease in capacitance was observed at cut off time of 50 min for the tannic acid and for alginic acid the cut off time was 45 min.

When comparing the results obtained (fig 5.1 – fig 5.3) and the calibration curves in chapter 4 there is a correlation in results. The unmodified polysulfone membrane showed to be non-linear, lowest sensitivity, lowest limit of detection (LOD) and the shortest cut-off time. For the modified polysulfone with metal nanoparticles showed linearity, improved sensitivity, highest LOD and longer cut-off time than the unmodified polysulfone. Unmodified polysulfone membrane takes the shortest time to fouls which is due to its hydrophobic nature and the contact angle suggested that the unmodified polysulfone is hydrophobic because of the highest contact angle value obtained (87°). The modification of the polysulfone with

metal nanoparticles improved the hydrophilicity of the polysulfone because of the high sensitivity, longer cut-off time and also the low contact angle values obtained.

Material	Slope (F/m)	Standard Deviation (F/m)	Cut-off time (m)
Polysulfone	Alginate acid 3.25×10^{-9}	5.68×10^{-9}	20
	Tannic acid 6.31×10^{-9}	1.80×10^{-9}	35
Polysulfone/Co	Alginate acid 1.80×10^{-9}	4.32×10^{-9}	45
	Tannic acid 2.07×10^{-9}	1.93×10^{-9}	45
Polysulfone/Ni	Alginate acid 7.53×10^{-9}	2.2×10^{-9}	40
	Tannic acid 3.49×10^{-9}	1.55×10^{-8}	50

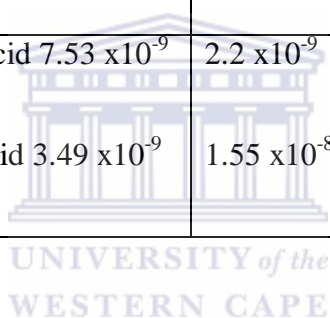


Table 5.1: Table of results of the polysulfone thin films prepared in the presence of tannic acid and alginate

These times indicate that polysulfone unmodified fouls in the shortest time and hence PSF/Co and PSF/Ni shows an improvement in performance because of higher hydrophilicity.

For the dynamic EIS studies the potential was fixed at 0.58V which represents the formal potential for tannic acid oxidation at these thin films. For alginate acid the potential was fixed at 0.37 V which represents the formal potential for alginate acid reduction. The frequency range used was from 100 mHz – 1KHz. The Randles circuit was used to model the data, where R_s represent the solution resistance, R_{ct} represent charge transfer resistance. The CPE was used instead of pure capacitor to model the capacitance.

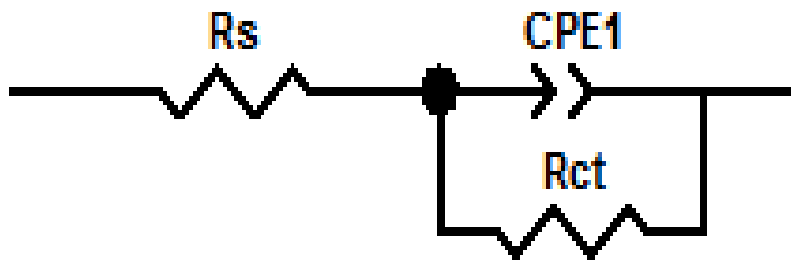


Fig5.4: Randles circuit

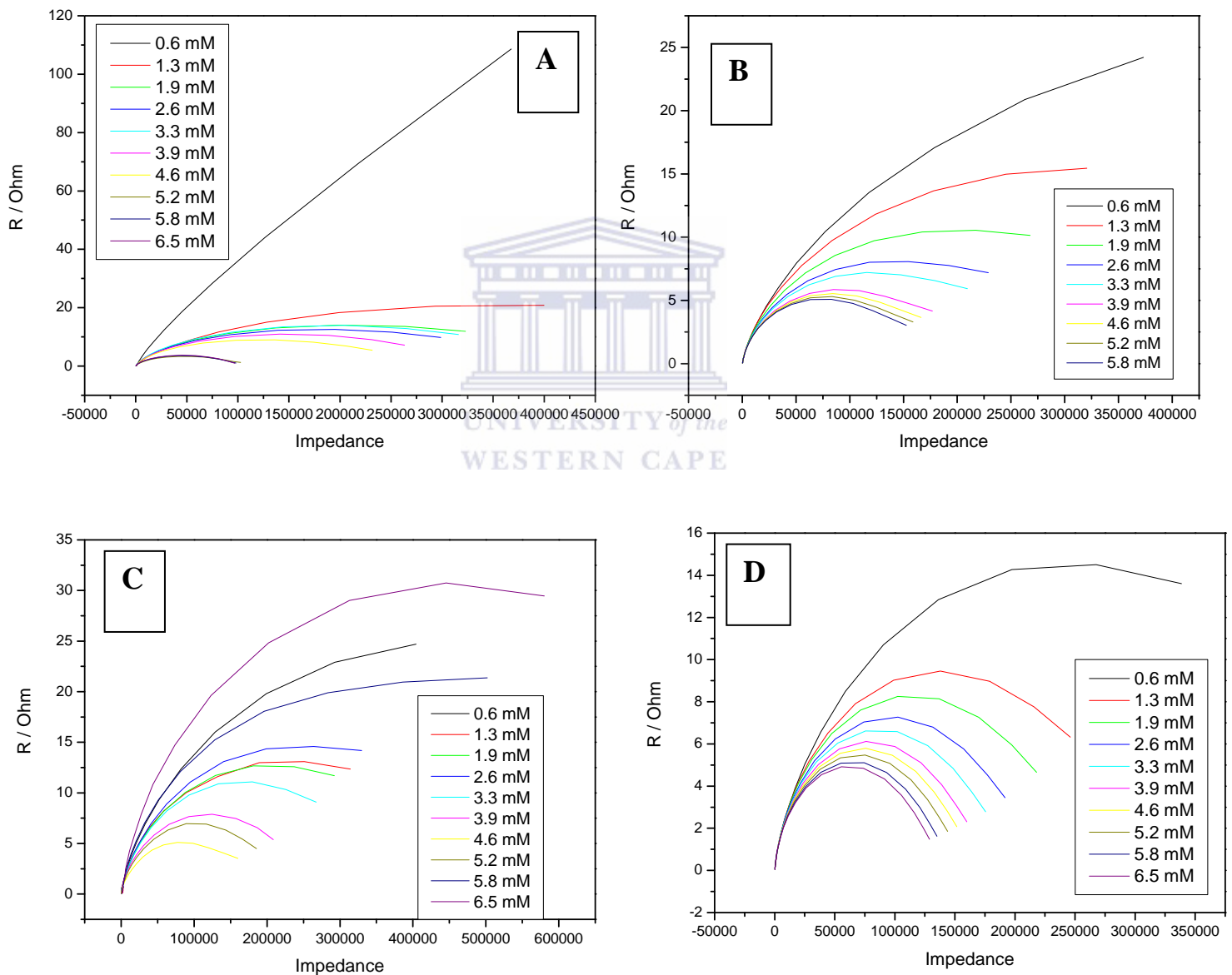


Fig5.5: EIS plot of (A) PSF, (B) PSF/Co, (C) PSF/Ni and (D) PSF/Ag in the presence of tannic acid

Tannic acid at fixed potential of 0.58 V and over a frequency of 100 mHz to 1 KHz was evaluated as concentration dependent response. The electrocatalysis of TA followed typical diffusion control kinetics as evidenced by semi circle at low frequency in the concentration range evaluated and was modelled as Randles circuit using CPE to model non-homogenous adsorptic at the interface.

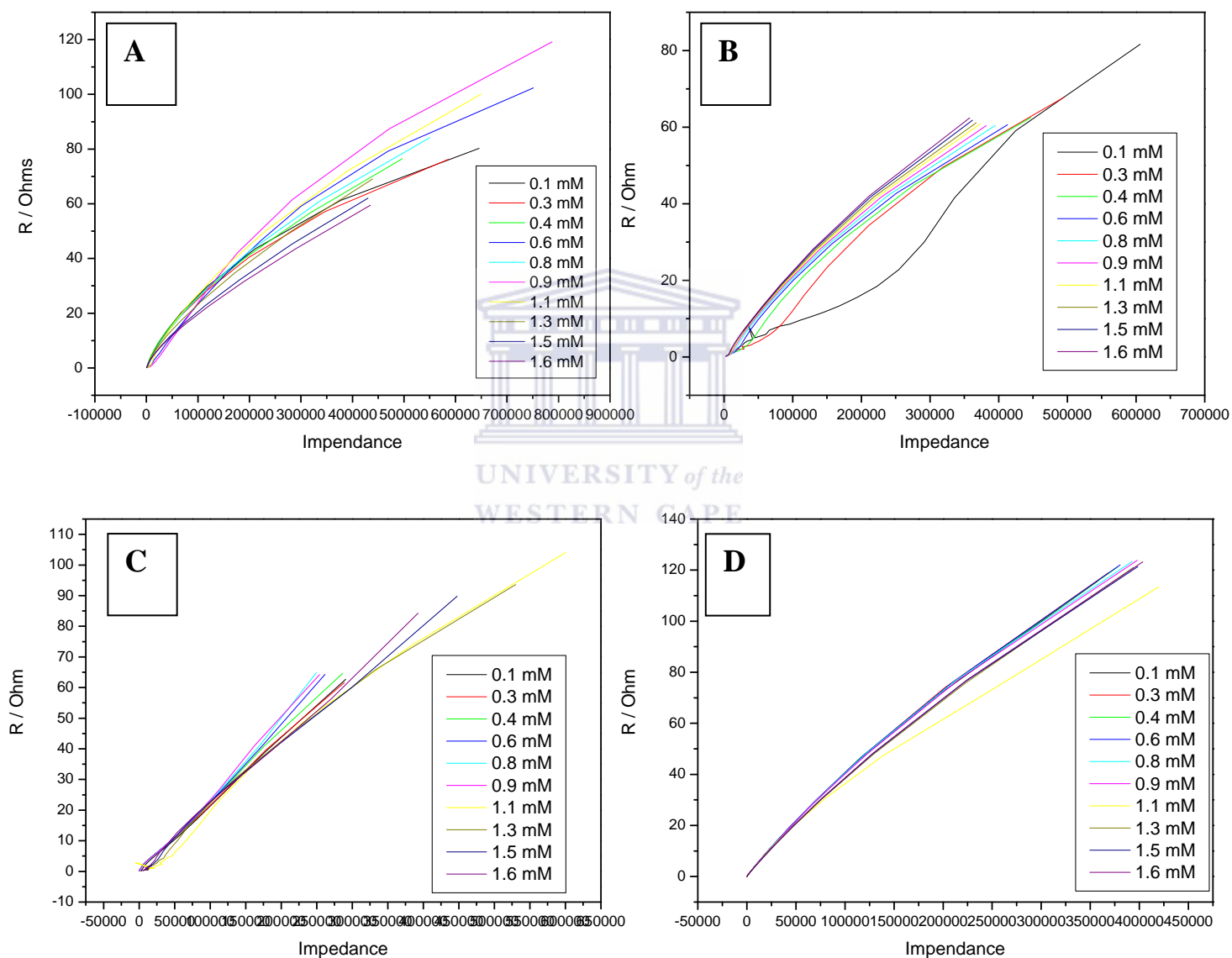


Fig5.6: EIS plot of (A) PSF, (B) PSF/Co, (C) PSF/Ni and (D) PSF/Ag in the presence of alginate acid

Alginic acid electrocatalysis at fixed potential of 0.37 V and over a frequency range of 100 mHz to 1 KHz was evaluated as a concentration dependent response. Alginic acid electrocatalysis appeared to be influenced by passivating infinite diffusive behaviour as evidenced by unresolved low frequency impedance arcs. This type of data should best be modelled as infinite Warburg diffusion, but for consistency in data interpretation, the same RCT circuit was used as for tannic acid.

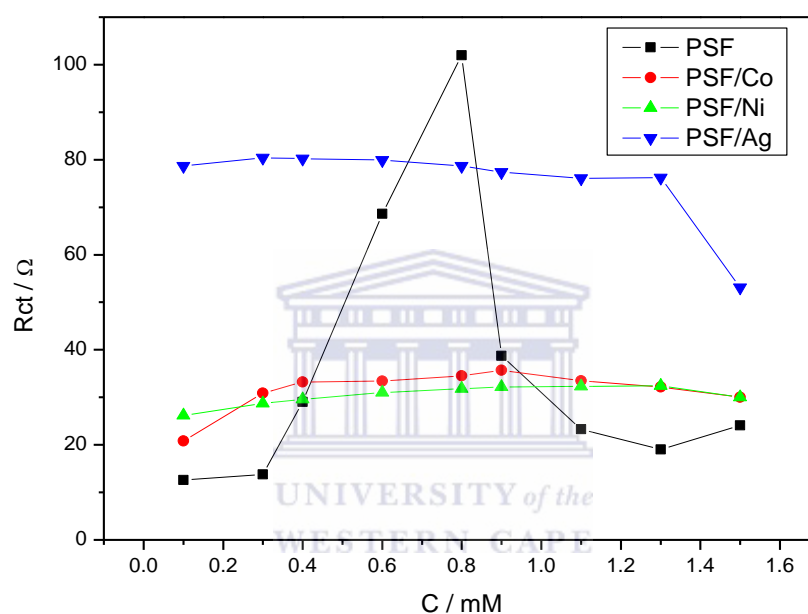


Fig 5.7: Rct plot of alginic acid at the polysulfone thin films

The PSF/Ag appeared to be insensitive to alginic acid whereas PSF/Co displayed the highest sensitivity towards alginic acid as evidenced by initial slope. The PSF unmodified was inconsistent in its response to alginic acid and may require further controlled evaluation. However the same inconsistency in concentration response was also observed in voltammetric evaluation (CV, SWV).

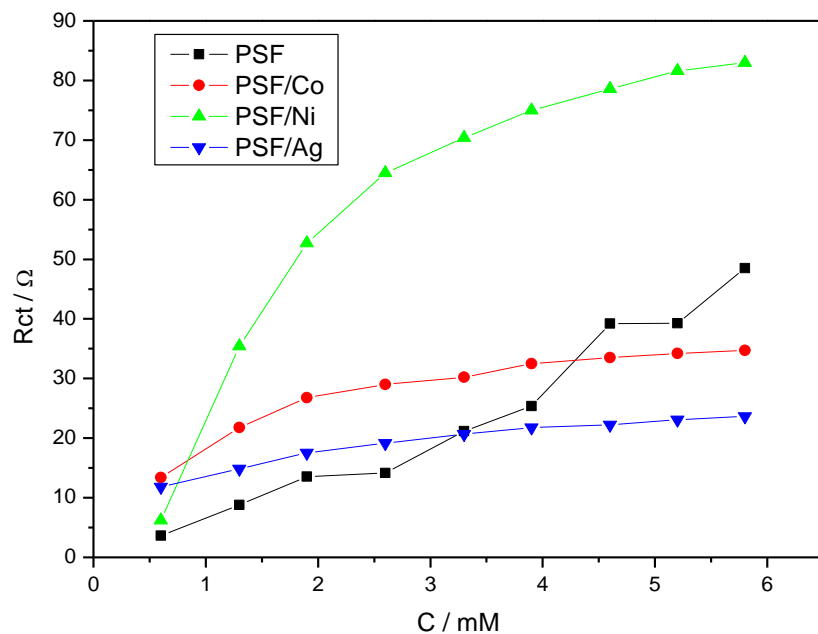
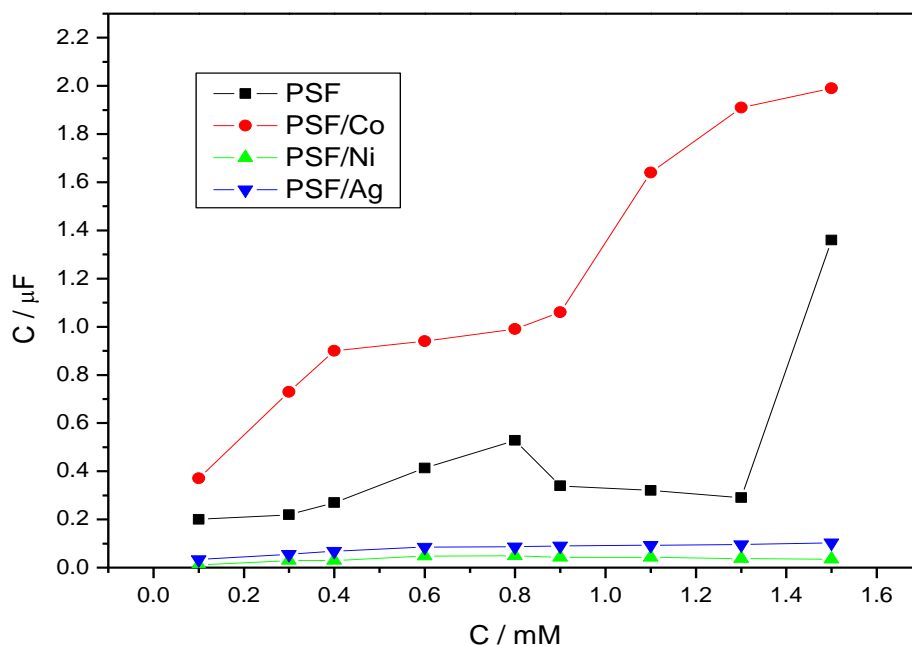


Fig5.8: Rct plot of tannic acid at the thin films

The adsorptive behaviour of tannic acid at the different polysulfone films was evaluated under electrochemical stimulation to induce catalysis. The PSF/Ni films showed the best quantitative response indicated by the limit of detection which was 2.6 mM when compared to PSF/Ag and PSF/Co, and highest sensitivity towards tannic acid indicated by the highest slope which was found to be $2.91 \times 10^{-6} \Omega / \text{mM}$. However all films showed a tendency towards fouling above 2 mM of tannic acid added.



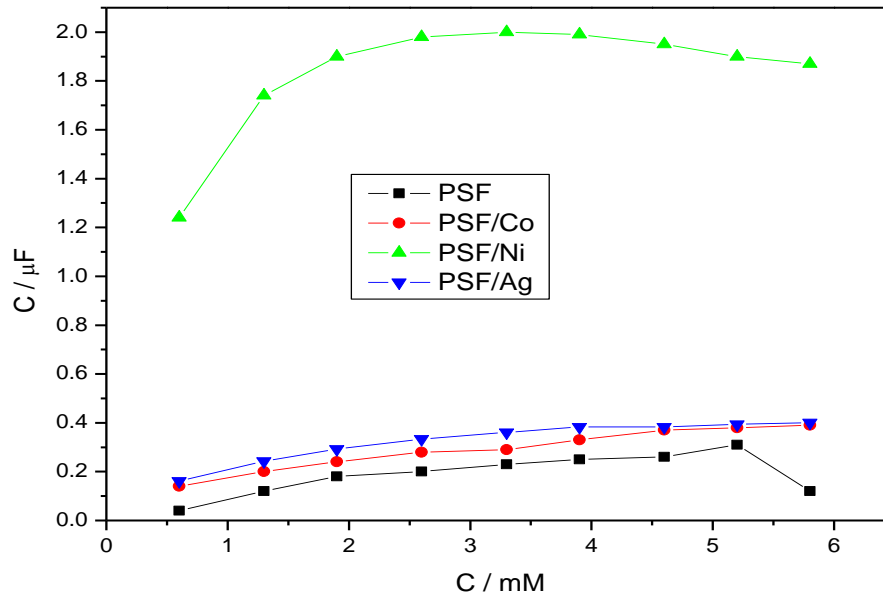


Fig 5.9: Caps plot of PSF, PSF/Co, PSF/Ni and PSF/Ag in the presence of (A) alginic acid and (B) tannic acid

The capacitance response range for the PSF and modified thin films were consistently in the range of $1.0\mu\text{F}$ to $0.1\mu\text{F}$ as previously detailed by the fixed frequency impedance. However, further analysis of capacitance under electrochemically was not attempted here since this would represent capacitance electrochemically induced catalytic control, which is not relevant to membrane fouling

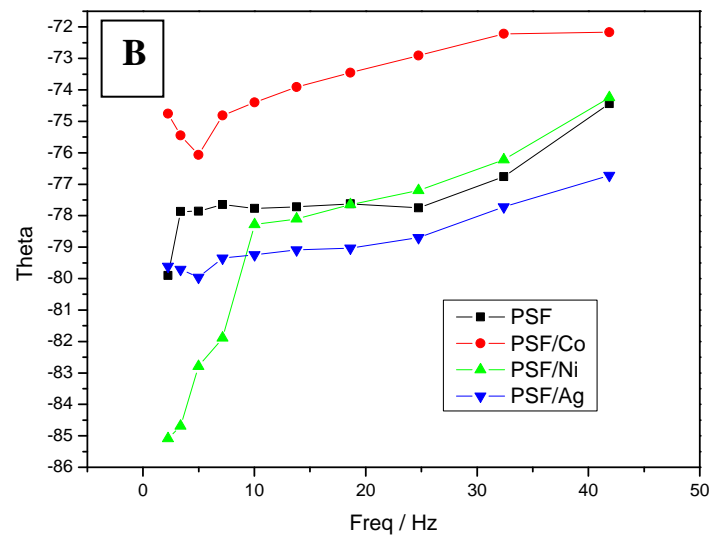
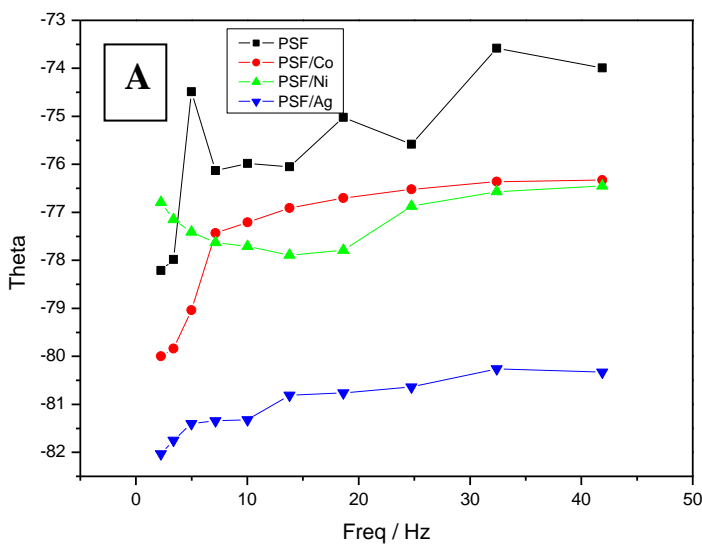


Fig5.10: Phase angle plot of PSF, PSF/Co, PSF/Ni and PSF/Ag in the presence of (A) alginic acid and (B) tannic acid

Evaluating the above plot, phase angle change during the catalysis events confirmed that the PSF and modified PSF thin films retained their semiconducting nature and hence fouling was dominated by interfacial film properties such as surface area and analyte loading.

From the fixed frequency, the PSF/Ni showed to have the longest slope of 7.53×10^{-9} . The R_{ct} result shows that PSF/Ni films showed the best quantitative response and highest sensitivity towards tannic acid.



Chapter 6

This chapter draws the conclusion of the whole work that was done and also the future work.

6.1 Conclusion

Briefly in this study three metal nanoparticles were successfully synthesized by the chemical reduction method. Three nanocomposites of polysulfone thin films were prepared and characterized by means of cyclic voltammetry, square wave voltammetry, electrochemical impedance spectroscopy, contact angle and scanning electron microscope.

The SEM, TEM and EDS confirmed the synthesis of nanoparticles. The SEM images of both Ni and Co nanoparticles were agglomerated, the agglomeration of the nanoparticles may be to incomplete reaction or the metal salts were not fully reduced by the reducing agent that was used. The TEM image of Ag nanoparticles showed the nanoparticles to be well dispersed and non-agglomerated with the average size of 20 – 50 μm . The nanoparticles showed different shapes like cubic, rods and spherical. In comparing the SEM images of the unmodified polysulfone membrane with the metal modified polysulfone, the PSF/Ag nanocomposite showed have larger pores than the PSF/Co and PSF/Ni, followed by the PSF/Co and the PSF/Ni showed small pores. The unmodified polysulfone membrane didn't show pores. The EDS of the modified polysulfone membrane confirmed the incorporation of the metal nanoparticles into the polysulfone.

The contact angle measurements were done to study the hydrophilicity of the modified and unmodified polysulfone membrane. From the results obtained in contact angle confirmed that when the polysulfone is modified with metal nanoparticles the hydrophilicity of the unmodified polysulfone was improved. The contact angle of the unmodified polysulfone

membrane was 87.5° and when the PSF was modified with metal nanoparticles the contact decreased, the PSF/Co showed to be the most hydrophilic (31.7°) when compared with PSF/Ni and PSF/Ag. The PSF/Ni showed to be the second most hydrophilic PSF nanocomposite with the PSF/Ag being the least hydrophilic PSF membrane.

The electrochemical characterisation of the PSF unmodified and PSF modified was done in the presence of an analyte (alginic acid and tannic acid), to study the fouling behaviour of the prepared polysulfone thin films. Cyclic voltammetry studies of the different thin films that were prepared were done at the presence of the electrolyte which was the HCl. The polysulfone unmodified thin film showed to have the highest diffusion coefficient followed by the polysulfone modified with Ni nanoparticles. From the cyclic voltammetry showed that both analytes behaves differently at the membrane thin films prepared, the tannic acid showed an oxidation peak at 0.58 V where as the alginic acid had a reduction peak at 0.37 V.

Calibration curves were constructed using the peak measurements for the analytes from the square wave voltammetry results. The PSF/Co showed to be the most sensitive polysulfone nanocomposite in the presence of both the alginic acid and tannic acid because of the highest slope when compared with the PSF/Ni and PSF/Ag. The PSF/Ni showed better performance for quantitative detection studies in the presence of both analytes.

From the fixed frequency, unmodified polysulfone thin films had the longest cut off time when compared to the PSF/Co and PSF/Ni, indicating that modification with metal nanoparticles into the polysulfone improved the cut off time because of the hydrophilic membranes. The R_{ct} result shows that PSF/Ni films showed the best quantitative response and highest sensitivity towards tannic acid. The phase angle of the prepared polysulfone thin films was observed to be $75^\circ - 86^\circ$, indicating that the thin films retained their

semiconducting nature and hence the fouling was dominated by the interfacial film properties such as surface area and analyte leaching.

6.2 Future Work

For future work:

- For this research the EIS was used to evaluate the fouling mechanisms of the prepared thin films of polysulfone, the other method that can be used to study the fouling mechanism of the thin films is the rotating disk electrode. The results obtained for EIS can be compared with the RDE results.
- Two model organic acids were chosen to study the fouling caused by them in ultrafiltration membranes. The other model organic acid to be used is the humic acid to study the fouling it causes to membranes of water treatment. A solution of humic acid will be prepared and the fouling behaviour will be tested using impedance spectroscopy.
- The fixed frequency EIS of PSF/Ag in the presence of both tannic acid and alginic acid will be done for full comparison of the unmodified polysulfone and the modified polysulfone membrane. The experiment will be done by drop-coating the PSF/Ag onto a Pt electrode, fixing the frequency at 10 mHz – 1 KHz and using the both tannic acid and alginic acid as analytes.

References

Absar Ahmada, Priyabrata Mukherjee, Satyajyoti Senapati, Deendayal Mandal, M. Islam Khanb, Rajiv Kumar, Murali Sastry , 2003, Colloids and Surfaces B: Biointerfaces 28, 313–318

Adou, A.F.Y., Muhandiki, V.S., Shimizu, Y., Matsui, S., 2001, Water Science and Technology 43, 1–7.

Alam J, Dass L.A, Alhoshan M.S, Ghasemi M, Mohammad A.W, (2012), Applied Water Science 2, 37-46

Allen J. Bard, Larry R. Faulkner, 2002, Electrochemical Methods: Fundamentals and Applications, 2nd edition, John Wiley & Sons, New York, USA

Aryanti P.T.P, Wenten G.I, Khoiruddin, 2013, Journal of Water Sustainability 3, 85-96

Ayse Asatekin a, Seoktae Kangb, Menachem Elimelech b, Anne M. Mayesc, 2007, Journal of Membrane Science 298, 136–146

Baker R.W, Membrane Technology and Applications, JohnWiley, Chichester, 2004.

Boksoon Kwon, H.K. Shon, Jaeweon Cho, 2009, Desalination and Water Treatment 8, 177–187

Byoung-Yong Chang and Su-Moon Park, 2010, Anal. Chem. 3, 207–29

Castro E.F Vidaurre, C.A. Acheteb, F. Gallob, D. Garciac, R. Simãob A.C. Habertc, 2002, Materials Research 5, 37-41

Choong Jeon , Young Je Yoo , Wolfgang H. Hoell, 2005, Bioresource Technology 96, 15–19.

Choong Jeon, Jae Yeon Park, Young Je Yoo, 2002, *Biochemical Engineering Journal* 11, 159–166

Chowdhury S.R., 2001, *Separation/ Purification Technology* 24271-282

Combe C., E. Molisa, P. Lucasa, R. Riley, M.M., Clark, 1999, *Journal of Membrane Science* 154, 73-87

D.A. Skoog, F.J. Holler, T.A. Nieman, *Principles of Instrumental Analysis*, Brooks/Cole Publishing Co., 5th edition, 1997, chapter 25.

Derek A. Long. *The Raman Effect*. John Wiley & Sons, New York, 2002.

Ehsan Saljoughi, Toraj Mohammadi, 2009, *Desalination* 249, 850–854

Geisse, Nicholas A. (July-August 2009). *Materials Today* 12, 40–45

Giessibl, Franz J., 2003, *Reviews of Modern Physics* 75: 949

Goosen M.F.A, S.S. Sablani, H. Ai-Hinai, S. Ai-Obeidani, R. Al-Belushi, D. Jackson, 2004 *Sci. Technol.* 39, 2261–2297.

Gordeyev S. A., G. Yu. Nikolaeva, K. A. Prokhorov, R. Withnall, I. R. Dunkin, S. J. Shilton, and P. P. Pashinin, 2001 , *Laser Physics* 11, 82–85.

Guezguez, I., Mrabet, B. Ferjani, E., 2013, *Desalination* 313, 208-211

Hamid N.A.A, A.F. Ismail , T. Matsuura , A.W. Zularisam , W.J. Lau, E. Yuliwati , M.S. Abdullah N.A.A. Hamid, 2011, *Desalination* 273, 85–92

<http://www.jtbaker.com/msds/englishhtml/t0065.htm> (12/04/2012)

Jae Weon Cho, Gary Amy, John Pellegrino, Yeomin Yoon, 1998, *Desalination* 118, 101-108

Jeon, C., Park, J, Y. and Yoo Y.J., *Immobilization of Alginic Acid Using PVA for Lead Adsorption*, 216th ACS National Meeting, Boston, August 21-28 (1998).

Kabsch-Korbutowicz M., 1994, Sep. Sci. Technol 29, 2345.

Kim J and Van der Bruggen B., 2010, Environmental Pollution 158, 2335-2349.

Kim K.S., 2002, Journal of Membrane Science 199, 135–145

Kim, James H. Herman J. Gibb, Paul D, Concise international chemical assessment document; 69

Lang, K.M.; D. A. Hite, R. W. Simmonds, R. McDermott, D. P. Pappas, and John M. Martinis, (2004), Review of Scientific Instruments 75, 2726–2731

Lee J, Ahn W and Lee C. (2001), Water Research 35, 2435-2445.

Lowe J., Hossain Md.M, (2008), Desalination (218), 343–354

Lucian Baia and Simion Simon, (2007), *UV-VIS and TEM assessment of morphological features of silver nanoparticles from phosphate glass matrices*, Modern Research and Educational Topics in Microscopy.

Macdonald J. Ross, 1992, Annals of Biomedical Engineering 20, 289-305

Madaeni S.S. & Akbarzadeh Arbatan T., 2010, Iran. J. Chem. Chem. Eng 29, 105-111

Matveev V.V. et al., (2006) , Chemical Physics Letters 422, 402–405

Maximous N, Nakhla G, Wan W and Wong K, 2010, Journal of Membrane Science 352, 222-230.

Mulder J, “*Basic Principles of Membrane Technology*,” 2nd Edition, Kluwer Academic Publishers, Dordrecht, 1996, p. 584.

N.B. Colthup, L.H. Daly, S.E. Wiberley. *Introduction to Infrared and Raman Spectroscopy*. (Third Edition) Academic Press, 1990.

Odegaard, H., Eikebrokk, B., Storhaug, R., 1999, *Water Science and Technology* 40, 37–46.

Perron R.N, Brumaghim J.L, 2009, *Cell Biochem Biophys* 53, 75-100

Puntesa Victor F., Kannan Krishnanb and A. Paul Alivisatos, 2002, *Topics in Catalysis* 19,

Rahimpour A., Madaeni S.S. (2007), *Journal of Membrane Science* 305, 299–312

Rama Chemnamsetty, Isabel Escobar, Xinglong Xu, (2006), *Desalination* 188, 203-212

Reckhow, D.A., Singer, P.C., Malcolm, R.L., (1990), *Environmental Science and Technology* 24,1655–1664.

Rong Guan, Hua Zou , Deping Lu, Chunli Gong, Yanfang Liu, 2005, *European Polymer Journal* 41, 1554–1560

Sabine Vico, Barbara Palys, and Claudine Buess-Herman, 2003, *Langmuir* 19, 3282-3287

Salazar-ALvarez, 2007 , *Chem. Mater* 19, 4957-4963

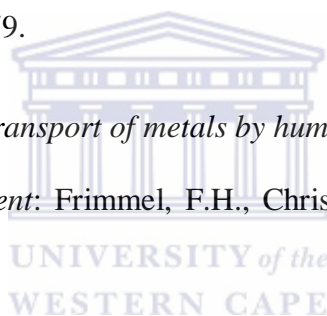
Sangyoun Lee and Menachem Elimelech, 2006, *Environ. Sci. Technol* 40, 980-987

Schafer, A.I., Fane, A.G., Waite, T.D., 2005. *Nanofiltration: Principle and Application*. Ed, Elsevier Ltd, Oxford.

Selby Maphutha, Kapil Moothil, M. Meyyappan, & Sunny E. Iyuke, (2013) *A carbon nanotube-infused polysulfone membrane with polyvinyl alcohol layer for treating oil-containing waste water,*

Sheppard Patrick, *Preparation and Characterization of composite PES/Nanoparticle Membrane,*

- Srisudha M, K. Karthik and S. Ponnuswamy, 2013, Nano Vision, Vol.3 (1), 37-43
- Stevenson, F.J., 1994. Humus Chemistry: Genesis, Composition, Reactions, second ed. John Wiley & Sons, New York.
- Summers G.J., M.P. Ndawuni, C.A. Summers, 2001, Polymer 42, 397–402
- Sutton, A., Harrison, B. E., Carr, T. E., and Barltrop, D.(1971) Int.J.Radiat.Biol.Relat Stud.Phys.Chem.Med. 19, 79-85.
- Suzuki, E. (2002), *Journal of Microscopy* 208 (3): 153–157.
- Weber A (Editor). *Raman Spectroscopy of Gases and Liquids*. Topics in Current Physics. John Springer-Verlag, Berlin, 1979.
- Weber, J.H., 1988. *Binding and transport of metals by humic materials*. In *Humic Substances and Their Role in the Environment*: Frimmel, F.H., Christman, R.F. (Eds.), John Wiley & Sons, Chichester.
- Yamaguchi, H., Higasida, R., Higuchi, M., Sakata, I., 1992, J. Appl. Polym. Sci. 45, 1463–1472.
- Yoshichiko Bandu and Takahito Terashima, 1986 , Bull. Chem. Soc, Japan 59, 607-612,
- Yoshichiko Bandu and Takahito Terashima, Preparation and Coercivity of Cobalt ultrafine particles by reduction of multilayered CoO-SiO films, Bull. Chem. Soc, Japan, 59, 607-612, 1986
- Yuehua Deng, Lin Wang, Xiaobin Hu, Benzhi Liu, Zhongbo Wei, Shaogui Yang, Cheng Sun, 2012, Chemical Engineering Journal 181– 182, 300– 30



Yunan Zhou , Xin-Hui Xing, Zehua Liu , Liwen Cui b, Anfeng Yu , Quan Feng a, Haijun Yang, 2008, Chemosphere 72, 290–298

Zhao C. et al. 2004, Desalination 170, 263-270

Zhao Lijun, Liang Xiaoming, *Room-temperature synthesis of air-stable cobalt nanoparticles and their high-efficient adsorption ability for Congo red*, Electronic Supplementary Material (ESI) for RSC Advances, 2012

