Ain Shams University
Faculty of Science
Chemistry Department

Preparation and Characterization of Some Nanomaterials for Waste Water Treatment and Their Use in Chemical Sensors for Environmental Pollutants Monitoring

Thesis Submitted by

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M. Sc. (2013)

Chemistry Department, Faculty of Science, Ain Shams University

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In

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To

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Dedication

This thesis is dedicated first of all to my God and creator who on and on supporting me to achieve this work and supporting me in all my life "thanks for Allah"

To my supervisors for their continuous encouragement during this work

To my parents (God prolong their age) and all my family

To My friends who encourage and supported me

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Novel Flow-Through Potentiometric System for Dimethyamine Assessment Using New Ion Exchangers Doped-Polymeric Membrane Sensors

Saad S. M. Hassan,*[a] Ayman H. Kamel,*[a] and Heba Abd El-Naby[a]

Abstract: New simple potentiometric sensing systems are described for the sensitive and selective monitoring of dimethylamine (DMA). These systems are based on using polymeric membranes doped in some ion exchangers such as dimethylamine/phosphomolybdate $[(CH_3)_2NH_3]_2^{2+}$ $[MP]^{2-}$ (Sensor I), dimethylamine/tetraphenylborate $[(CH_3)_2NH_3]^+[TPB]^-$ (Sensor II) and dimethylamine/phosphotungstate $[(CH_3)_2NH_3]^+[TP]^-$ (sensor III). All the sensing systems are incorporated in poly(vinyl chloride) matrix plasticized with o-NPOE. In a Trizma buffer solution of pH 7.1, the sensors exhibit a stable, fast and linear response for 5.0×10^{-6}–1.0×10^{-2}, 2.5×10^{-5}–1.0×10^{-2}, and 5.0×10^{-6}–1.0×10^{-2} mol L^{-1} DMA^+ with slopes of 53.2 ± 0.4, 49.4 ± 0.6, and 53.8 ± 0.3 mV decade^{-1}, and detection limits of 2.0×10^{-6} (0.16 μg mL^{-1}), 1.6×10^{-5} (1.3 μg mL^{-1}), and 1.4×10^{-6} (0.11 μg mL^{-1}) mol L^{-1} for sensors (I), (II), and (III), respectively. Potentiometric selectivity measurements of these sensors reveal negligible interferences from most common aliphatic and aromatic amines. Satisfactory results are obtained with an average accuracy of 99.5% and a mean precision of ±0.5%. Validation of the proposed assay methods are examined by measuring the limit of detection, linearity range, accuracy, precision, within-day repeatability, between-days reproducibility and method ruggedness. Good performance characteristics and applicability of these sensors for DMA assessment in different matrices under static and hydrodynamic modes of measurements are demonstrated. The proposed sensors are also prepared in a tubular form and used as DMA detector in a two-channel flow injection setup for continuous monitoring. The frequency rate is 27–53 samples h^{-1}. The sensors are satisfactory applied for DMA quantification in both biological matrices and environmental samples with recoveries ranging between 95.0 and 104.0%.

Keywords: Potentiometric sensors · Flow injection analysis · determination of dimethylamine.

POTENTIOMETRIC STUDY FOR RAPID CONTINUOUS MONITORING OF TRACE LEVEL THIOCYANATE USING SOLID AND CONVENTIONAL TYPES PVC MEMBRANE SENSORS

Saad S. M. Hassan[a]*, Ayman H. Kamel[a]*, Heba Abd El-Naby[a] and M. Abdelwahab Fathy[a]

Key words: Potentiometry, conventional sensors, solid state; thiocyanate, flow injection analysis, biological fluids.

A comparative study using two different thiocyanate electrode designs was conducted; a solid type electrode (type A) and conventional liquid inner contact electrode (type B). The fabrication of these electrodes was based on Al (III) [4-(2-Pyridylazo) resorcinol] (Al/PAR) and Mg (II) phthalocyanine (MgPC) complexes as a charged carrier, aliquate 336S and TDMAC as ion exchangers in plasticized poly (vinyl chloride) membrane. Electrodes type (A) revealed significantly enhanced response towards SCN^- ions with displayed near-Nernstian slope of -53.7 - -55.8 mV decade^{-1} over the concentration range $5.0x10^{-6}$-$1.0x10^{-2}$ mol L^{-1} and a detection limit of 0.4-3.7 μg mL^{-1}. Type (B) sensors revealed near-Nernstian potential response to SCN^- with a slope of -45.9 - -62.4 mV decade^{-1} over a linear range of $5.0x10^{-5}$-$1.0x10^{-2}$ mol L^{-1} and a detection limit of 0.12-0.3 μg mL^{-1}. Membrane sensors based on (Al/PAR) and (MgPC) using the so called "fixed interference method" (FIM) exhibited a good selectivity over different anions which differ significantly from the classical Hofmeister series. All sensors were integrated in a flow system for continuous monitoring of thiocyanate under hydrodynamic mode of operation. The sensors revealed a frequency of ~ 54 samples h^{-1}. Application of the proposed sensors for SCN^- determination in biological fluid samples such as saliva collected from some non-smoker and smoker donors. Determination of cyanide content in electroplating wastewater samples after its conversion into thiocyanate was also applied. The results obtained from the proposed sensors were agreed with that obtained using the standard methods of thiocyanate and cyanide analysis.

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ABSTRACT

Abstract

This thesis entitled with "Preparation and characterization of some nanomaterials for waste water treatment and their use in chemical sensors for environmental pollutants monitoring" includes six chapters.

Chapter one:

This chapter is divided into two parts: part (A) deals with general background, characterization and applications of nanomaterials, part (B) includes the basic principles, historical background, classifications, selectivity, applicability, some strategies used in fabrication and application of potentiometric sensors.

Chapter two:

This chapter describes the synthesis of a new SnO_2/CeO_2 nano-composite sample and itscharacterization to be used for the removal of alizarin dyes from aqueous solutions. The composite material was prepared using a co-precipitation method. Under optimized experimental conditions, the removal of alizarin yellow, alizarin red and alizarin-3-methylimino-diacetic acid dyes from aqueous solutions was about 96.4% ,87.8% and 97.3 %, respectively.

The adsorption isotherms were agreed with Langmuir, Freundlich and Temkin isotherms.

Chapter three:

In this chapter copper ferrite nanoparticles ($CuFe_2O_4$) and copper ferrite polyaniline nanocomposite ($CuFe_2O_4$/PAN) were synthesized using co-precipitation methodology and utilized as sorbent materials for the removal of total inorganic mercury. The Nanosorbents were characterized showing the formation of $CuFe_2O_4$ with 20.8 nm size. Several removal parameters for mercury have been studied and exhibited high performance with high removal percentage of up to 99 %. The adsorption isotherms were investigated using Langmuir, Freundlich and Temkin isotherms.

Chapter four:

A potentiometric study using different thiocyanate sensors was conducted based on the use of Al (4-(2-pyridylazo) resorcinol) (Al/PAR) and Mg (II) phthalocyanine (MgPC) complexes as charged carriers. Copper (II) neocuproin/SCN^- ion association complex, aliquate 336S and TDMAC were also used as ion exchangers in plasticized poly (vinyl chloride) membranes. The sensors exhibited near-Nernstian slopes of -45.9 — -62.4 mV $decade^{-1}$ for SCN^- ions

with detection limits of 0.25 — 0.3 µg ml^{-1}. The developed sensors were applied to determine the cyanide content in electroplating wastewater samples after conversion into thiocyanate.

Chapter five:

New simple potentiometric sensing systems are described for the sensitive and selective monitoring of dimethylamine (DMA). The first system is based on using polymeric membranes doped with some ion exchangers such as dimethylamine/phosphomolybdate $[(CH_3)_2NH_2)_2]^{2+}$ $[PM]^{2-}$ (Sensor I), dimethylamine/tetraphenylborate $[(CH_3)_2NH_2)]^{+}[$ $TPB]^{-}$ (Sensor II) and dimethylamine/phosphotungstate $[(CH_3)_2NH_2)]^{+}[PT]^{-}$ (Sensor III). The second system involves the fabrication of a molecularly imprinted polymer, with a pre-defined specific cavity suitable to accommodate DMA (Sensor IV). The sensors exhibit a stable, fast and linear response with near-Nernstian potential response to DMA^{+}. Slopes of 53.2±0.4, 49.4±0.6, 53.8±0.3 and 51.3±0.3 mV $decade^{-1}$ and detection limits of 2.0 x 10^{-6} (0.16 µg ml^{-1}), 1.6 X 10^{-5}(1.3 µg ml^{-1}), 1.4 x 10^{-6} (0.11 µg ml^{-1}) and 4.6 x 10^{-6} (0.37 µg ml^{-1}) mol L^{-1} are obtained with sensors (I), (II), (III) and (IV), respectively. The sensors are satisfactory applied for DMA quantification in both biological matrixes and

environmental samples with recoveries ranging between 95.0 and 102.0%.

Chapter six:

This chapter deals with the development of novel biomimetic potentiometric membrane sensors for the assessment of aminoacridine (ACR). The membranes of sensors (I) and (II) consist of MIP based methacrylic acide (MAA) and acrylamide (AM), respectively. The sensors exhibit near-Nernstian potential response to ACR^+ with slopes of 51.2±1.3 and 50.5±1.4 mV per decade and detection limits of 0.05 and 0.17 µg ml^{-1} for sensors (I) and (II) , respectively. The sensors are used for the assessment of aminoacridine in some pharmaceutical preparations and biological samples.

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