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Synthesis and application of molecular imprinted polymers for online monitoring of textile dyes in wastewater

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ABSTRACT

A large quantity of dyes is being used in different industries like textile, leather, tanning, paper, plastics, food, cosmetics and printing, etc. which cause water pollution. The impedance of water pollution has special implications for both human life and livestock. Different spectroscopic and chromatographic techniques are used to determine the concentration of dyes. However, these techniques are expensive due to the cost of instruments and time-consuming with regard to sampling and sample preparation. In the present research project, selected dyes in industrial wastewater were quantified and online-monitored via molecularly imprinted polymers. For this purpose, polystyrene and polyvinylpyrrolidone and their composite with graphene oxide were synthesized. These sensors layers were combined with mass-sensitive transducer-quartz crystal microbalance. The composite of polyvinylpyrrolidone with graphene oxide showed 2.5 times better sensor response than its molecular imprinted polymers. The polystyrene composite with graphene oxide showed 13 times better sensor response as compared to its molecularly imprinted polymers. The composite of polyvinylpyrrolidone with graphene oxide have lesser response toward selected dyes (methyl red and methyl orange) as compared to polystyrene composite with graphene oxide. Especially the sensitivity of molecular imprinted polymer-based composite sensors is detected up to 5 ppm toward selected dyes in industrial wastewater.

Keywords: Molecular imprinted polymer; Vinyl pyrrolidone; Polystyrene; Ethylene glycol dimethacrylate; 2,2-azobis isobutyronitrile; Quartz crystal; Microbalance

1. Introduction

A large quantity of dyes is being used in different industries like textile, leather, tanning, paper, plastics, food, cosmetics, printing, among others for the coloration of their related products. Wastewater of these industries causes water pollution. These dyes have toxic effects on human beings and animals. Most of the dyes have a carcinogenic effect. Water pollution is being caused by the wastewater of these industries [1]. The consumption of these dyes in the leather tanning, textile and plastic industry is increasing and their demand increased 20%–30% in the market [2].

The detection methodologies of dyes from industrial wastewater are time-consuming, expensive and are not easily available especially in underdeveloped countries where they are needed desperately. Molecularly imprinted polymers (MIPs) coated on sensors have emerged as a promising alternative for low-cost, faster, and simpler methods of various dyes detection in water. The preparation of these MIPs is cost-effective and these could be stored after drying at room temperature for longer periods of time without any

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change in their chemistry or functioning. The imprinted polymers have long-term stability to pH, high pressures, organic solvents and temperatures [3].

The principle of MIPs could be explained best by the lock and key model of Emil Fischer, which says, as a specific key could fit only a specific lock, thus explaining the enzyme-substrate interaction, similarly, a MIP has specific sites in which only a specific analyte could bind. These sites could be made by making an imprint on the polymer material with functional monomers binding on it. The template is washed away and an empty space is left behind where the analyte could specifically bind. These MIPs are coated on different sensors that could be mass-based, electrochemical, optical or thermal [4]. When the analyte binds to MIP, the binding force is increased by the addition of graphene in molecularly imprinted polymers. The transducer detects the change, whether it is optical, electrochemical, mass change, etc. and converts it into an electrical signal. The amplifier in the chemical sensor responds to a very small input signal coming from the transducer and produces a large output signal which contains the important waveform features of an input signal. The signal that has been amplified is then processed through the signal processor where it can be displayed, stored or analyzed later [5–10].

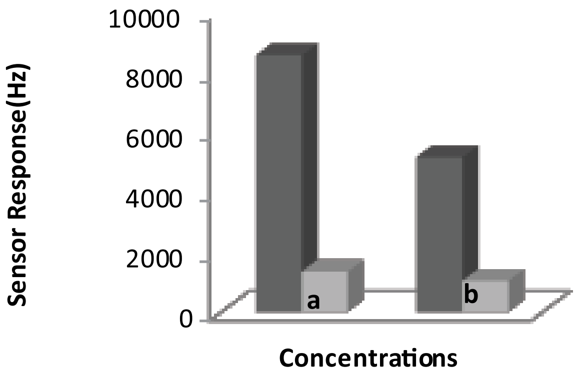


Fig. 1. Polystyrene (MIPs + GO) composite MIPs based sensor response towards 400 and 300 ppm, respectively concentrations of methyl orange and methyl red.

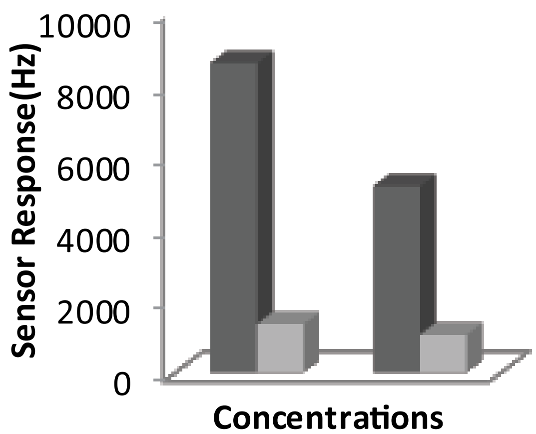


Fig. 2. Polyvinylpyrrolidone MIPs + GO sensor response towards 400 and 300 ppm, respectively concentrations of methyl red and methyl orange.

2. Experimental

2.1. Chemicals

Styrene (St), ethylene glycol dimethacrylate (EGDMA), 2,2-azobis isobutyronitrile (AIBN), vinyl-2-pyrrolidone, bisphenol A, ethanol (95%), methanol (95%), methyl red, methyl orange were purchased from Sigma-Aldrich (Germany) and graphene oxide (GO) which was self synthesized, with maximum available purity and used as received.

2.2. Synthesis of polystyrene MIP

0.5 mL solution of both the analytes were prepared in methanol as a solvent. 0.2 mL of this solution was mixed with 0.01 mL of the monomer, styrene. This mixture was thoroughly shaken on a vortex. 0.2 mL of the cross-linker, bisphenol A and 5 mg of the initiator, AIBN was added to the prepolymerized mixture. This mixture was then polymerized under ultraviolet light for 45 min. The monomer:crosslinker was 40:60.

2.3. Synthesis of polyvinylpyrrolidone MIP

0.5 mL solution of both the analytes were prepared in methanol as a solvent. 0.2 mL of this solution was mixed with 0.01 mL of the monomer, n-vinylpyrrolidone. This mixture was thoroughly shaken on a vortex. 0.2 mL of the cross-linker, EGDMA and 5 mg of the initiator, AIBN were added in the prepolymerized mixture. This mixture was then polymerized under ultraviolet light for 45 min. The monomer:crosslinker was 40:60. The polymer was divided in two half portion and added 1 mg of GO was in one fraction [11–13].

2.4. Coating on quartz crystal microbalance

The diluted solution was spin-coated on one of the two electrodes of the (QCM – quartz crystal microbalance) QCM.02 5 mL of this solution was used for coating. The

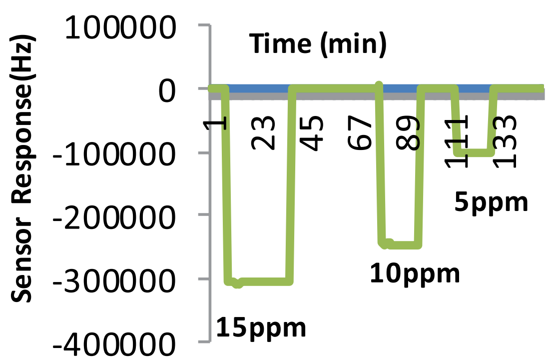


Fig. 3. QCM sensor responses of polyvinylpyrrolidone (MIPs + GO) towards 15, 10 and 5 ppm, respectively concentrations of methyl red.

QCM is then again left under ultraviolet light to ensure polymerization. It is further dried in the oven. The washing of the polymer is done using water. The washed polymer is again dried in the oven at 70°C. This mass-sensitive sensor was then ready to be used.

3. Results

Molecularly imprinted polymers are compared with its composite of graphene oxide and coated on the surface of the mass-sensitive transducer. The sensor's response is noted. And sensitivity and selectivity have been checked by using the molecularly imprinted-based sensor. The sensor response has increased by using a composite of molecularly imprinted-based sensors [14–16].

3.1. Selectivity

The selectivity will be checked by using the other dyes solutions. The selectivity will be checked the MIPs + GO composite and MIPs methyl orange templates with methyl red on 400 and 300 ppm concentration which is explain in the Fig. 1. MIPs-GO sensor lesser response.

In case of MIPs + GO composite based sensor of polystyrene shows more superior result as compared polyvinylpyrrolidone. Polyvinylpyrrolidone (MIPs + GO) composite based sensor and polyvinylpyrrolidone (MIPs). MIPs-GO of polyvinylpyrrolidone highly selective as compared to MIPs of polyvinylpyrrolidone (Fig. 2).

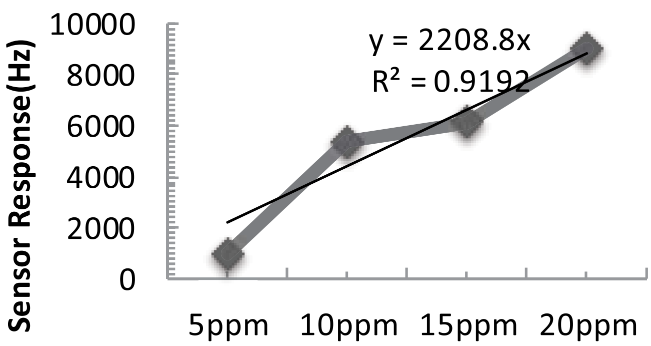


Fig. 4. Regression analysis of sensitivity.

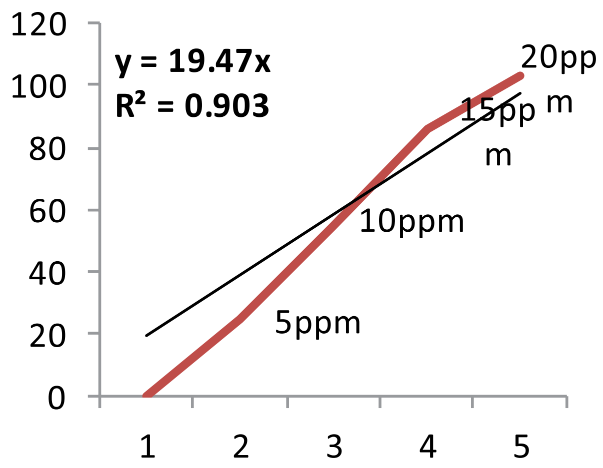


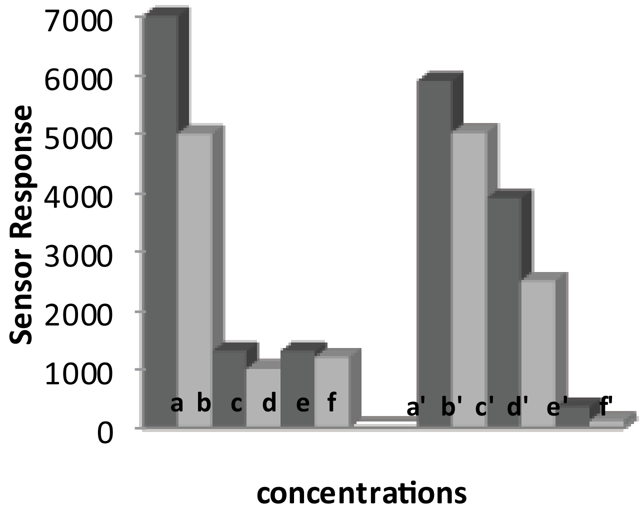
Fig. 5. Regression analysis of sensitivity (polystyrene system).

3.2. Sensitivity

MIPs + GO-based sensor is highly sensitive towards analytes. Sensitivity will be checked by using 15, 10, and 5 ppm of methyl red (Fig. 3). We can online monitor up to 5 ppm. Sensitivity is analyzed by regression analysis in Fig. 4 (polyvinylpyrrolidone-GO based sensor) and Fig. 5 (polystyrene-GO based sensor).

MIPs + GO of polystyrene-based sensors is highly sensitive towards analytes. We can online monitor up to 5 ppm.

The sensitivity of MIPs increases by using the GO composite. We can detect analytes up to 5 ppm.



Polystyrene system MIPS-GO [a] 400 ppm, [b] 300 ppm, selectivity [f] 400 ppm, polystyrene system MIPs [c] 400 ppm, [d] 300 ppm, selectivity [e] 400 ppm, polyvinylpyrrolidone MIPs-GO [a′] 400 ppm, [b′] 300 ppm, selectivity [f′] 400 ppm polyvinylpyrrolidone-MIPs [c′] 400 ppm, [d′] 300 ppm, selectivity [e′] 400 ppm.

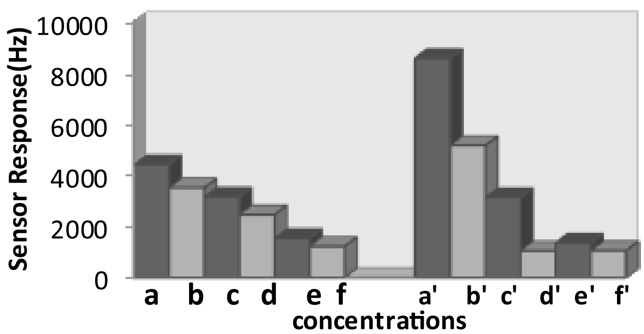


Fig. 7. Polystyrene system MIPS-GO [a] 400 ppm, [b] 300 ppm, selectivity [f] 400 ppm, polystyrene system MIPs [c] 400 ppm, [d] 300 ppm, selectivity [e] 400 ppm, polyvinylpyrrolidone MIPs-GO [a′] 400 ppm, [b′] 300 ppm, selectivity [f′] 400 ppm, polyvinylpyrrolidone-MIPs [c′] 400 ppm, [d′] 300 ppm, selectivity [e′] 400 ppm.

3.3. Comparison study of polystyrene and polyvinylpyrrolidone for methyl red

Two polymeric systems have been used for the online monitoring of methyl red [17–20]. Polystyrene polymers show better results as compare polyvinylpyrrolidone. Composite MIPs with GO shows better results as compared to MIPs. MIPs + GO-based sensor shows more sensitivity and selectivity. The MIPs-GO composite polystyrene towards methyl red show much better response (Fig. 6). MIPs-GO composite polyvinylpyrrolidone is more selective toward to another analyte.

3.4. Comparison study of polystyrene and polyvinylpyrrolidone for methyl orange

Two polymeric systems have been used for the online monitoring of methyl orange. Polystyrene polymers show better results as compared to polyvinylpyrrolidone. Composite MIPs with GO shows better results as compared to MIPs. MIPs + GO-based sensor shows more sensitivity and selectivity [21,22].

Polyvinylpyrrolidone (MIPS-GO based sensor) show better result as compare polystyrene polymer (MIPS-GO based sensor) for methyl orange. MIPs-GO based sensor shows more sensitivity and selectivity. The MIPs-GO composite based sensor Polyvinylpyrrolidone towards methyl orange show much better response (Fig. 7). MIPs-GO composite based sensor polystyrene is more selective toward to another analyte.

4. Discussion

Molecularly imprinted polymers sensors are used for the detection of metals ions, microorganisms [5]. In the present work, molecularly imprinted-based sensors have been prepared for online monitoring of textile dyes in wastewater. Polystyrene and polyvinylpyrrolidone systems have been used for the preparation of the sensing layer for dyes. Molecularly imprinted polymers have been coated on the surface of the mass-sensitive transducers, for example, quartz crystal microbalance. Coated quartz crystal microbalance has been put in quartz crystal microbalance cell which is connected with read-out system [23–27]. QCMs cell has an inlet and outlet. From the inlet added analyte and after taking reading then QCMs were washed and checked the selectivity and sensitivity. Two dyes have been used as templates, for example, methyl red and methyl orange. A composite of molecularly imprinted polymers with graphene oxide has been prepared. This composite has been used for detections of methyl orange and methyl red. Molecularly imprinted polymers are less sensitive as compared to a composite of molecularly imprinted polymers with graphene oxide. The concentrations of molecularly imprinted polymers and graphene oxide have been optimized. The diluted molecularly imprinted polymers were mixed with 1 mg of graphene oxide. The sensitivity and selectivity of the sensor have increased by using composite molecularly imprinted based and graphene oxide. The composite of polystyrene with graphene oxide has shown superior results to the composite polyvinylpyrrolidone. The composite of polystyrene is highly sensitive and selective towards textile dyes.

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