

pH EFFECTS ON REACTIVE ORANGE 16 ADSORPTION OF M-POLY(DIVINYLBENZENE–N-VINYLMIDAZOL) MICROBEADS

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ABSTRACT

In this study, Reactive Orange 16, which is a reactive dye, was investigated by using magnetic poly (DVB-VIM) to determine the effect of pH on adsorption. For this reason, the effect of pH on adsorption has been investigated in detail in pH: 2 and pH: 12. Magnetic poly (DVB-VIM) microbeads were characterized by scanning electron microscopy (SEM), fourier-transform infrared spectroscopy (FTIR) studies and swelling studies.

Keywords: pH, reactive dye, reactive orange 16, magnetic poly (DVB-VIM), adsorption.

INTRODUCTION

The textile industry is the largest dyestuff consumer. [1]. It is known that water quality is greatly influenced by color. Textile industry causes many pollutants. One of the largest pollutants is textile dyestuffs. [2,3]. Textile waste water is ranked among the most harmful pollutants in relation to the high discharge volume, the chemical structures contained therein and the amount of paint passing through the paint during the paint process. [4].

Many dye wastes are toxic and can be carcinogenic [5-7]. The dyes in very low concentrations in water (less than 1 mg/l) are undesirable and bad. [8]. Reactive dyes are the most problematic dyestuffs, especially compared to other dye types. It causes both aesthetic and serious environmental pollution. Because of its toxic effect, it should be completely removed from the waste water because it causes serious health risks for some organisms and human. [8-11]. Dyes can have negative and toxic effects such as skin irritation and cancer in humans. [12-14]. Untreated wastewater causes biological and chemical changes in the water system and thus affects the activities of photosynthesis. [16] These colored compounds are not only aesthetic, they also prevent sunlight from penetrating into the stream and reducing the photosynthetic reaction. [14] Therefore, environmental regulations need to be adhered to before discharge of textile wastewater into the environment and further processing is required. [12,16,17]

Reactive dyes are classified as water soluble azo reactive dyes. Azo dyes are characterized by the presence of N = N, easy to apply and are known for their bright colors. [15]. It also has one or more azo boundaries (-N = N-) and is widely used in many applications due to their solubility, low costs, stability and color variations. [16,17]. Azo reactive dyes with two azo groups are known to be toxic, carcinogenic and mutagenic. [18]. The reactive dyes have very low fixing rates and high concentration of reactive dyes are discharged into the waste water. They are water-soluble and cannot be readily biodegradable and therefore reactive dyes may remain in the waste water even after intensive processing. [19-25].

Reactive dyes are typically azo-based chromophores combined with different types of reactive groups. They are different from all other classes of dye because they are covalently bonded to textile fibers. [26,27] The use of reactive dyes over the last decade is resistant to biodegradation, ie, heat and light under aerobic conditions and biodegradable, which is usually due to poor biodegradation of such dyes (especially those containing azo groups). [28] A wide variety of treatment methods are used to remove dyestuffs from wastewater. [29]. Traditional treatment methods for waste water include biological, chemical and physical methods. [30-32].

Adsorption is widely used in wastewater treatment due to its ability to remove different types of paint, high quality purified water and easy handling. Adsorption technique is the most suitable method for the removal of dyes

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due to its simple design, easy operation and relatively simple regeneration. [33] Several different adsorbent source materials have shown potential for dye adsorption [34] and there is a need to investigate adsorbents with the potential to bind with reactive dyes. The adsorption method is widely used in the removal of synthetic dyes from industrial wastes. [35] Recently, magnetic sorbents have been used to remove some metals from aqueous solutions. These methods are cheap and highly scalable. Moreover, techniques using magnetism are more suitable for automation. [36,37].

Applications of magnetic polymer microspheres have been a new research topic. Magnetic polymer microspheres have high strength because they can benefit from both components: magnetic particles and polymer. Magnetic particles enable fast and easy separation in a magnetic field. Applications of magnetic polymer microspheres have been a new research topic since Dynabeads was successfully synthesized by Professor Ugelstad (Norway). [38].

Magnetic polymers have several potential advantages over conventional approaches. [39]. Magnetic separation is relatively quick and easy, cost effective and highly efficient. To take full advantage of the magnetic separation technology, magnetic carriers with good features are required and indispensable. One is coating or encapsulating magnetic particles with the polymer being performed. The other uses the more widely used monomer polymerization. [40-48].

The magnetic separation technique has some advantages such as high efficiency, cost efficiency. Magnetic carriers usually consist of magnetic nuclei to provide a strong magnetic response and a polymeric shell to provide functional groups and properties suitable for various applications. In addition, magnetite (Fe₃O₄) is widely used as magnetic material due to its excellent magnetic properties, chemical stability and biocompatibility. [49-50].

The aim of this study is to investigate the effect of pH effect on the adsorption capacity of Reactive Orange 16 (RO16) which is a reactive dye using magnetic polymers under optimum experimental conditions.

MATERIAL AND METHODS

MATERIALS

The dye used in this study is Reactive Orange 16. Reactive Orange 16 is an anionic dye and azo belongs to the class. In Table 1 its characteristics are summarized. Its general characteristics are shown. Figure 1.

Table 1. Characterization of Reactive Orange 16 (Lee, Choi ve ark.; 2006)

Generic name	Reactive Orange 16
Molecular Formula	C ₂₀ H ₁₇ N ₃ Na ₂ O ₁₁ S ₃
Molecular weight (g/mol)	617,54
Chemical Name	2-((4-(7-Asetamido-1-Hidroksi-3-Sülfo-2-naftilazo)Fenil) Sülfonil) Etil Sulfat
Application Class	Reactive
Chromophore	Azo
λ max(nm):	494

Divinilbenzene (DVB) was obtained from Aldrich (Steinheim, Germany), and inhibitor was rendered by washing with NaOH solution (3%, w/w) prior to use. 1-Vinyl-imidazole (VIM), (Aldrich, Steinheim, Germany) was distilled under vacuum (74–76°C, 10 mmHg). Benzoyl peroxide (BPO) was obtained from Merck (Darmstadt, Germany). Poly(vinyl alcohol) (PVAL; Mw: 89,000-98,000, 99 % hydrolyzed) was supplied by Sigma- Aldrich (Steinheim, Germany). Magnetite nanopowder (Fe₃O₄; diameter 20–50 nm) was obtained from Aldrich, (Steinheim, Germany). All other reagents were of analytical grade and were used without further purification.

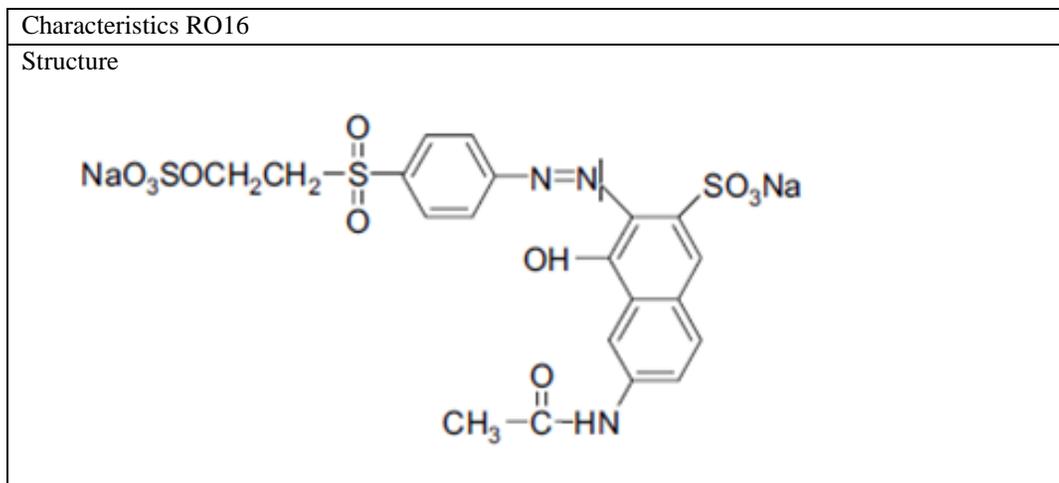


Figure 1. General characteristics of RO16 used dye in this study

SYNTHESIS OF THE m-POLY(DVB-VIM) MICROBEADS

DVB and VIM were copolymerized as initiators and stabilizers by suspension using BPO and poly (vinyl alcohol), respectively. Toluene was included as diluent (as pore former) in the polymerization description. A typical preparation procedure is then exemplified in the article. The sustained environment was prepared by dissolving in poly (vinyl alcohol) (200 mg) purified water (50 ml). To prepare the dispersion phase, DVB (2.9 ml; 20 mmol), magnetite Fe₃O₄ nanopowder (0.5 g) and toluene (10 ml) were stirred at room temperature for 10 minutes. Then, VIM (7.3 ml; 80 mmol) and BPO (100 mg) were dissolved in the homogeneous organic phase. The organic phase was dispersed in aqueous environment by stirring the mixture magnetically (500 rpm) in a closed cylindrical pyrex polymerization reactor. The reactor content was heated to the polymerization temperature (ie 65 ° C) within 4 hours and the polymerization was carried out for 2 hours at a stirring speed of 600 rpm at 80 ° C. The resulting microbeads were washed extensively with ethanol and water to remove any unreacted monomer or diluent, and then dried in a vacuum oven at 50 ° C. The microbeads were then sieved in different sizes. A microscope examination showed that almost all microbeads were completely spherical. Table 2 shows the description and polymerization conditions for the preparation of m-poly (DVBVIM) microbeads.

Table 2. Recipe and polymerization conditions for preparation of the m-poly (DVBVIM) microbeads.

<u>Aqueous Dispersion Phase</u>	<u>Organic Phase</u>
Distilled water: 50 mL	DVB: 2.9 ml; 20 mmol
PVAL : 200 mg	VIM : 7.3 ml; 80 mmol
	Toluene: 10 mL
	BPO : 100 mg
	Fe ₃ O ₄ : 0.5 g
	<u>Polymerization Conditions</u>
	Reactor volume: 100 ml
	Stirring Rate: 600 rpm
	Temperature and Time: first at 65°C for 4 h, and then at 80°C for 2 h

CHARACTERIZATION EXPERIMENTS OF THE m-POLY(DVB-VIM) MICROBEADS

To characterize synthesized the m-poly(DVB-VIM) microbeads, Fourier transform infrared spectrophotometer (FTIR), scanning electron microscopy (SEM) analysis and swelling test were performed.

FTIR ANALYSIS

m-poly(DVB-VIM) microbeads was analysed using a Fourier transform infrared spectrophotometer-FTIR (Shimadzu IR Prestige21). The samples were recorded at room temperature with spectral region of 4,000 to 400 cm^{-1} . The FTIR results are shown Figure 2.

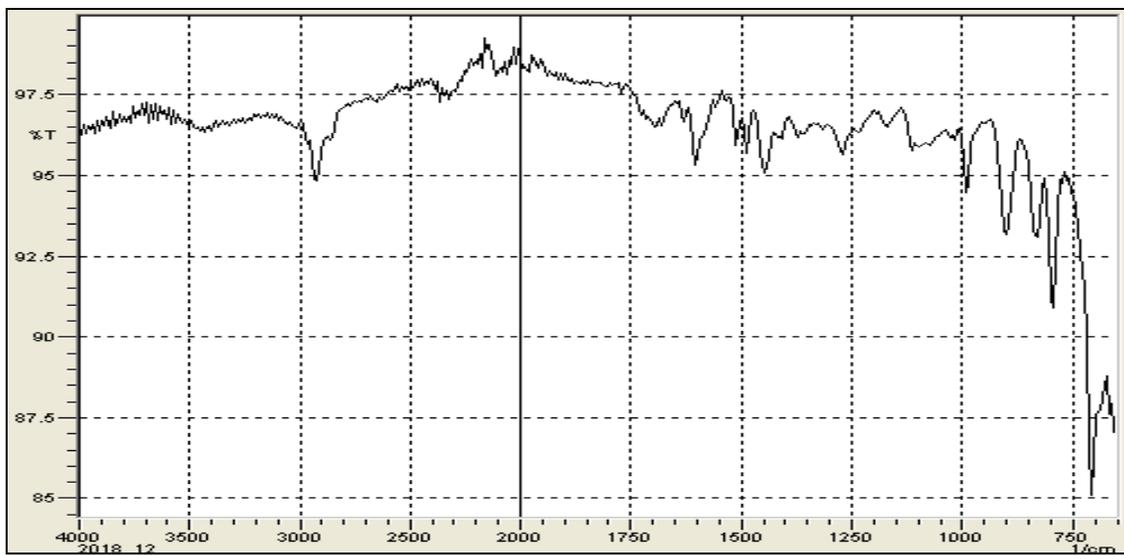


Figure 2. FTIR results of m-poly(DVB-VIM) microbeads.

According to the results obtained from the FT-IR spectrum, the characteristic vibration frequencies in the FT-IR spectrum of the Reactive Orange 16 staining indicate the tension of the OH tension of 2995 cm^{-1} , N = N stretching of 1570 cm^{-1} , the tension of the stretching of SO and SOC. 998 cm^{-1} , 900 cm^{-1} , 848 cm^{-1} , 800 cm^{-1} can also be observed.

SEM ANALYSIS

The surface morphology of the m-poly(DVB-VIM) microbeads were analysed using scanning electron microscopy ((SEM, CARL ZEISS EVO 40, UK). The surface of the samples were then scanned at the desired magnification to study the morphology of the microbeads. The SEM micrographs of the m-poly(DVB-VIM) microbeads are illustrated in Figure 3 (a) and Figure 3(b). All the m-poly(DVB-VIM) microbeads have a spherical form and rough surface.

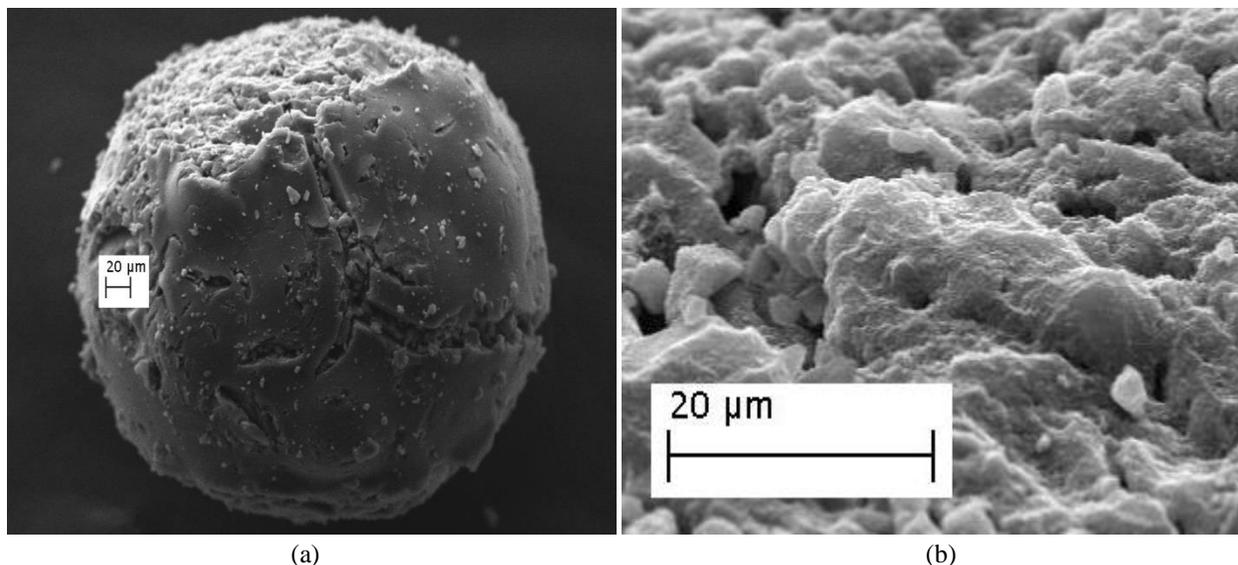


Figure 3. SEM micrographs of the m-poly(DVB-VIM) microbeads in (a) and (b).

SWELLING TEST

Water uptake ratio of the m-poly(DVB-VIM) beads was determined in distilled water. The experiment was conducted as follows—initially dry beads were carefully weighed before being placed in a 50ml vial containing distilled water. The vial was put into an isothermal water bath with a fixed temperature (25 ± 0.5 °C) for 2 h. The bead sample was taken out from the water, wiped using a filter paper, and weighed. The weight ratio of dry and wet samples was recorded. The equilibrium-swelling ratio for the m-poly(DVB-VIM) microbeads is 41%.

MAGNETIC FE₃O₄ CONTENT TEST

Magnetic characteristics of magnetic materials are related to their type generally, while those of non-magnetic materials are usually related to the content of magnetic component inside. So, Fe₃O₄ content is very important to the magnetic responsibility of magnetic materials. In general, the higher Fe₃O₄ content shows the stronger magnetic responsibility (Şenel et al. 2008). For this reason, the average Fe₃O₄ content of the m-poly(DVB-VIM) microbeads was determined by density analysis. The hydrated density of the m-poly(DVB-VIM) microbeads measured at 25 °C was 1.43 g/ml. By the same procedure, the density of Fe₃O₄ particles was found to be 4.89 g/ml at 25 °C. The density of non-magnetic poly(DVB-VIM) microbeads measured at 25 °C was 1.02 g/ml. The magnetic particles volume fraction in the mesoporous m-poly(DVB-VIM) microbeads can be calculated from the following equation derived from the mass balance:

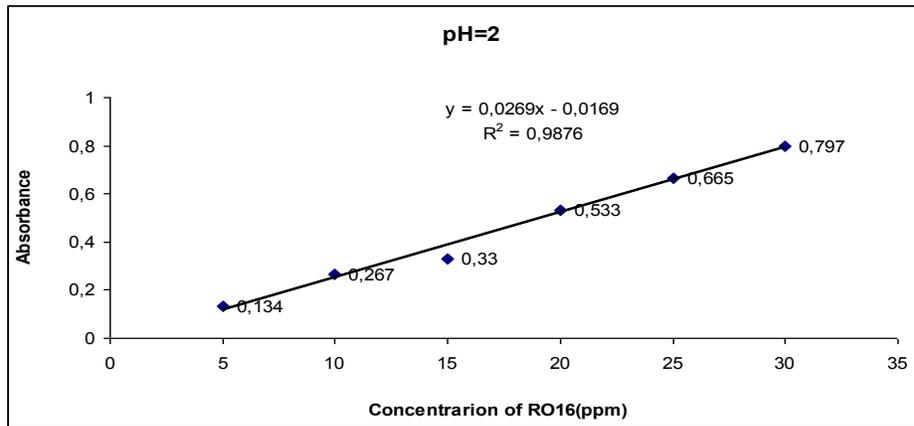
$$\phi = (\rho_C - \rho_M) / (\rho_C - \rho_A) \quad (1)$$

where, ρ_A , ρ_C and ρ_M are the densities of non-magnetic poly(DVB-VIM) microbeads, Fe₃O₄ nanopowder, and the m-poly(DVB-VIM) microbeads, respectively. Thus, with the density data mentioned above, the m-poly(DVB-VIM) microbeads gel volume fraction in the magnetic beads was estimated to be 89.4%. Therefore, the average Fe₃O₄ content of the resulting m-poly(DVB-VIM) microbeads was 10.6%.

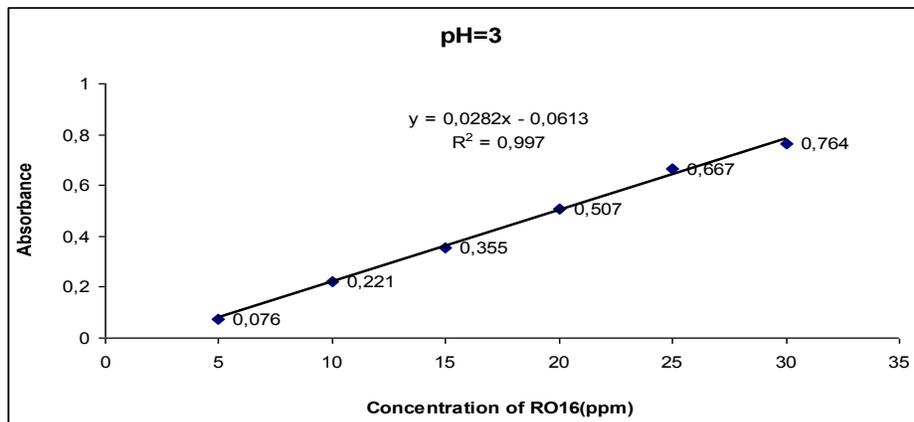
RESULTS AND DISCUSSION

Linear regression analysis of pH effects are very important factor that affects the adsorption process. The linear regression analysis of pH effects on RO16 adsorption of the m-poly(DVB-VIM) microbeads are shown. In this study, the linear regression analysis of pH effects on adsorption has been examined in detail in pH (2-12). To

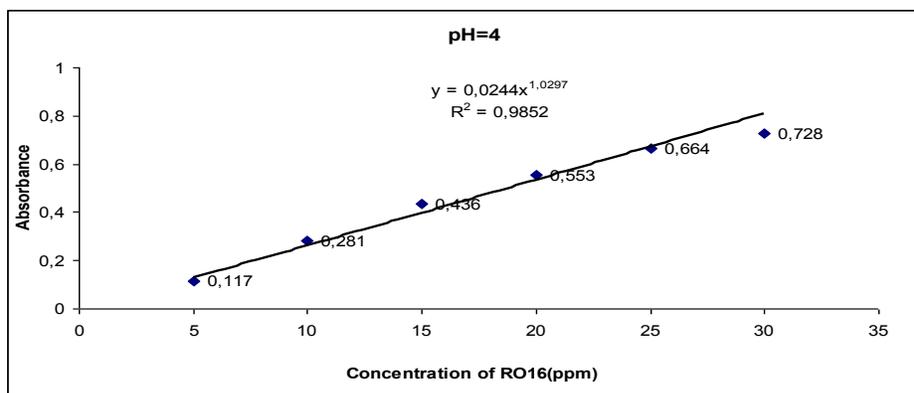
determine the optimum pH, pH was changed in the range of (2-12). Figure 4 (a), (b), (c), (d), (e), (f), (g), (h), (i), (j), and (k) show the linear regression analysis of pH effects of RO16 concentrations.



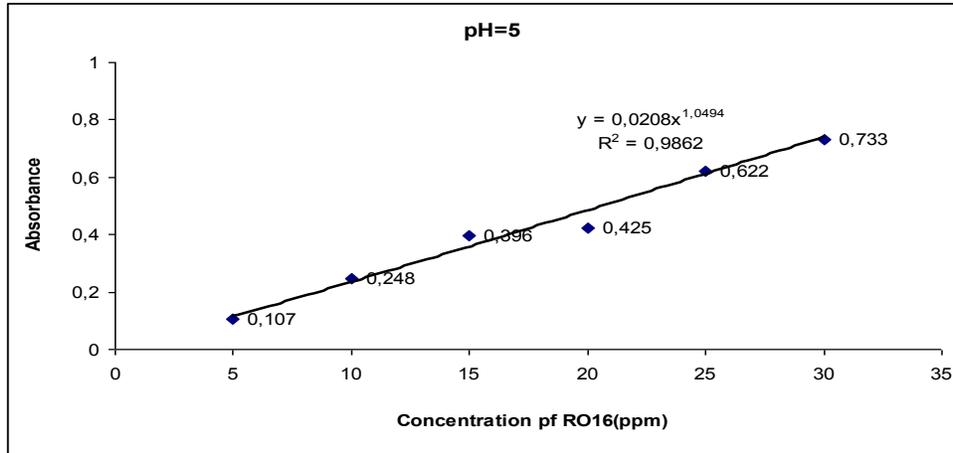
(a)



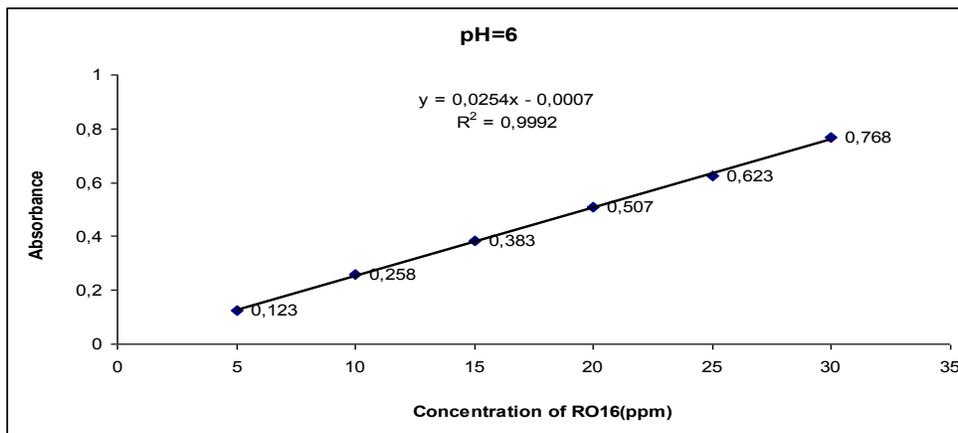
(b)



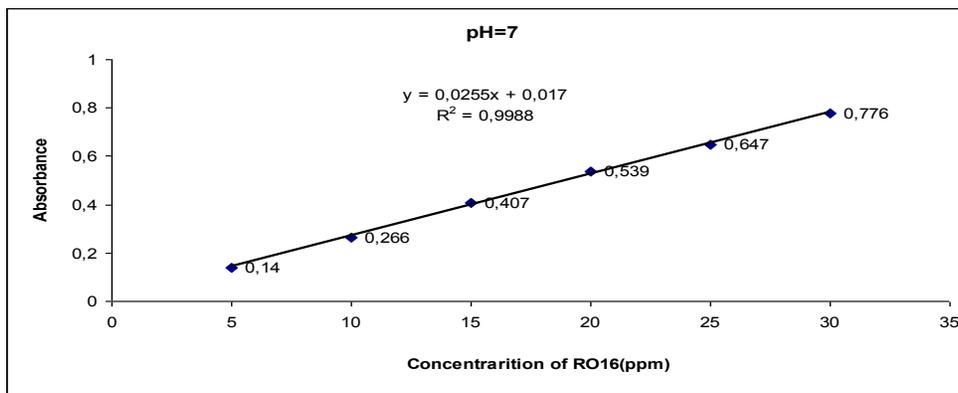
(c)



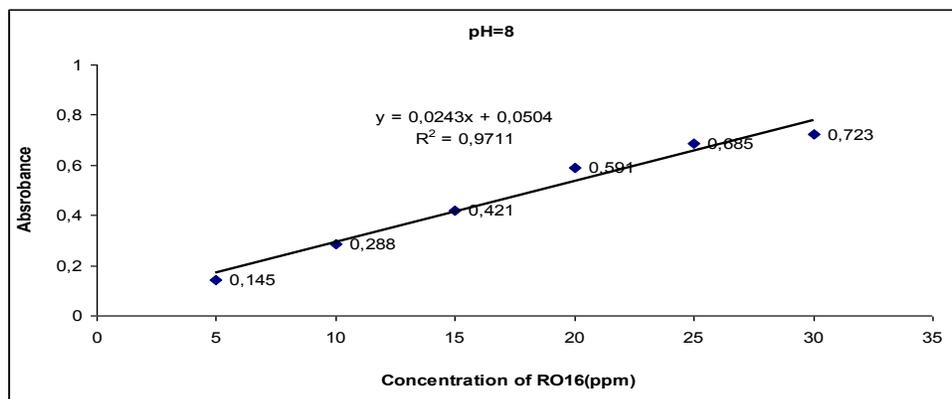
(d)



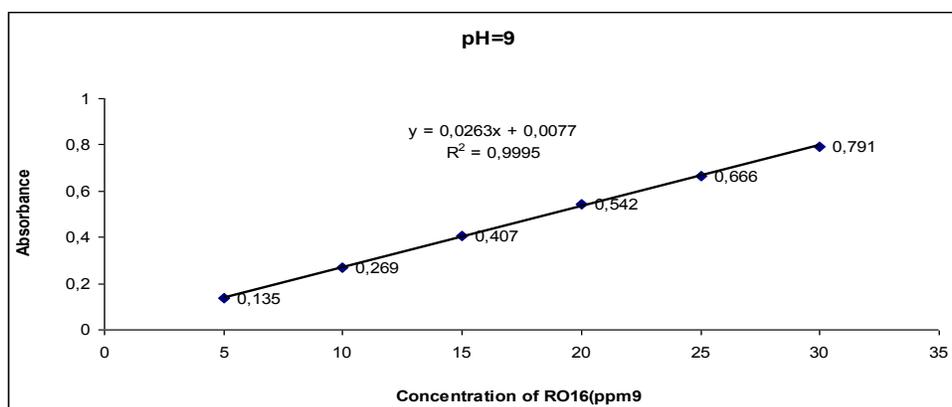
(e)



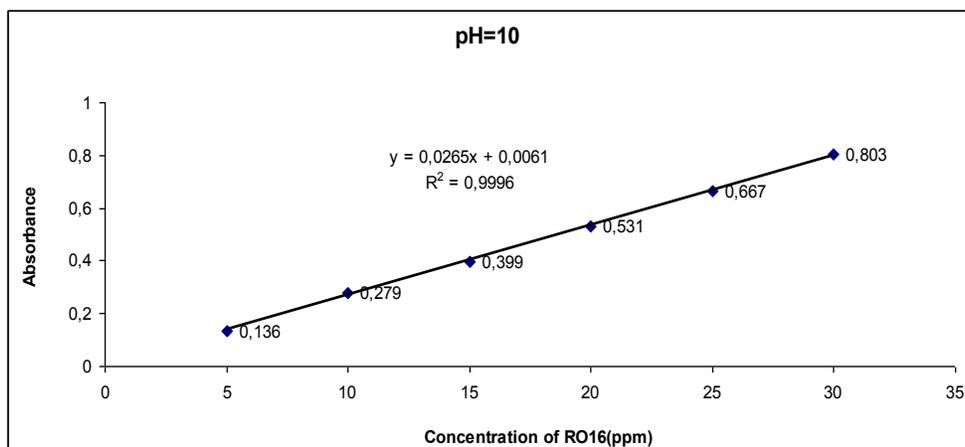
(f)



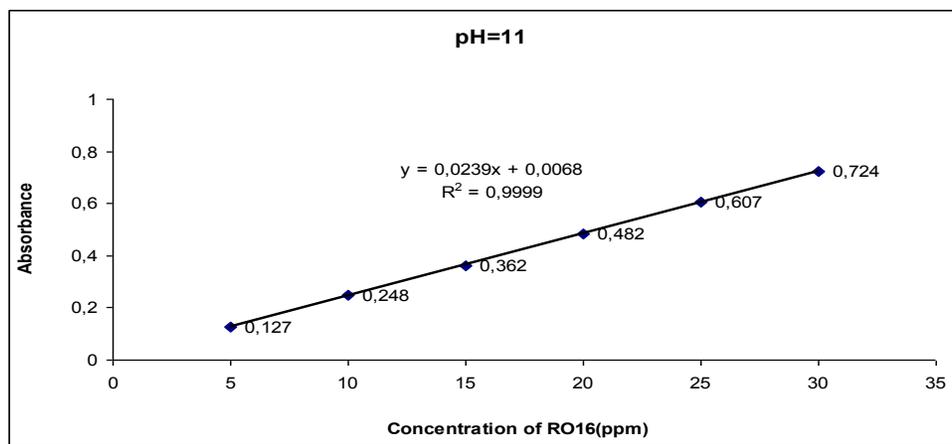
(g)



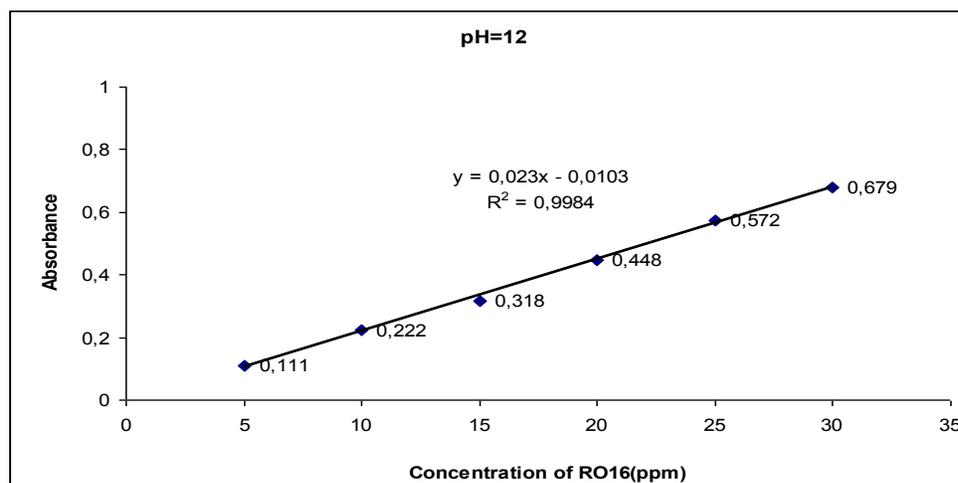
(h)



(i)



(j)



(k)

Figure 4. The linear regression analysis of pH effects of RO16 concentrations in (a), (b), (c), (d), (e), (f), (g), (h), (i), (j), and (k).

From this added linear regression analysis values, the maximum adsorption at which pH was calculated. The results are depicted in Figure 5, showing that the maximum adsorption on the m-poly(DVB-VIM) microbeads are 4.73 m g g⁻¹ occurred at pH 2, it dropped to 1.63 m g g⁻¹ at pH of 12.0, respectively. The adsorption RO16 of the m-poly(DVB-VIM) microbeads increases with decreasing pH.

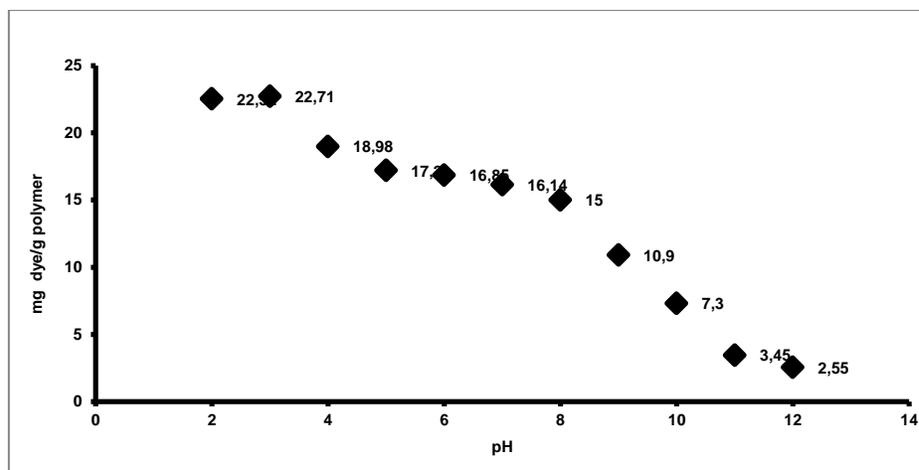


Figure 5. Effect of pH on adsorption of RO16 of the m-poly(DVB-VIM) microbeads (initial solution concentration: 30 mg L^{-1} ; temperature: $4 \text{ }^\circ\text{C}$).

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