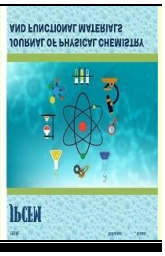
Journal of Physical Chemistry and Functional Materials

Home Page of Journal: https://dergipark.org.tr/jphcfum



Temperature Effects on the Adsorption with Microbeads In Reactive Black 5 m-Poly (EGDMA-VIM)

[a] *B.E. Kaplan* *, [b] *A. Kara*, [a] *H.A. Eren*

[a] *Department of Textile Engineering, University of Bursa Uludag, 16059 Bursa Turkey*

[b] *Department of Chemistry, University of Bursa Uludag, 16059 Bursa Turkey*

Received: 19-May-2019, **Accepted**: 24-May-2019
ISSN: 2651-3080

ABSTRACT

In this study m-poly(ethylene glycol dimethacrylate-vinyl imidazole) [m-poly(EGDMA–VIM)] microbeads were employed as adsorbent for reactive dye black 5. Temperature effects of reactive black 5, from aqueous solutions were studied by adsorption on m-poly(EGDMA-VIM). The m-poly(EGDMA-VIM) microbeads were synthesized and characterized; their use as adsorbent of temperature effects were investigated. The m-poly (EGDMA-VIM) microbeads were characterized by scanning electron microscope (SEM), Fourier-transform infrared spectroscopy (FTIR) studies and swelling studies. In this study, the effects of temperature on adsorption were investigated. In this study, 4, 25, 45 and 65 degree temperatures were studied.

ARTICLE INFO

Keywords:

pH
temperature
reactive dye
reactive black 5
m-poly(EGDMA-VIM)
adsorption

1. Introduction

Many important sources of environment contamination are synthesis of dye, leather, cosmetics, papers, food processing, pulp mill, pharmaceuticals, and plastics industries [1].

The water contaminated by dye at even a concentration of 1.0 mg/L would cause a change in color and make it improper for human usage. [2].

Reactive dye is one of the most important identified contaminants among the various dye pollutants of industrial effluents. Due to its good solubility, reactivity, high toxicity and possible accumulation in the environment, Reactive dye is a common water pollutant and it may frequently be found in trace quantities in industrial wastewater [3-4].

Reactive dyes have been extensively used in many industries such as textile. [5-7]. Although the exact number and amount of dyes produced in the world is not known,it is estimated to be more than 100,000 commercially available dyes with over of dye-stuff produced annually [5-8]

Large volumes of water are consumed by textile industries for wet processing of textiles. [9]

Discharging dyes to water sources can cause a number of problems as they have serious health risks on living organisms. [10]

Azo reactive dyes, which have two azo groups, represent about half of all reactive dyes such as RB 5. These types of dyes are known to be toxic, carcinogenic, and mutagenic. Their removal from the environment can result in nonaesthetic pollution. Moreover, these dyes are not easily degraded by conventional aerobic wastewater treatment due to their recalcitrance [11].

However, it has to be emphasized that the overwhelming majority of synthetic dyes currently used are the highly water soluble azo reactive dyes. Azo dyes are characterized by the existence of nitrogen nitrogen double bonds and the presence of bright colour is due to these azo bonds and associated chromospheres. Even the presence of very low concentrations of dyes (less than 1 mg/l) in the effluent is highly visible and is considered undesirable. These reactive dyes are the most problematic compared to other forms of dyes and must be removed from wastewater completely. These synthetic dyes cause considerable environmental pollution, are toxic to some aquatic organisms and are of serious health risk to human beings. They lead to greater public concern and present legislation problems. However, removal of these dyes from wastewater is a major environmental challenge and there is a constant need to have an effective process that can efficiently remove these dyes. Moreover, tightening government legislation is enforcing to treat textile wastewater to an increasingly high standard. [12].

Removal of azo dyes from colored effluents due to their complex composition, toxicity, poor degradability and high solubility, have attracted great interest in the last few years. [13].

Wastewater industries may contain a variety of organic compounds and toxic substances that exhibit toxic effects for microbial populations and can be toxic and carcinogenic for animals [14].

Several methods which treat dye wastewater with various biological, chemical, and physical technologies prove to be very useful for environmental purification. [15]

There are many processes available for the removal of dye by conventional treatment technologies.[16-19].Remove dyes from wastewaters, there are various methods of development, including chemical oxidation, biodegradation, ultrafiltration , and adsorption [20-27].

However, most of the dyes used in the textile industry are difficult to remove by conventional physicochemical and biological treatment methods, since they are stable against the light and oxidizing agents and resist biodegradation.[28].

The adsorption technique is the most favorable method for the removal of dyes because of its simple design, easy operation, and relatively simple regeneration [29].

Adsorption process has been extensively examined for the elimination of the organic substances or heavy metal ions from water and waste water [30].

The applications of magnetic polymer microspheres became a new topic of research. Magnetic polymer microsphere indeed has its strength because it can be benefit from both components: magnetic particles and polymer. The magnetic particles make the rapid and facile separation possible in an external magnetic field [31].

The aim of this study is to investigate the effect of pH effect on the adsorption capacity of Reactive Black 5(RB5) which is a reactive dye using magnetic polymers under change temperature conditions.

2. Material and Methods

2.1 Materials

The dye used in this study is Reactive Black 5, obtained from a textile form in Turkey. In Table 1 its characteristics are summarized. Its general characteristics are shown in Figure 1. Absorbance values were recorded at the corresponding maximum absorbance wavelength [32]

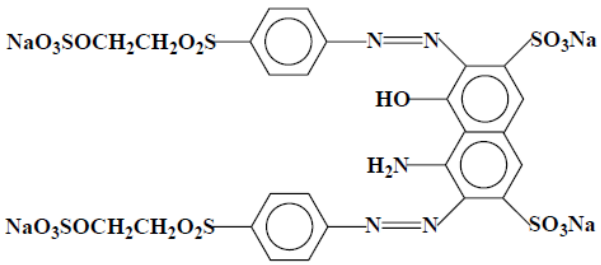


Figure 1. General characteristics of RB5 [33]

Table 1. Characterization of Reactive Black5 [32]

Generic name	CI Reactive Black 5
Formula	C26H21N5Na4O19S6
Percentage of pure dye	66
Anchor	Vinylsulfone
Chromophore	Azo
λmax, nm	598
Molecular weight (g/mol)	991.82

Ethylene glycol dimethacrylate (EGDMA) was obtained from Merck (Darmstadt, Germany), purified by passing through active alumina and stored at 48◦Cuntil use.N-Vinyl imidazole (VIM, Aldrich, Steinheim, Germany) was distilled under vacuum (74–76°C, 10 mm Hg). Benzoyl peroxide (BPO) was obtained from Merck (Darmstadt, Germany). Poly(vinyl alcohol) (PVAL;Mw: 100.000, 98% hydrolyzed) was supplied from Aldrich Chem. Co. (USA).Magnetite nanopowder (Fe_3O_4, diameter: 20–50 nm) was obtained from Sigma. All other chemicals were of reagent grade and were purchased from Merck AG (Darmstadt, Germany).

2.2 Synthesis of the m-poly(EGDMA-VIM) Microbeads

EGDMA and VIM were polymerized in suspension by using BPO and poly(vinyl alcohol) as the initiator and the stabilizer, respectively. Toluene was included in the polymerization recipe as the diluent (as a pore former). A typical preparation procedure was examplified below. Continuous medium was prepared by dissolving poly(vinyl alcohol) (200 mg) in the purified water (50 ml). For the preparation of dispersion phase, EGDMA (4 ml) and toluene (4 ml) were stirred for 15 min at room temperature. Then, VIM (3 ml) and BPO (100 mg) were dissolved in the homogeneous organic phase. The organic phase was dispersed in the aqueous medium by stirring the mixture magnetically (400 rpm), in a sealed-cylindrical pyrex polymerization reactor. The reactor content was heated to polymerization temperature (i.e., 70°C) within 4 h and the polymerization was conducted for 2 h with a 600 rpm stirring rate at 90 °C. Final beads were extensively washed with ethanol and water to remove any unreacted monomer or diluent and then stored in distilled water at 4 °C. [35]

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

Aqueous Dispersion Phase	**Organic Phase**	**Polymerization Conditions**
Distilled water: 50 mL PVAL : 200 mg	EGDMA: 4 ml VIM : 3 mL Toluene: 10 mL BPO : 100 mg Fe_3O_4: 0.5 g	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

2.3 Characterization Experiments of the m-poly (EGDMA-VIM) Microbeads

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

2.3.1. FTIR Analysis

m-poly(EGDMA-VIM) microbeads was analyzed 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.

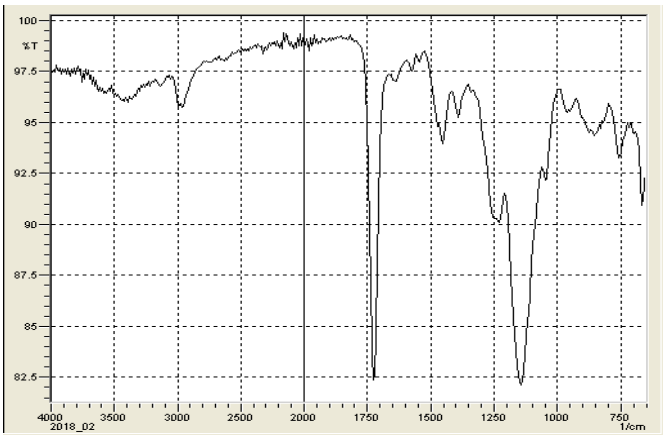
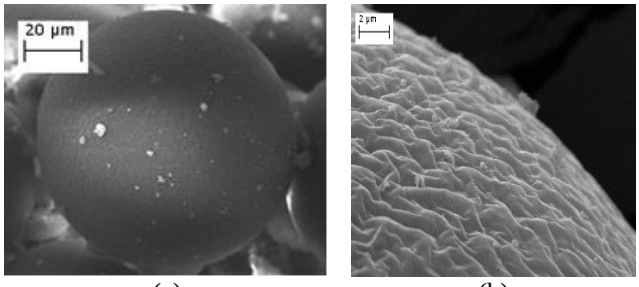


Figure 2. FTIR results of m-poly (EGDMA-VIM) microbeads.

Figure 2 illustrates the infrared spectrum measured for chitosan. Its absorption band at 3502 cm-1 is rather intense as a consequence of OH and water stretching vibrations, whereas the band at 2995 cm-1 corresponds to C-H stretching vibrations. The bands at 1730 and 1380 cm-1 may be attributed to deformation vibrations of medium intensity of N-H bonds from primary amines and of low intensity from C-H bonds of the CH3 group. Small contents of residual acetamide groups may be found in the polymeric chain as a consequence of incomplete deacetylation of chitosan. The band at 1050 cm-1 corresponds to the stretching vibrational of C-O bonds from primary alcohol [36].

2.3.2. SEM Analysis

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



(a) (b)

Figure 3. SEM photomicrographs: (a) m-poly(EGDMA-VIM) microbeads at 20 µm;(b) external surface at 2 µm

2.3.3. Swelling test

Water uptake ratio of the m-poly(EGDMA–VIM) beads was determined in distilled water. The experiment was conducted as follows—initially dry beads were carefully weighed before being placed in a 50 ml 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(EGDMA–VIM) microbeads is 36%.

2.3.4. Magnetic Fe3O4 Content Test

Magnetic characteristics of magnetic materials are related to their type generally, while those of magnetic materials are usually related to the content of magnetic component inside. So, Fe_3O_4 content is very important to the magnetic responsibility of magnetic materials. In general, the higher Fe_3O_4 content shows the stronger magnetic responsibility [36]. (Şenel et al. 2008). For this reason, the average Fe_3O_4 content of the m-poly(EGDMA-VIM) microbeads was determined by density analysis. The hydrated density of the m-poly(EGDMA-VIM) microbeads measured at 25°C was 1.60 g/ml. By the same procedure, the density of Fe_3O_4 particles was found to be 4.89 g/ml at 25°C.The density of non-magnetic poly(EGDMA-VIM) microbeads measured at 25°C was 1.05 g/ml. The magnetic particles volume fraction in the mesoporous m-poly(EGDMA-VIM) microbeads can be calculated from the following equation derived from the mass balance:

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

where, dA, dC and dM are the densities of non-magnetic poly(DVB-VIM) microbeads, Fe_3O_4 nanopowder, and the m-poly(EGDMA-VIM) microbeads, respectively. Thus, with the density data mentioned above, the m-poly(EGDMA-VIM) microbeads gel volume fraction in the magnetic beads was estimated to be 85.7%. Therefore, the average Fe_3O_4 content of the resulting m-poly(EGDMA-VIM) microbeads was 14.3%.[37].

3 Results and Discussion

This section discussed on effect of temperature on the adsorption of RB5 in the range 4 to 65 °C and the results are presented in Figure 4(a),(b),(c) and (d).

Maximum reactive black 5 adsorption to m-poly (EGDMA-VIM) microspheres in the experiments was observed at pH 2.0. The relationship between the amount of reactive black 5 adsorbed to the polymer microbeads and the starting pH is shown in Figure 4(a),(b),(c) and (d).The adsorption values of pH 2- pH 12 at 25,25,45 and 65°C are given in the Table 3-Table 6.

The adsorption values from pH 2 to pH 12 at 4°C are shown in the Figure 4(a). The adsorption values of pH 2- pH 12 at 25°C are given in the Table 3.

When the initial pH value of the solution of Reactive black 5 is increased from 2.0 to 12.0; The amount of reactive black 5 which is adsorbed per unit mass of adsorbent is decreasing. For example; When the pH value is increased from 2.0 to 12.0, the amount of reactive black 5 adsorbed per adsorbent decreases from 25.55 mg / g to 4.49 mg / g.

Table 3. The adsorption values of pH 2- pH 12 at 4°C

*Reactive Black 5 *m-poly(EGDMA-VIM)-Fe3O4	Start conditions =30 ppm
pH	**mg/g**
2	25,55
3	24,85
4	21,52
5	20,90
6	19,43
7	18,09
8	16,04
9	11,6
10	9,78
11	5,10
12	4,49

The adsorption values from pH 2 to pH 12 at 25°C are shown in the Figure 4(b). The adsorption values of pH 2- pH 12 at 25°C are given in the Table 4.

When the initial pH value of the solution of Reactive black 5 is increased from 2.0 to 12.0; the amount of reactive black 5 which is adsorbed per unit mass of adsorbent is decreasing. For example; When the pH value is increased from 2.0 to 12.0, the amount of reactive black 5 adsorbed per adsorbent decreases from 28,35 mg / g to 6,4 mg / g.

Table 4. The adsorption values of pH 2- pH 12 at 25°C

*Reactive Black 5 *m-poly(EGDMA-VIM)-Fe3O4	Start conditions =30 ppm
pH	**mg/g**
2	28,35
3	28,02
4	23,76
5	22,8
6	20,34
7	19,96
8	18,75
9	13,5
10	11,69
11	7,5
12	6,4

The adsorption values from pH 2 to pH 12 at 45°C are shown in the Figure 4(c). The adsorption values of pH 2- pH 12 at 25°C are given in the Table 5.

When the initial pH value of the solution of Reactive black 5 is increased from 2.0 to 12.0; The amount of reactive black 5 which is adsorbed per unit mass of adsorbent is decreasing. For example; When the pH value is increased from 2.0 to 12.0, the amount of reactive black 5 adsorbed per adsorbent decreases from 28,98 mg / g to 8,6 mg / g.

Table 5. The adsorption values of pH 2- pH 12 at 45°C

*Reactive Black 5	Start conditions =30 ppm
*m-poly(EGDMA-VIM)-Fe3O4	
pH	**mg/g**
2	28,98
3	28,62
4	24,9
5	24,14
6	22,7
7	21,35
8	19,71
9	15,67
10	13,88
11	9,01
12	8,6

The adsorption values from pH 2 to pH 12 at 65°C are shown in the Figure 4(d). The adsorption values of pH 2- pH 12 at 25°C are given in the Table 6.

When the initial pH value of the solution of Reactive black 5 is increased from 2.0 to 12.0; The amount of reactive black 5 which is adsorbed per unit mass of adsorbent is decreasing. For example; When the pH value is increased from 2.0 to 12.0, the amount of reactive black 5 adsorbed per adsorbent decreases from 29,4 mg/g to 10,3mg/g.

Table 6. The adsorption values of pH 2- pH 12 at 65°C

*Reactive Black 5 *m-poly(EGDMA-VIM)-Fe3O4	Start conditions =30 ppm
pH	**mg/g**
2	29,4
3	28,99
4	26,34
5	25,71
6	23,66
7	22,07
8	20,05
9	17,18
10	15,12
11	11,8
12	10,3

4. Conclusion

In this study m-poly(ethylene glycol dimethacrylate-vinyl imidazole) [m-poly(EGDMA–VIM)]microbeads were employed as adsorbent for reactive dye black 5. Adsorption technology enables the use of polymeric microbeads for rapid.m-poly(EGDMA–VIM) were prepared and, was applied to the removal of reactive black 5 from aqueous solutions.

Temperature effects of reactive black 5, from aqueous solutions were studied by adsorption on m-poly(EGDMA-VIM). The m-poly (EGDMA-VIM) microbeads were synthesized and characterized; their use as adsorbent of temperature effects were investigated. The m-poly(EGDMA-VIM) microbeads were characterized by scanning electron microscope (SEM), fourier-transform infrared spectroscopy (FTIR)

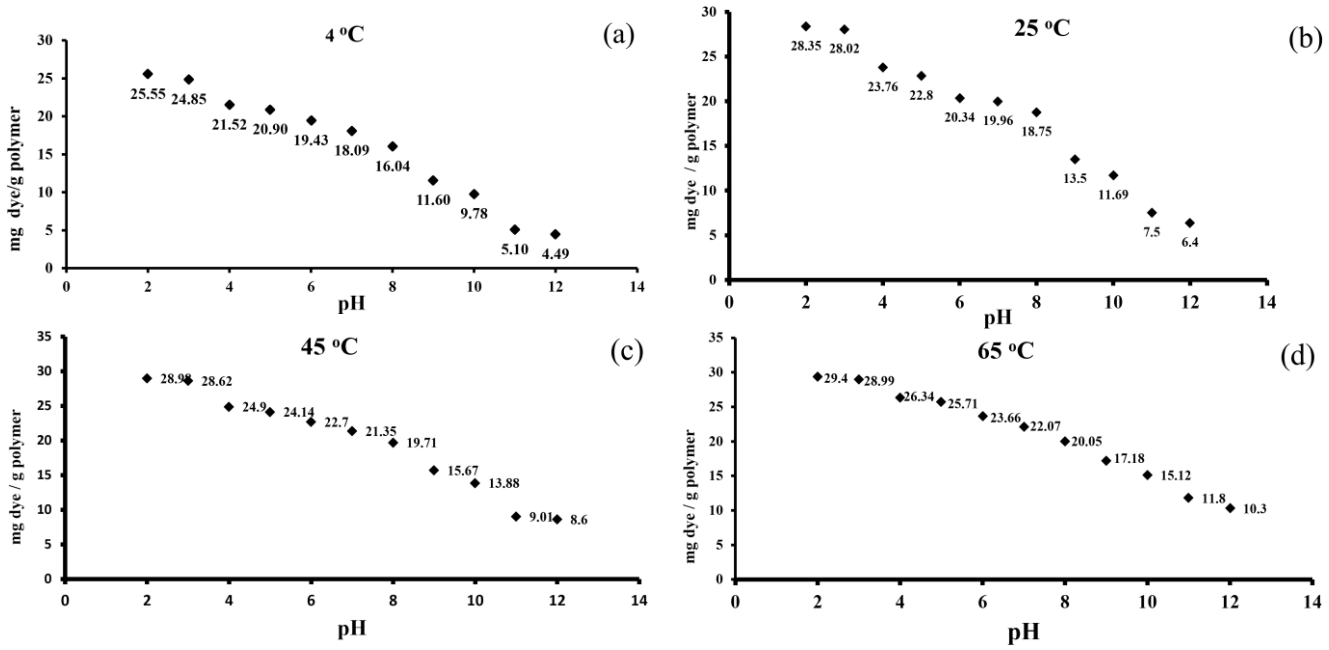


Figure 4(a) pH effect of RB5 adsorption of m-poly (EGDMA-VIM) microbeads at 4°C. **(b)** pH effect of RB5 adsorption of m-poly (EGDMA-VIM) microbeads at 25°C. **(c)** pH effect of RB5 adsorption of m-poly (EGDMA-VIM) microbeads at 45°C. **(d)** pH effect of RB5 adsorption of m-poly (EGDMA-VIM) microbeads at 65°C.

studies and swelling studies. In this study, the effects of temperature on adsorption were investigated. In this study, 4, 25, 45 and 65 °C temperatures were studied.

In this study for this reason, the effect of temperature on adsorption has been investigated in detail in pH: 2 and pH: 12. Maximum reactive black 5 adsorption to m-poly (EGDMA-VIM) microspheres in the experiments was observed at pH 2.0. Also, maximum reactive black 5 adsorption to m-poly (EGDMA-VIM) microspheres in the experiments was observed at 25.

Our results suggest that m-poly(EGDMA–VIM) can be good reactie black 5 adsorbers and have great potential applications in environmental protection.

REFERENCES

[1] Y. Yao, F. Xu, M. Chen, Z. Xu, and Z. Zhu, "Adsorption behavior of methylene blue on carbon nanotubes," Bioresource Technology, vol. 101, no. 9, pp. 3040–3046, 2010

[2]. R. Malik, D. S. Ramteke and S. R. Wate, Adsorption of malachite green on groundnut shell waste based powdered activated carbon, Waste Manage., 2007, 27, 1129–1138.

[3]. Y. Zhang, P. Su, J. Huang, Q. Wang and B. Zhao, A magnetic nanomaterial modi ıı ed with poly-lysine for efficient removal of anionic dyes from water, Chem. Eng. J., 2015, 262, 313–318.

[4] M. Shanehsaz, S. Seidi, Y. Ghorbani, S. M. R. Shoja and S. Rouhani, Polypyrrole-coated magnetic nanoparticles as an efficient adsorbent for RB19 synthetic textile dye: Removal and kinetic study, Spectrochim. Acta, Part A, 2015,149, 481–486.

[5] Forgacs E, Cserhati T, Oros G. Removal of synthetic dyes from wastewaters: a review. Environ Int 2004;30:953-71.

[6] Papic S, Koprivanac N, Bozic AL, Metes A. Removal of some reactive dyes from synthetic wastewater by combined Al(III) coagulation/carbon adsorption process. Dyes Pigments 2004;62:293-300.

[7] Nakagawa K, Namba A, Mukai SR, Tamon H, Ariyadejwanich P,Tanthapanichakoon W. Adsorption of phenol and reactive dye from aqueous solution on activated carbons derived from solid wastes. Water Res 2004;38:1791-8.

[8] Kim TH, Park CH, Shin EB, Kim SY. Decolorization of disperse and reactive dye solutions using ferric chloride. Desalination 2004;161:49-58.

[9]- M. L. Parisi, E. Fatarella, D. Spinelli, R. Pogni and R. Basosi, Environmental impact assessment of an eco-efficient production for coloured textiles, J. Cleaner Prod., 2015, 108,514–524.

[10] A. C. S. Rocha, M. A. Reis-Henriques, V. Galhano, M. Ferreira and L. Guimar˜aes, Toxicity of seven priority hazardous and noxious substances (HNSs) to marine organisms: Current status, knowledge gaps and recommendations for future research, Sci. Total Environ., 2016, 542, 728–749.

[11] S. Chatterjee, S.-R. Lim, and S. H. Woo, "Removal of reactive black 5 by zero-valent iron modified with various surfactants,"Chemical Engineering Journal, vol. 160, no. 1, pp. 27–32, 2010.

[12] Vandevivere PC, Bianchi R, Verstrete W. Treatment and reuse of wastewater from wet-processing industry:

review of emerging technologies. J Chem Technol Biotechnol 1998;72:289e302

[13]. Q. Baocheng, Z. Jiti, X. Xuemin, Z. Chunli, Z. Hongxia and Z. Xiaobai, "Adsorption behavior of Azo Dye C. I. Acid Red 14 in aqueous solution on surface soils", J. Env. Sci., 20 (2008) 704.

[14] X. Han, W. Wang, and X. Ma, "Adsorption characteristics of methylene blue onto low cost biomass material lotus leaf," Chemical Engineering Journal, vol. 171, no. 1, pp. 1–8, 2011.

[15] J. He, S. Hong, L. Zhang, F. Gan, and Y. S. Ho, "Equilibrium and thermodynamic parameters of adsorption of methylene blue 10 Journal of Nanomaterials onto rectorite," Fresenius Environmental Bulletin A, vol. 19, no.

[16] Forgacs E, Cserhati T, Oros G. Removal of synthetic dyes from wastewaters: a review. Environ Int 2004;30:953e71.

[17] Papic S, Koprivanac N, Bozic AL, Metes A. Removal of some reactive dyes from synthetic wastewater by combined Al(III) coagulation/carbon adsorption process. Dyes Pigments 2004;62:293e300.

[18] Kim TH, Park CH, Shin EB, Kim SY. Decolorization of disperse and reactive dye solutions using ferric chloride. Desalination 2004;161:49e58.

[19]Nakagawa K, Namba A, Mukai SR, Tamon H, Ariyadejwanich P,Tanthapanichakoon W. Adsorption of phenol and reactive dye from aqueous solution on activated carbons derived from solid wastes. Water Res 2004;38:1791e8.

[20] L. Chengtang, X. Hui, L. Huaming, L. Ling, X. Li, and Y.Zhixiang, "Efficient degradation of methylene blue dye by catalytic oxidation using the Na8Nb6O19 ·13H2O/H2O2 system,"Korean Journal of Chemical Engineering, vol. 28, no. 4, pp. 1126– 1132, 2011.

[21] S. A. Ong, E. Toorisaka, M. Hirata, and T. Hano, "Biodegradation of redox dye methylene blue by up-flow anaerobic sludge blanket reactor," Journal of Hazardous Materials B, vol. 124, no. 1–3, pp. 88–94, 2005.

[22] A. K. Golder, N.Hridaya, A. N. Samanta, and S. Ray, "Electrocoagulation of methylene blue and eosin yellowish using mild steel electrodes," Journal of Hazardous Materials, vol. 127, no. 1–3, pp. 134–140, 2005.

[23] I. Fatimah, S.Wang, and D.Wulandari, "ZnO/montmorillonite for photocatalytic and photochemical degradation ofmethylene blue," Applied Clay Science, vol. 53, no. 4, pp. 553–560, 2011.

[24] G. Muthuraman, T. T. Teng, C. P. Leh, and I.Norli, "Extraction and recovery of methylene blue from industrial wastewater using benzoic acid as an extractant," Journal of Hazardous Materials, vol. 163, no. 1, pp. 363–369, 2009.

[25] M. Bielska and K. Prochaska, "Dyes separation by means of cross-flow ultrafiltration of micellar solutions," Dyes and Pigments, vol. 74, no. 2, pp. 410–415, 2007.

[26] A. M. M. Vargas, A. L. Cazetta, M. H. Kunita, T. L. Silva, and V. C. Almeida, "Adsorption of methylene blue on activated carbon produced from flamboyant pods (Delonix regia): study of adsorption isotherms and kinetic models," Chemical Engineering Journal, vol. 168, no. 2, pp. 722–730, 2011.

[27] V. Gupta, Application of low-cost adsorbents for dye removal—a review, J. Environ. Manage., 2009, 90, 2313–2342.

[28] V. K. Gupta, R. Kumar, A. Nayak, T. A. Saleh and M. A. Barakat, Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: A review, Adv. Colloid Interface Sci., 2013, 193–194, 24–34.

[29] A. L. Ahmad, M. M. Loh, and J. A. Aziz, "Preparation and characterization of activated carbon fromoil palm wood and its evaluation on methylene blue adsorption," Dyes and Pigments, vol. 75, no. 2, pp. 263–272, 2007.

[30] J.-Y. Tseng, C.-Y. Changa, Y.-H. Chenb, C.-F. Changc, P.-C. Chiang, Synthesis of micro-size magnetic polymer adsorbent and its application for the removal of Cu(II) ion, Colloid Surf. A: Physicochem. Eng. Aspects 295 (2007) 209–216

[31] Y. Yi, C. Lai, Y. Jiang, J. Mei, H. Wang, Preparation of amino-reserved magnetic chitosan microsphere and its application in adsorbing endotoxin, J. Appl. Polym. Sci. 125 (2012) 248–254.

[32] Zeynep Eren, Filiz Nuran Acar, Adsorption of Reactive Black 5 from an aqueous solution:equilibrium and kinetic studies, Department of Environmental Engineering, Engineering Faculty, Ataturk University, Erzurum 25240, Desalination 194 (2006) 1–10, Turkey

[33]-Kimura, Fávere,Martins,Spinelli and Josué; Adequacy of isotherm adsorption of black 5 reactive dye for crosslinked chitosan microspheres ;2001,

[34]- Ali Kara , Lokman Uzun, Necati Besirli , Adil Denizli , Poly(ethylene glycol dimethacrylate-n-vinyl imidazole) beads for heavy metal removal; Journal of Hazardous Materials 106B (2004) 93–99

[35]-Irene Yukiko Kimura, Valfredo Tadeu Fávere, Amarildo Otávio Martins2, Viviane Aparecida Spinelli2 and Atche Josué; Adequacy of isotherm adsorption of black 5 reactive dye for crosslinked chitosan microspheres, Acta Scientiarum Maringá, v. 23, n. 6, p. 1313-1317, 2001

[36] Şenel, S., Uzun, L., Kara, A., & Denizli, A. (2008). Heavy metal removal from synthetic solutions with magnetic beads under magnetic field. Journal of

Macromolcular Science Pure & Applied Chemistry, A45, 635–642.

[37] Ali Kara and Emel Demirbel, Kinetic, Isotherm and Thermodynamic Analysis on Adsorption of Cr(VI) Ions from Aqueous Solutions by Synthesis and Characterization of Magnetic-Poly (divinylbenzene-vinylimidazole) Microbeads, Water Air Soil Pollut (2012) 223:2387–2403 DOI 10.1007/s11270-011-1032-1.