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Development of novel acid–base ions exchanger for basic dye removal: phosphoric acid doped pyrazole-g-polyglycidyl methacrylate

M.S. Mohy Eldin[a,b,*], K.M. Aly[c,d], Z.A. Khan[a], A.E. Meky[a], T.S. Saleh[a], A.S. Elbogamy[a]

[a] *Faculty of Science, Chemistry Department, University of Jeddah, Osfan P.O. Box 80203, Jeddah 21589, Saudi Arabia, Tel. +966 569006640; emails: m.mohyeldin@mucsat.sci.eg (M.S. Mohy Eldin), ziyaakhan@gmail.com (Z.A. Khan), ataher2211@yahoo.com (A.E. Meky), tamsaid@yahoo.com (T.S. Saleh), chem_org@hotmail.com (A.S. Elbogamy)*
[b] *Polymer Materials Research Department, Advanced Technology and New Materials Research Institute, MuCSAT, New Borg El-Arab City, 21934 Alexandria, Egypt*
[c] *Faculty of Science, Physics Department, University of Jeddah, Osfan P.O. Box 80203, Jeddah 21589, Saudi Arabia, email: khalid_ali_nis@yahoo.com*
[d] *Thermal Meteorology Department, National Institute of Standards-Egypt, Giza, Egypt*

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ABSTRACT

Novel acid–base ions exchanger for basic dye removal developed through three subsequent steps. First, glycidyl methacrylate (GMA) was polymerized to have poly glycidyl methacrylate particles. Second, pyrazole derivative was grafted onto poly glycidyl methacrylate particles to have pyrazole-g-poly glycidyl methacrylate. Finally, orthophosphoric acid was doped onto the pyrazole-g-poly glycidyl methacrylate matrix. Factors affecting the pyrazole derivative grafting process were studied. Structure verification was conducted using FT-IR and thermogravimetric analyses. A fundamental investigation of the removal of methylene blue (MB) from aqueous solutions by orthophosphoric acid-doped pyrazole-g-poly glycidyl methacrylate (OPA-py-g-PGMA) and PGMA particles was conducted under batch conditions. Operational conditions such as initial MB concentration, contact time and temperature, adsorbent dosage, and finally agitation speed have been investigated and correlated to the MB removal percentage and adsorption capacity. OPA-py-g-PGMA particles show higher MB removal percentage and adsorption capacity in comparison with PGMA particles. Maximum adsorption capacities found 11 and 5 mg/g for OPA-py-g-PGMA and PGMA particles, respectively.

Keywords: Basic dye removal; Methylene blue; Acid–base ions exchanger; PGMA; Pyrazole; Grafting; FTIR; TGA

1. Introduction

The effluents from textile, leather, food processing, dyeing, cosmetics, paper, and dye manufacturing industries are important sources of dye pollution [1]. The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable [2]. During the past three decades, several physical, chemical, and biological decolorization methods have been reported; few, however, have been accepted by the paper and textile industries. Among

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*Corresponding author.

the numerous techniques of dye removal, adsorption using different adsorbents is the procedure of choice and gives the best results as it can be used to remove different types of coloring materials [3–5].

Adsorption employs adsorbent—a substance that attaches the substrate or solvent molecule to its surface, and several materials applied as an adsorbent for the treatment of waste water. Agricultural waste and activated carbon have proven very efficient as an adsorbent for many compounds including various classes of dyes.

In the last few decades, however, polymers and polymeric gels which have attracted much interest in the field of biotechnology and medicine [6] directed toward separation work, and many studies on dye adsorption by polymers have been published. In comparison with classical adsorbents such as activated carbon and clay, the synthetic polymeric adsorbent is more attractive because of its favorable physicochemical stability, high selectivity and structural diversity, eco-friendliness, and regeneration abilities [7–9]. The application of polymers as an adsorbent for the removal of cationic/anionic dyes is found in the literature. For instance, Malana et al. [10] reported the removal of industrially important dyes from aqueous media onto polymeric gels by adsorption process. In recent years, a wide variety of polymers and polymer composites reported as excellent adsorbents for the removal of various dyes and organic contaminants from aqueous solution. For example, cyclodextrin polymer [11], novel polymer—Jalshakti [12], polystyrene-block-poly(N-isopropyl acrylamide) [13], PVA hydrogels, and PVA/AC composites [14].

For heavy metals removal, the ability of pyrazole and its derivatives to act as ligands with sp2 hybrid nitrogen donors have been the research subjects for many researchers [15–17].

In this study, pyrazole derivative was grafted onto polyglycidyl methacrylate particles to have pyrazole-g-polyglycidyl methacrylate and then doped the base nitrogen moieties with orthophosphoric acid to have acid–base ions exchanger and apply finally in the removal of MB from the synthetic dye aqueous solution for the first time.

2. Materials and methods

2.1. Materials

Glycidyl methacrylate (GMA), DMF, DMSO, ethyl alcohol, sodium persulphate (SPS), 4-(4-chlorophenyl) azo-1*H*-pyrazole-3,5-diamine, and methylene blue.

2.2. Methods

2.2.1. Preparation of pyrazole derivative

4-(4-chlorophenyl) azo-1*H*-pyrazole-3,5-diamine [18] prepared according to the reported literature.

2.2.2. Preparation of orthophosphoric acid-doped pyrazole-g-PGMA

Three consequent steps were followed to have orthophosphoric acid-doped pyrazole-g-PGMA. First, glycidyl methacrylate was polymerized to have poly glycidyl methacrylate particles. Second, pyrazole derivative was grafted onto polyglycidyl methacrylate particles to have pyrazole-g-polyglycidyl methacrylate. Finally, orthophosphoric acid was doped onto the pyrazole-g-polyglycidyl methacrylate matrix.

2.2.2.1. Polymerization process. Polymerization was carried out with a monomer concentration of 10% (v/v) through the dissolution of GMA in an alcohol solution (1:1; ethanol/water) of sodium persulfate (0.1 M). Polymerization was carried out at 55˚C in a water bath for 4 h.

2.2.2.2. Pyrazole grafting process. The epoxy group of the PGMA chains reacted with different molar concentrations of pyrazole derivative dissolved in DMF: DMSO (1:1) at 50˚C for two hours. The reaction of pyrazole derivative with epoxy rings of PGMA component illustrated in Fig. 1.

2.2.2.3. Orthophosphoric acid doping process. Pyrazole-g-polyglycidyl methacrylate particles reacted with 3% orthophosphoric acid solution at 50˚C for one hour.

2.3. Preparation of basic dye solution

MB, $C_{16}H_{18}N_3SC_{13}H_2O$, the stock solution was prepared by dissolving 0.01 g of MB in 1,000 mL distilled water. The dye concentration in the supernatant and residual solutions determined by measuring their absorbance at 1 cm light-path cell at Max wavelength 660 nm using a spectrophotometer.

2.3.1. Batch MB adsorption experiments

The adsorption experiments were carried out in a batch process using MB aqueous solution. The variable parameters, namely the initial MB concentration, the adsorbent dosage, the contact time, the stirring rate, and the adsorption temperature were studied.

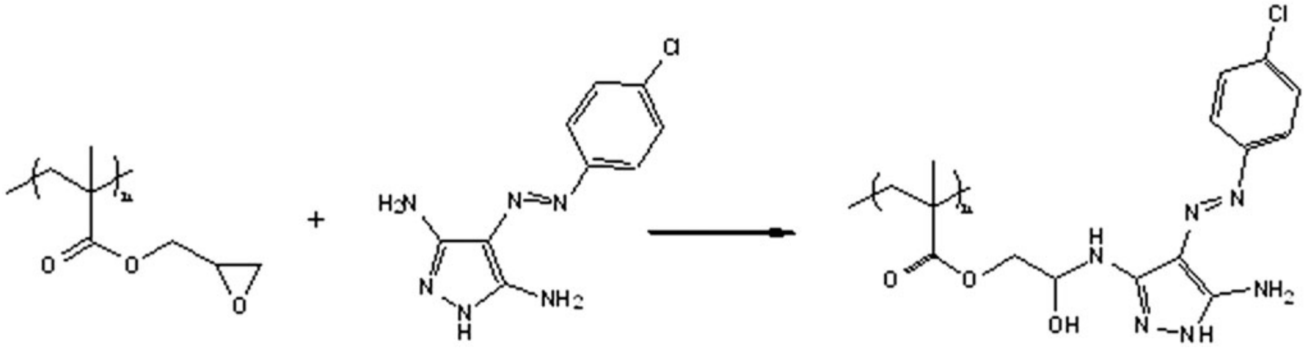

Fig. 1. Reaction of pyrazole derivative with PGMA epoxy ring.

The MB adsorption studies were performed by mixing 0.1 g of OPA-py-g-PGMA and PGMA with 20 mL of fixed MB concentration. The mixture was magnetically stirred at R.T for selected time and then centrifuged at 6,000 rpm for 10 min to separate the adsorbent out of the liquid phase. The dye concentration, before and after the adsorption, for each solution, was determined by measuring the absorbance at the maximum wavelength ($\lambda_{\max} = 660$ nm) using UV–vis spectrophotometer. Dye removal percentage is calculated according to the following formula:

$$\text{Dye removal}\,(\%) = [(C_0 - C_t)/C_0] \times 100$$

where C_0 and C_t (mg L^{-1}) are the initial concentration at zero time and the final concentration of MB at a definite time, respectively.

2.4 Infrared spectroscopic analysis

The polymer functional groups were investigated using a Fourier-transform infrared spectrophotometer (Shimadzu FTIR-8400 S, Japan) connected to a PC, and the analysis of the data was accomplished using the IR Solution software, version 1.21.

2.5. Thermogravimetric analysis

Thermogravimetric analysis (TGA) of the polymer was carried out using a thermogravimetric analyzer (Shimadzu TGA-50, Japan); the samples were heated at 10˚C/min in the temperature range from 20 to 600˚C under nitrogen flowing at 20 mL/min.

3. Results and discussion

3.1. Characterization of the synthesized matrices

The success of the pyrazole grafting process was verified by conducting FT-IR and TGA analyses of pyrazole-g-PGMA. The FT-IR spectra of PGMA (Fig. 2) show the absorption bands at 1,725, 1,300–1,100 cm^{-1}, caused by the stretching vibration of the ester carbonyl groups, C–O–C stretching in addition to the characteristic bands of the epoxy ring at 1,260 and 950–815 cm^{-1} [19]. After performing pyrazole grafting process, absorption bands of the epoxy rings at 1,260 cm^{-1} and 950–815 cm^{-1} start to disappear, while the band at 760 cm^{-1} of weak intensity still noticed the shift to 780 cm^{-1}. That may refer to a minor fraction of epoxy rings that may have taken part in the formation of the cross-linking structure during polymerization [20]. The new characteristic band appearing at 2,300 cm^{-1} of grafted pyrazole derivative was recognized. C=C, C=N, NH absorption bands at 1,650–1,550 cm^{-1} characteristics of pyrazole compounds recognized and the presence of aromatic rings indicated by bands at 1,589, 1,600, and 1,512 cm^{-1}. For orthophosphoric acid-doped matrix, P=O stretch band

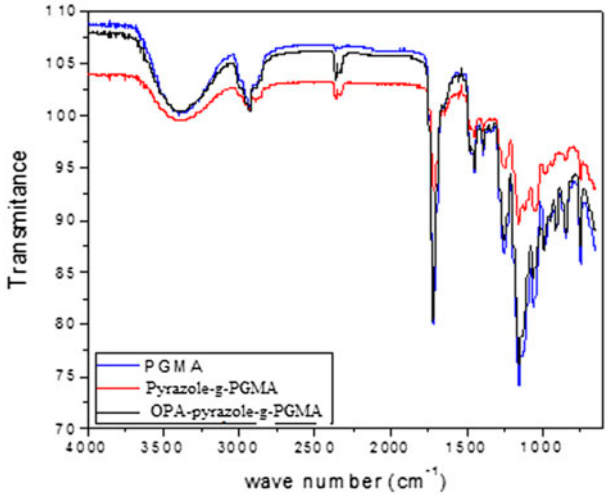

Fig. 2. FTIR spectra of PGMA, pyrazole-g-PGMA, and OPA- pyrazole-g-PGMA particles.

at 1,415–1,085 cm^{-1} and P–OH stretch bands at 1,740–1,600 cm^{-1} while P–O stretch at 1,030–972 cm^{-1} and 950–917 cm^{-1}.

On the other hand, TGA thermograms (Fig. 3) showed the weight loss of samples at 120˚C, due to water evaporation. PGMA grafted with pyrazole derivative show a significant increase in weight loss. A remarkable decrease in thermal stability was observed for the pyrazole grafted sample. A negative shift of characteristic thermogram of PGMA was recognized. At 400˚C, the PGMA sample lost 50% of its weight. Pyrazole grafted sample lost 50% of its weight at 330˚C. OPA-doped pyrazole-g-PGMA sample regains thermal stability where it lost 50% of its weight at 400˚C.

3.2. Pyrazole grafting process

The impact of different factors affecting the pyrazole grafting process on the MB removal efficiency was studied. These factors include pyrazole concentration, grafting time, and temperature.

3.2.1. Effect of the pyrazole concentration

Table 1 shows the effect of variation the pyrazole derivative concentration on the MB removal efficiency from 0.2 to 1 M. From the tabulated results, it is clear that the variation of pyrazole derivative concentration has no significant effect on the MB removal efficiency within the studied range. Different MB synthetic solution concentrations were tested. This behavior is explained by the limitation of the grafting reaction by the exposed epoxy group numbers on the PGMA particles surface. For comparison, PGMA particles have been tested under the same conditions. In general, all the pyrazole grated samples show higher MB removal efficiency than PGMA one. The difference in favor of pyrazole grafted samples was detected only in testing MB solution concentration higher than 25 ppm. This observation confirms the occurrence of the adsorption process on the polymer particles surface.

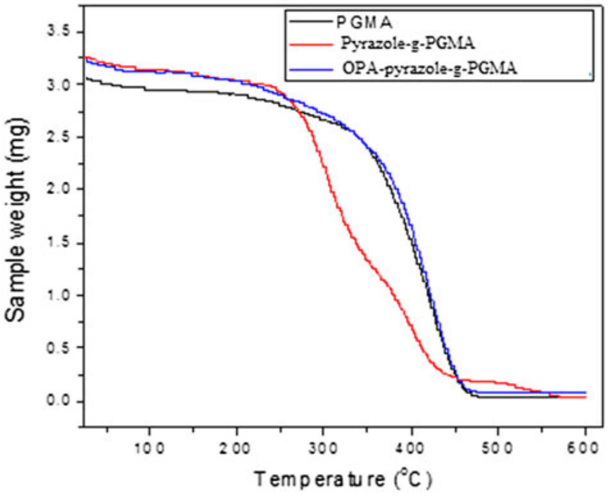

Fig. 3. TGA of PGMA, pyrazole-g-PGMA, and OPA-pyrazole-g-PGMA particles.

3.2.2. Effect of the grafting time

The effect of variation of the grafting time on the removal efficiency of MB is shown in Table 2. From the obtained results, it is clear that minimum grafting time, 0.5 h, is comparable with 2.0 h that confirmed our assumption that the grafting process occurs only on the surface, and the number of epoxy groups on the PGMA particle surface is the grafting limiting factor.

3.2.3. Effect of the grafting temperature

Table 3 shows the effect of variation the grafting temperature on the MB removal efficiency. No effect was noticed which confirmed our assumption about the occurrence of the pyrazole grafting on the PGMA particles surface and the limitation of the process by the surface epoxy groups. That presents an advantage of the prepared matrices that did not need any additional energy for preparation that reduced the cost of the matrix.

3.3. Methylene blue removal process

The operational conditions affecting the MB removal process, namely MB concentration, MB removal time and temperature, adsorbent dosage, and agitation speed were investigated.

3.3.1. Effect of the MB concentration

The effect of the initial dye concentration factor depends on the immediate relation between the dye concentration and the available binding sites on an adsorbent surface [21]. Fig. 4 shows the effect of initial dye concentration. The percentage of dye removal decreases with an increase in initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface [22]. At low concentration, there will be unoccupied active sites on the adsorbent surface, and when the initial dye concentration increases, the active sites required for adsorption of

Table 1
Effect of variation the pyrazole concentration on the removal efficiency of MB

	Methylene blue concentration (ppm)						
Pyrazole concentration (M)	10	18	25	30	40	50	60
0.0	100	90	83	78	63	50	33
0.2	100	100	100	98	99	92	83
0.4	100	100	100	97	97	87	84
0.6	100	100	100	98	98	88	84
0.8	100	100	100	98	99	94	84
1.0	100	100	100	97	98	90	84

Table 2
Effect of variation the grafting time on the MB removal efficiency

	Methylene blue concentration (ppm)						
Functionalization time (h)	10	18	25	30	40	50	60
0.5	100	100	100	98	99	97	85
1.0	100	100	100	98	99	92	83
1.5	100	100	100	98	99	96	84
2.0	100	100	100	99	99	92	84

the dye molecules will disappear [23]. However, the increase in the initial dye concentration will cause an increase in the loading capacity of the adsorbent, and this may be due to the high driving force for mass at a high initial dye concentration [24]. In other words, the residual concentration of dye molecules will be higher for higher initial dye concentrations. In the case of lower concentrations, the ratio of an initial number of dye molecules to the available adsorption sites is low, and subsequently the fractional adsorption becomes independent of initial concentration. The MB removal efficiency of OPA-pyrazole-g-PGMA sample is much higher than the blank sample, PGMA. This behavior is very clear at the highest MB tested concentration (100 ppm) where the removal percentage was found 50 and 25% for the OPA-pyrazole-g-PGMA and the PGMA, respectively. That is due to the induced ion exchanger sites located on the surface of OPA-pyrazole-g-PGMA samples.

On the other hand, the adsorption capacity for OPA-pyrazole-g-PGMA and PGMA matrices is shown in Fig. 5. From the figure, it is clear that the adsorption capacity was increased linearly for PGMA matrix up to 5 mg/g at 30 ppm MB concentration where the adsorption capacity reached 10 mg/g for OPA-pyrazole-g-PGMA sample at 50 ppm MB concentration. Beyond these MB concentrations, the adsorption capacity started to level off. It expected that the presence of ionic sites over the OPA-pyrazole-g-PGMA particles surface was the main cause for the gained MB higher adsorption capacity. The lack of such ionic sites on the PGMA particles surface explains the limited adsorption capacity. Within the studied contact time, it seems that most of the adsorption sites over the polymeric particles surface have been occupied by MB molecules at 30 and 50 ppm for PGMA and OPA-pyrazole-g-PGMA, respectively.

3.3.2. Effect of the contact time

The effect of variation contact time on MB removal percentage was investigated as shown in Fig. 6. From the figure, it can be seen that the MB removal percentage of OPA-pyrazole-g-PGMA has been slightly affected by increasing contact time over 5 min. Very fast equilibrium was achieved due to a lot of available exchange sites. The removal percentage increases from 55 to 70% with increase time from 5 to 30 min. For PGMA, the removal percentage increases from 20 to 33% with increase time from 5 to 30 min. Beyond 30-min adsorption time, a slight increase in removal

Table 3
Effect of variation the functionalization temperature on the MB removal percentage

	Methylene blue concentration (ppm)						
Functionalization temperature (°C)	10	18	25	30	40	50	60
25	100	100	100	97	98	95	84
40	100	100	100	97	98	95	84

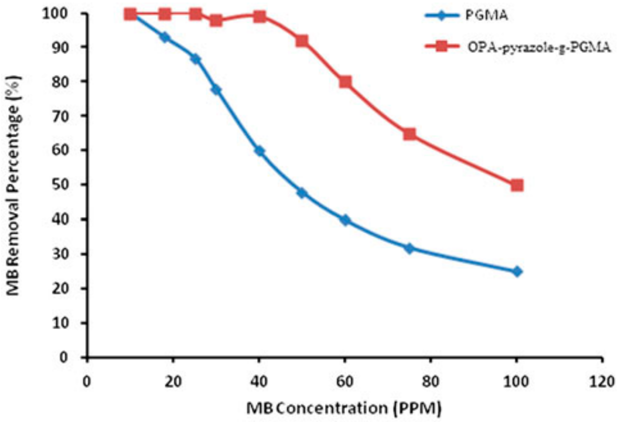

Fig. 4. Effect of the MB concentration on the MB removal percentage (%) of OPA-pyrazole-g-PGMA and PGMA particles.

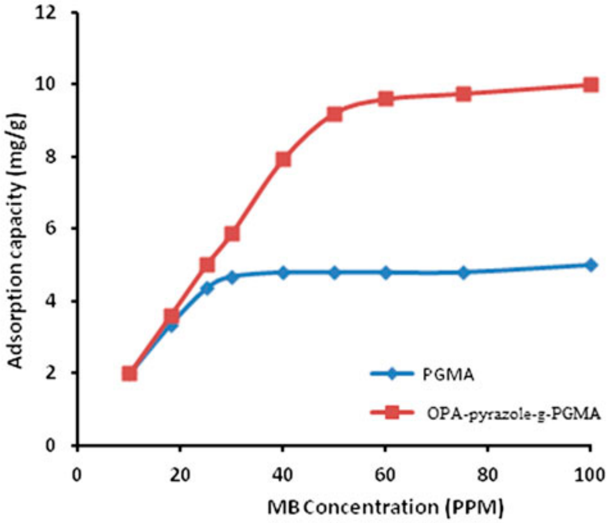

Fig. 5. Effect of the MB concentration on the adsorption capacity of OPA-pyrazole-g-PGMA and PGMA particles.

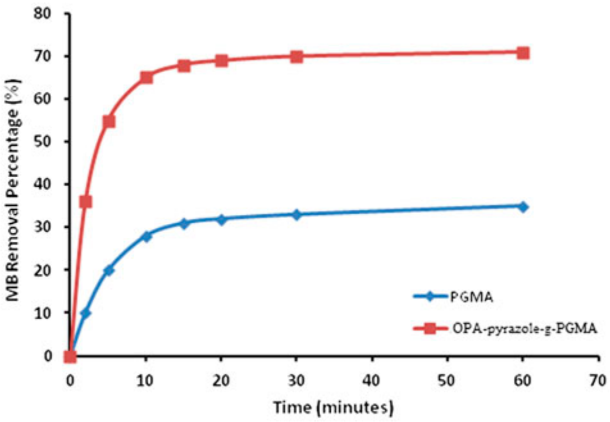

Fig. 6. Effect of the contact time on the MB removal percentage (%) of OPA-pyrazole-g-PGMA and PGMA particles.

percentage for both samples was observed. This behavior referred to the reduction of the concentration gradient between the liquid phase and the adsorbent surface. This behavior is shown by previously published results by the author [25,26] where MB adsorbed onto hydro-oxime polyacrylonitrile ions exchanger nanoparticles. The present results show equilibrium reach at the shorter time. Table 4 shows the adsorption capacity for both samples. From the obtained results, it is clear that the adsorption capacity for the OPA-pyrazole-g-PGMA sample is higher than its PGMA counterpart. The induced ionic centers over the OPA-pyrazole-g-PGMA particles' surface help in accelerating of the adsorption process and reach to almost equilibrium within fifteen minutes where adsorption capacity reaches to its almost maximum value after one hour contact time. PGMA sample shows a slower rate of adsorption while reaches to almost equilibrium within twenty minutes. Maximum adsorption capacities for OPA-pyrazole-g-PGMA and PGMA matrices were 10.65 and 5.25 mg/g, respectively.

3.3.3. Effect of the adsorbent dosage

The effect of variation of the adsorbent dosage on the MB percentage removal correlated with various MB concentrations (Fig. 7). It is evident from the curves that the percentage dye removal increases with adsorbent dosage. The OPA-pyrazole-g-PGMA sample shows an advantage over the PGMA sample. Such behavior is obvious because the number of active sites available for dye removal would be more as some adsorbent increases. From the curves, it can be

Table 4
Effect of variation of the contact time on the adsorption capacity for OPA-pyrazole-g-PGMA and PGMA matrices

Contact time (min)	PGMA	OP-pyrazole-g-PGMA
0	0	0
2	1.5	5.4
5	3	8.25
10	4.2	9.75
15	4.65	10.2
20	4.8	10.35
30	4.95	10.5
60	5.25	10.65

depicted that only 0.25 g of OPA-pyrazole-g-PGMA is enough to have the same MB removal percentage as 0.75 g of PGMA, 85%. Time-rate adsorption curve is single and continuous, suggesting the possibility of monolayer coverage of MB onto the surface of adsorbent [27].

Fig. 8 shows the variation of the adsorption capacity of both matrices with the adsorbent dosage. Within fixed amount of MB molecules and increased adsorbent dosage, it is expected that the adsorption capacity decreases. Accordingly, the adsorption capacities for both matrices are almost equal for adsorbent dosage 1 g where almost all of MB molecules were adsorbed from the medium.

3.3.4. *Effect of the agitation speed*

The effect of variation agitation speed from 0 to 1,000 rpm on the removal percentage of MB was studied (Fig. 9). From the figure, it is clear that the enhancing effect of agitation ranged from 0 to 250 rpm on the percentage of MB removal. That is because MB, through their transportation to the solid phase, meets resistance in the liquid phase, through the boundary layer. The motion induced through the agitation of suspensions during experiments leads to a decrease in the boundary layer thickness and a consequent decrease in the transportation resistance of MB [28]. That increases the transfer rate of the ions, and thus the MB removed percentage. However, a negligible increment in MB removal percentage was noticed for agitation speed above 150 rpm for OPA-pyrazole-g-PGMA and 200 rpm for PGMA samples, confirming that 200 rpm shaking rate is sufficient to expose all the polymer surface binding sites for MB molecules in the solution. Table 5 shows the effect of agitation speed on the adsorption capacities of PGMA and OPA-pyrazole-g-PGMA particles. The increment of the agitation speed was found most effective in the adsorption capacity of PGMA particles. That is may explain by the fact that the limitation of active sites over its surface compared with OPA-pyrazole-g-PGMA particles.

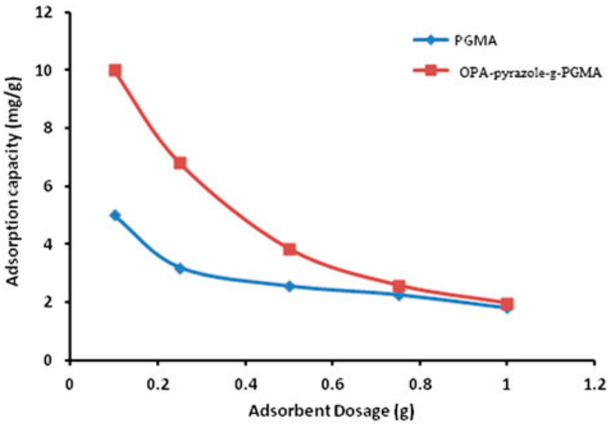

Fig. 8. Effect of the adsorbent dosage on the adsorption capacity of OPA-pyrazole-g-PGMA and PGMA particles.

3.3.5. *Effect of the adsorption temperature*

Table 6 shows the effect of variation of the adsorption temperature over a wide range, from 25 to 55˚C, on the MB removal percentage for both OPA-pyrazole-g-PGMA and PGMA particles. Almost constant removal percentages were observed. The obtained

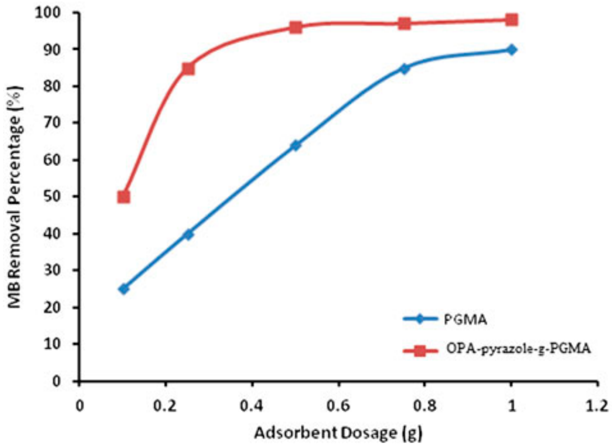

Fig. 7. Effect of the adsorbent dosage on the MB removal percentage (%) of OPA-pyrazole-g-PGMA and PGMA particles.

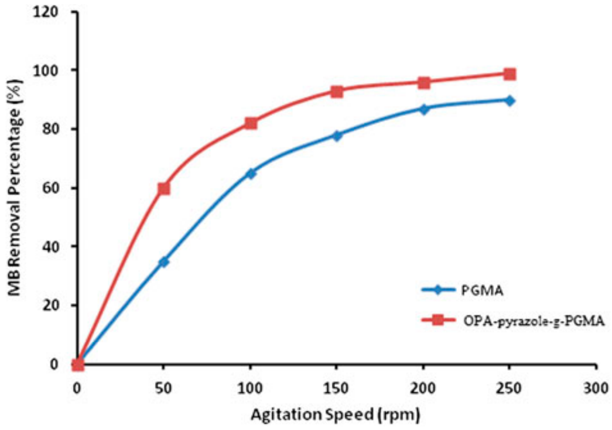

Fig. 9. Effect of the agitation speed on the MB removal percentage (%) of PGMA and OPA-pyrazole-g-PGMA particles.

Table 5
Effect of variation the agitation speed on the adsorption capacity of PGMA and OPA-pyrazole-g-PGMA

Agitation speed (rpm)	PGMA	OP-pyrazole-g-PGMA
0	0	0
50	0.7	1.2
100	1.3	1.64
150	1.56	1.86
200	1.74	1.92
250	1.8	1.96

Table 6
Effect of variation of the adsorption temperature on the MB removal percentage

	MB removal (%)	
Temperature (°C)	ABIE	PGMA
25	50	18
40	48	16
55	49	17

results are considered an advantage since the dye removal process does not need any additional heating and or other extra cost and could perform over a wide range of effluent temperature. This behavior may refer to the acceleration effect of temperature on the dye molecules adsorption on the surface of both OPA-pyrazole-g-PGMA and PGMA particles. This fast initial step reduces the concentration gradient between the MB dye liquid phase and the copolymer solid phase. MB concentration limitation from one side and high concentration of exchange sites over the particles surface on the other side contribute significantly to obtain this behavior. The absence of pore diffusion process also eliminates the effect of temperature [23].

4. Conclusion

Orthophosphoric acid-doped pyrazole-g-poly glycidyl methacrylate (OP-Py-g-PGMA) particles were developed as a novel acid–base ions exchanger for basic dye removal. The variation of different factors affecting the pyrazole derivative grafting process was studied. None of the studied factors has affected significantly the MB removal efficiency of the OPA-py-g-PGMA which revealed the surface nature of the grafting process. Operational conditions such as initial MB concentration, contact time and temperature, adsorbent dosage, and finally agitation speed have been investigated and correlated to the MB removal percentage and adsorption capacity. OP-Py-g-PGMA particles show higher MB removal percentage and adsorption capacity in comparison with PGMA particles. The OP-Py-g-PGMA particles show a faster rate of MB adsorption and higher removal percentage. Maximum adsorption capacities found 11 and 5 mg/g for OP-Py-g-PGMA and PGMA particles, respectively.

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