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Removal of Phenol and Nitrophenols from Aquatic System with Cibacron Blue F3GA Attached mPHEMA

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Abstract: Phenol and nitrophenols are toxic to other organisms in aqueous media even at very low concentrations. In this work, the removal of phenols and nitrophenols by using Cibacron Blue F3GA attached of magnetic poly(2-hydroxyethylmethacrylate) as an adsorbent from the aqueous media was investigated. The adsorption phenomenon of the phenol and nitrophenols on adsorbent at different time ranges (15, 20, 45, 60, 90 and 120 minutes) was investigated to elucidate the equilibrium times with increasing phenol and nitrophenols concentration. The parameters such as pH (2-12), adsorbent dosage, adsorption time and initial concentration were studied. The maximum adsorption equilibrium time was found to be approximately 20 minutes. The amount of adsorbed substance on adsorbent was observed to decrease in the order of 4-nitrophenol> 3-nitrophenol> and 2-nitrophenol> phenol. The adsorbent was examined by using Fourier Transform Infra-Red, Scanning Electron Microscopy-Energy Dispersive X-ray techniques and Differential Thermal Analysis-Thermal Gravimetric Analysis Techniques before and after the adsorption. The adsorption process was observed to comply with the Langmuir isotherm. It was possible to use again and again Cibacron Blue F3GA-attached mPHEMA beads without any significant decreases in their adsorption capacities.

Keywords: Adsorption, phenols, wastewater, mPHEMA, Cibacron Blue F3GA

Cibacron Blue F3GA Bağlı mPHEMA ile Sulu Sistemden Fenol ve Nitrofenollerin Uzaklaştırılması

Öz : Fenol ve nitrofenoller, çok düşük konsantrasyonlarda bile sulu ortamdaki diğer organizmalar için toksiktir. Bu çalışmada, sulu ortamdan bir adsorban olarak manyetik poli (2-hidroksietilmetakrilat) bağlı Cibacron Blue F3GA kullanılarak fenollerin ve nitrofenollerin uzaklaştırılması araştırıldı. Farklı zaman aralıklarında (15, 20, 45, 60, 90 ve 120 dakika) adsorban üzerindeki fenol ve nitrofenollerin adsorpsiyon miktarı, artan fenol ve nitrofenol konsantrasyonu ile denge süreleri araştırıldı. pH (2-12 arasında), adsorban dozaj, adsorpsiyon süresi ve başlangıç konsantrasyonu gibi parametreler araştırıldı. Maksimum adsorpsiyon denge süresi yaklaşık 20 dakika olarak bulunmuştur. Adsorban üzerindeki adsorbe edilen madde miktarının, 4-nitrofenol> 3-nitrofenol> ve 2-nitrofenol> fenol sırasıyla azaldığı gözlendi. Adsorban, adsorpsiyon öncesi ve sonrasında Fourier Transform Infra-Red, Taramalı Elektron Mikroskopisi-Enerji Dağıtıcı X-ışını teknikleri ve Diferansiyel Termal Analiz-Termal Gravimetrik Analiz Teknikleri kullanılarak incelenmiştir. Adsorpsiyon işleminin Langmuir izotermine uygun olduğu gözlenmiştir. Adsorpsiyon kapasitelerinde önemli bir azalma olmadan tekrar tekrar Cibacron Blue F3GA'ya takılı mPHEMA mikrokürelerin kullanılması mümkün olmuştur.

Anahtar Kelimeler: Adsorpsiyon, fenoller, atık su, mPHEMA, Cibacron Blue F3GA

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1. Introduction

Phenolic substances (Ps) are very harmful, deleterious and are related to carcinogens [1,2]. A lot of poisonous or toxic wastewater is discharged in industrial factories (petrochemistry, coal, polymer, steel, pharmaceutical etc.) [3]. Phenolic compounds should be less than 1 mg/L in wastewater according to the US Environmental Protection Agency (EPA). Different techniques such as solvent extraction, physical, biological, and chemical treatments are used for elimination of phenolic pollutants [4]. These techniques have some advantage and disadvantage in the removal or contaminants. Adsorption technique is recently being utilized commonly for the elimination of contaminants at a low concentration [5]. In this technique some special sorbents, such as metal oxides, activated carbon, resins, silica, clinoptilolite have been utilized [6-9]. They have a ligand that interacts with pollutants specifically [10].

Organic substances such as phenol (P) and nitrophenols (NPs) are very hard or unfeasible to eliminate by using biological process. P and their derivatives are very harmful to living things, causing oxygen requirement in receiving waters [11, 12]. In literature, removing of P and NPs from wastewaters were studied with chemical oxidation, physicochemical treatment processes, and biological degradation [13-16]. Currently, magnetic adsorbents are generally used in adsorption processes [17]. The Cibacron Blue F3GA (CB-F3GA) dye has a ligand that cause high adsorption capacity (Figure 1) [18]. They have solved many problems such as eliminating poisonous materials, organic contaminants, heavy metals etc. In literature, scientists have used different sorbents for phenolic substances. Singh and Misra utilized $Fe(OH)_3$ attached marble to eliminated organic pollutants P, 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), pyrogallol, resorcinol, quinol, payrocatechol). They found an adsorption capacity from 14.7 to 76.5 mmol/g [1]. Saleh et al investigated statistical analysis of phenols adsorption on diethylenetriamine-modified-AC [19]. Denizli et al [20] studied with CB-F3GA carrying pHEMA microbeads for removal of chlorophenols (CPs) and trichlorophenol (TCP) [20]. Lin and Juang reviewed the elimination of P and NPs from wastewater by natural and synthetic adsorbents [21]. Kuralay et all investigated affinities of bovine serum albumin with modified CB-F3GA/Pencil graphite electrodes [22]. Tüzmen et al. prepared magnetic poly(2-hydroxyethylmethacrylate) (mPHEMA) beads and then connected CB-F3GA to mPHEMA beads (Figure 2). They evaluated adsorbed and desorbed beta-casein on the CB-F3GA@ mPHEMA beads. [23, 24]. Gu et al studied elimination of different NPs in aquatic media by modified MCM-48. They found that the adsorption of 2-NP, 3-nitrophenol (3-NP), and 4-NP by modified MCM-48 was spontaneous and exothermic in nature [25].

Chen et al synthesized an organometallic structure chromium (III) terephthalic acid (Cr-BDC) and used for removing of NP and 4-NP. They found that as-prepared Cr-BDC was an effective and low-cost adsorbent for 2-NP elimination [26]. Kordic et al studied the valorization of organic compounds in the adsorption process. In their study, affinity for desorption decreased in the following order: 4-NP 3-NP 2-NP [27]. Aazza et al examined removal of 2-NP from aqueous solutions with modified alumina [28].

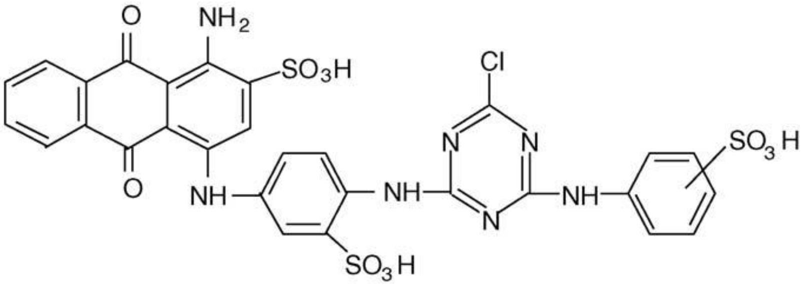


Figure 1. Molecular structure of CB-F3GA.

The aim of this paper is to research the adsorption behavior of P and NPs on the CB-F3GA@mPHEMA. Experimental parameters were studied such as the initial concentration, the adsorption rate, the equilibrium time, the pH and the regeneration. The adsorption of the P, NPs on CB-F3GA@mPHEMA was investigated. The equilibrium times with increasing P and NPs concentration were elucidated. A novel and cheap adsorbent was utilized for P and NPs.

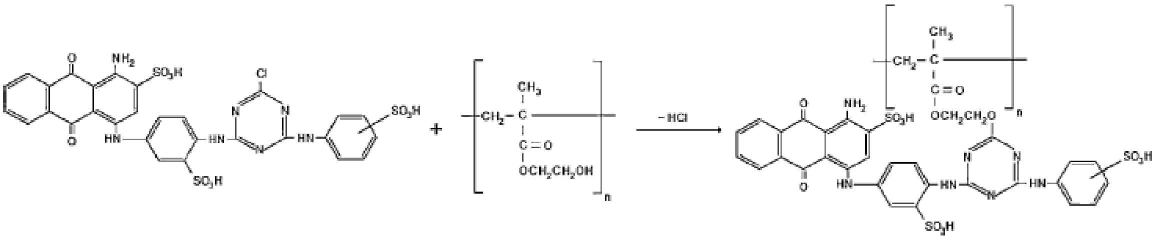


Figure 2. Attached of CB-F3GA to mPHEMA beads.

2. Experimental Methods

2.1. Materials

All chemicals were analytical grade and purchased from Merck. P, 2-NP, 3-NP, 4-NP, 4-Aminoantipyrine, Potassium ferricyanide (K_3FeCN_6), HCI and NaOH were used as received.
Concentrations of phenolic compounds were found as colorimetric assay by DR-5000 spectrophotometer [29, 30]. For each adsorption isotherm experiment was applied as described in our previous study [9, 30].

Distilled water was used to prepare a solution (ELGASTAT system). CB-F3GA@mPHEMA microbeads were synthesized as reported elsewhere [18]. A summary of the polymerization process is as follows. Poly(vinyl alcohol) (PVA; Mw: 50 000 kDa) was dissolved in distilled water. The desired amount of 2,2′-azobisisobutyronitrile (AIBN) was added to the monomer (EGDMA/HEMA/toluene) with 1.0 g of magnetite particles. This mixture was then poured to a glass polymerization reactor with a thermostatic water bath at 65 °C for 4 h. Then, the polymerization was finished at 90°C over 2 h [18]. SEM images of the prepared microbeads are given in Figure 3.

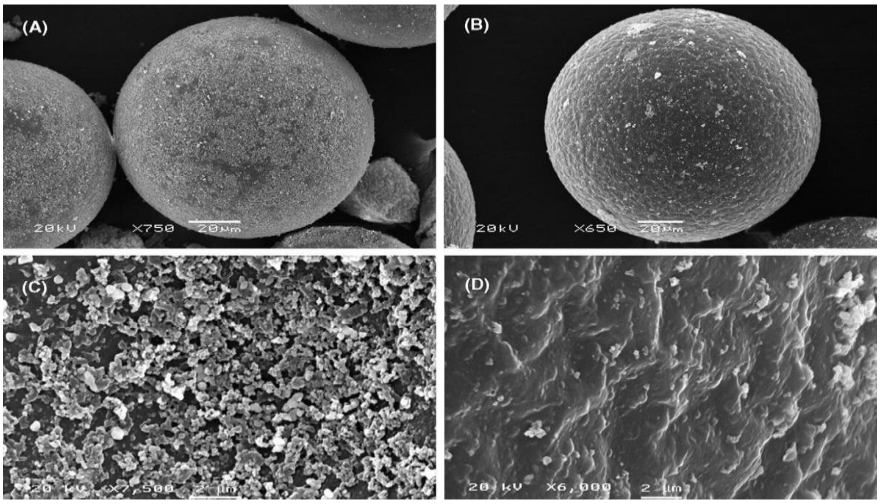


Figure 3. SEM images of (A) mPHEMA (B) PHEMA (C) cross section of mPHEMA (D) cross section of PHEMA

Some characteristics of the used microbeads are shown in Table 1 [31].

CB-F3GA@mPHEMA absorbances was observed according to presenting in our previous studies [9,20, 30]. P and NPs are vaporized at high temperature and in the experimental part was studied in three different temperatures (10, 25 and 40°C). Therefore, the ambient temperature was preferred in experimental studies because of ambient condition, easy and simplicity.

Table 1. Characteristics of prepared microbeads

Particle diameter	80-120 µm
Specific surface area	56 m^2/g
Average pore size	819 nm
Swelling rate	45%
Cibacron blue F3GA content	28.5 µmol/g
Density	1/1 g/ml
Volume fraction of the polymer	94.50%
Volume fraction of magnetic particle	5.5 % Fe_3O_4
Magnetic field resonance	2250 G

Desorption of P and NPs was performed by using ethyl alcohol solution (30% v/v).

Adsorbent dosage was examined such as 10, 50, 100, 200, 300, 400 and 500 mg/L. Then minimum adsorbent dosage was preferred as 200 mg/L to supply economical advantage. Because amount of adsorbed phenols was nearly constant for adsorbent dosages between 200-500 mg/L.

The morphological characterization of the CB-F3GA@mPHEMA were evaluated by a scanning electron microscope (SEM 1200 EX, JEOL).

3. Results and Discussion

3.1. DTA/TG Analysis

Thermal analysis of CB-F3GA@mPHEMA are shown in Figure. 4.

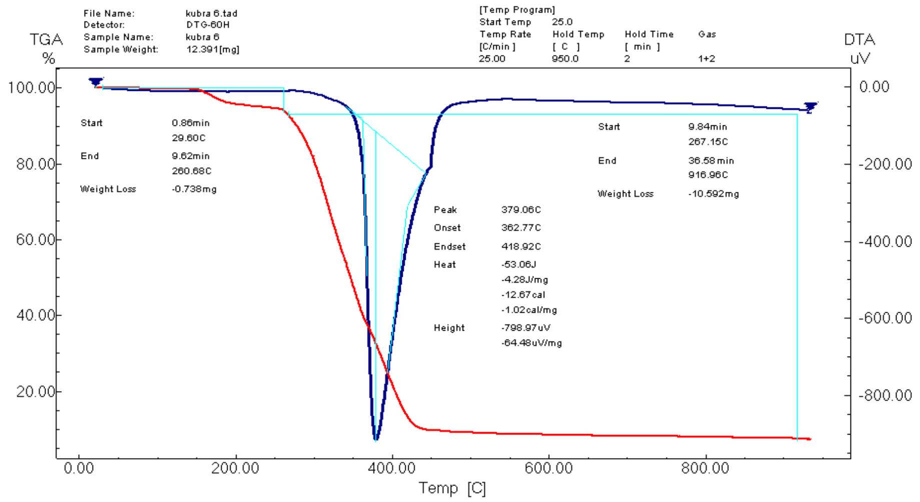
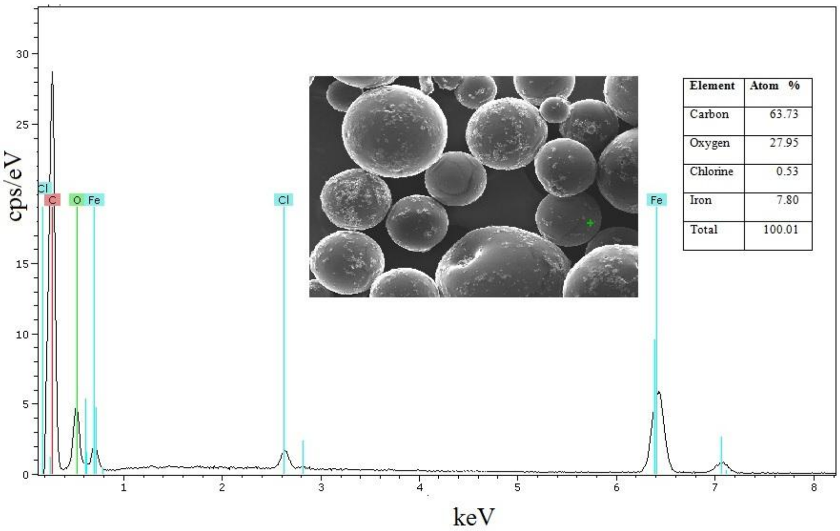


Figure 4. DTA/TG analysis of CB-F3GA@mPHEMA microbeads.

As a result of the DTA analysis, it was determined that the weak and strong bonded waters in the structure of the microbeads were thrown at 90-95°C and formed an endothermic peak. According to the information obtained from the literature, approximately all of waters remove away from the structure at 450°C without any phase transformation in the structure up to 800°C [32]. Also, when the DTA graph of the polymer is examined, it is seen that there is an endothermic peak before 400°C and then there is no phase change from 450°C to 800°C. The results obtained are compatible with previous researches [33].

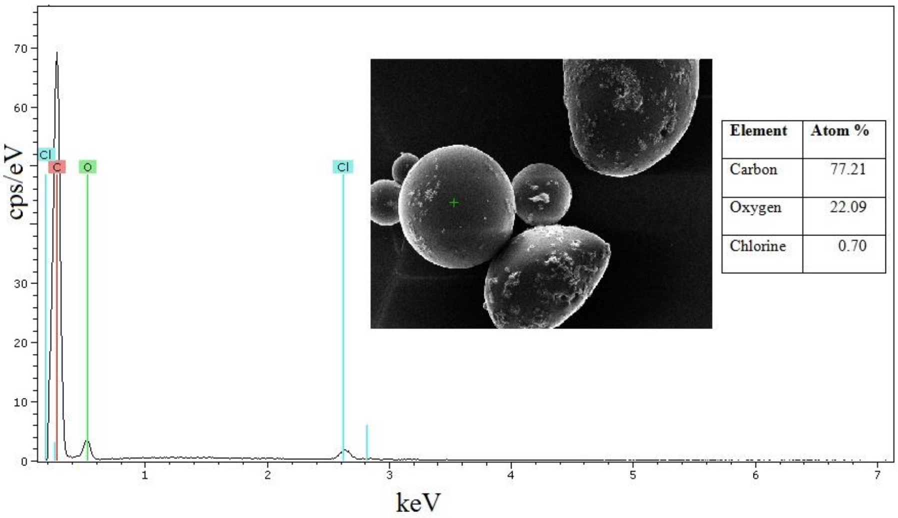
3.2. SEM-EDX Analysis

Morphological analysis of before and after adsorptions of 4-NP are shown in Figure. 5 and 6. The article shape was homogeneous and spherical. After adsorption process iron element disappeared from structure. Non-magnetic PHEMA microbeads displayed spherical shapes with a smooth surface. The presence of magnetite particles in the polymeric structure was confirmed by EDX.



Element	Atom %
Carbon	63.73
Oxygen	27.95
Chlorine	0.53
Iron	7.80
Total	100.01

Figure 5. EDX analysis of CB-F3GA@mPHEMA microbeads (before adsorption).



Element	Atom %
Carbon	77.21
Oxygen	22.09
Chlorine	0.70

Figure 6. EDX analysis of CB-F3GA@mPHEMA microbeads (after adsorption for 4-NP).

3.3. FTIR Analysis

Assessment the infrared analysis for 4-NP (Figure. 7(a)) of crosslinked CB-F3GA@mPHEMA beads gives sharp peaks between 400-4000 cm^{-1}. At 3448 ± 8 cm^{-1} peak was evaluated particularly the O-H stretching vibration. A sharp C=O bond stretching of monomer occurs at 1733 ±2 cm^{-1}. There is a characteristic band of C-C stretching of monomer at 1650 cm^{-1}. The C-O stretching vibration bands of monomer are exhibited at 1148 ± 100 cm^{-1}. IR spectrum of microbeads is characterized in the spectrum of the composite at 753 cm^{-1} and characterizes the Fe-O stretching vibration. FTIR analysis of CB-F3GA@mPHEMA is shown in Figure 5 (b) that same strong peaks were detected. The broad peak of O-H stretching vibration of CB-F3GA@mPHEMA monomer at 3448 cm^{-1} has disappeared after adsorption CB-F3GA@mPHEMA. FTIR analysis of same polymer is supported with our studies [29, 34-36].

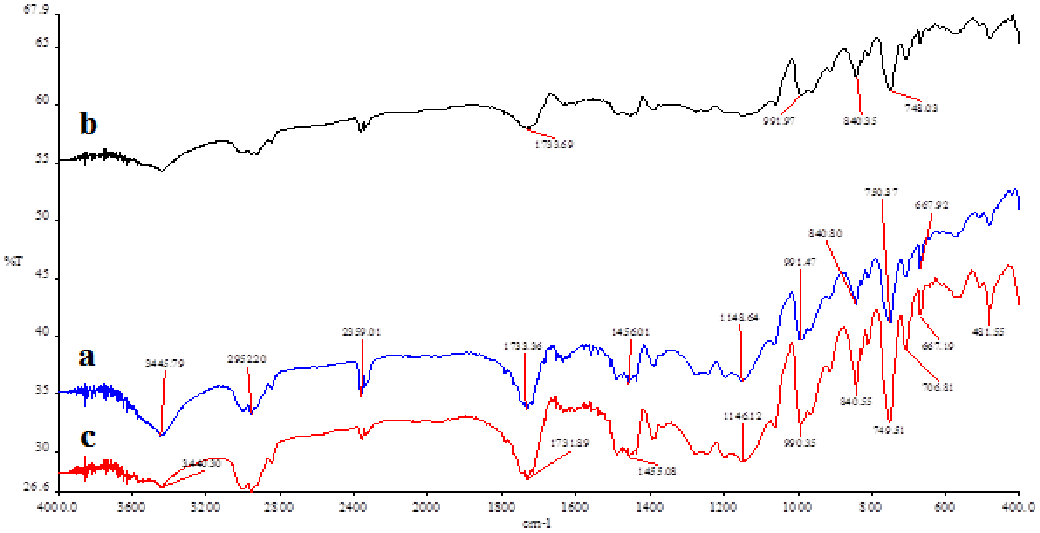


Figure 7. FTIR results (a) mPHEMA, (b) CB-F3GA@mPHEMA (c) after adsorption CB-F3GA@mPHEMA for 4-NP.

3.4. Adsorption of Nitrophenols

The initial concentration and pH versus adsorption capacity were investigated as presented elsewhere [20]. The concentration of adsorbed P and NPs was calculated according to equation 1:

$$q_e = [(C_o - C_A)V]/m \qquad (1)$$

where C_o and C_A show the initial and equilibrium P and NPs concentrations (mg/L), respectively; V is the volume of the solution (mL) and m is the amount of CB-F3GA@mPHEMA (mg) [9, 20, 30].

3.4.1. Effect of Contact Time

Contact time of P and NPs on CB-F3GA@mPHEMA was studied (Figure. 8). Batch experiments were investigated by using their solutions in 25 mg/L concentration at pH=2.0. As shown in Figure. 8, adsorption rate was firstly fast, and saturation degree was step by step achieved in about 20 min for all P and NPs. 4-NP was adsorbed much faster than other NPs. 4-NP has high affinity to CB-F3GA@mPHEMA microbeads because of far from the central atom. Their arrangement of adsorption rate was as follows: 4-NP> 3-NP >2-NP > P.

Previous studies on the adsorption of phenolic pollutants by different materials have given in different adsorption times. Ravi et al have found 20 h equilibrium adsorption time for P and cresol isomers adsorption on activated carbon (AC) [5]. Furuya et al. have examined 2 weeks equilibrium adsorption for nitro- and NPs on granular AC [7].

The adsorption rates received with the CB-F3GA@mPHEMA developed by us look like to be more useful. Therefore, the adsorption that we obtained was comparable with the data presented in the previous articles about CPs and NPs [9, 20, 30,37].

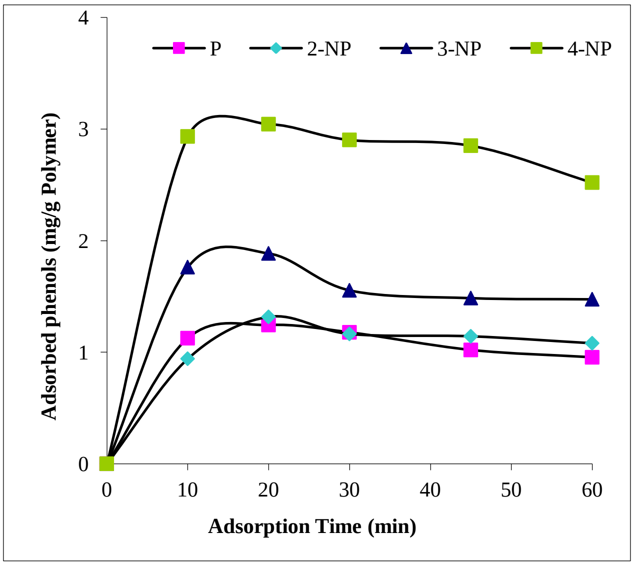


Figure 8. Adsorption rates of P and NPs on the CB-F3GA@mPHEMA (initial concentration 25 mg/L, T 25°C, pH 2, agitation rate 400 rpm).

3.4.2. Effects of Initial Concentration of NPs

The P and NPs adsorption versus the initial concentration of NPs is given in Figure. 9. It is clear that the amount of adsorbed phenol notable raised with the initial NPs concentration.

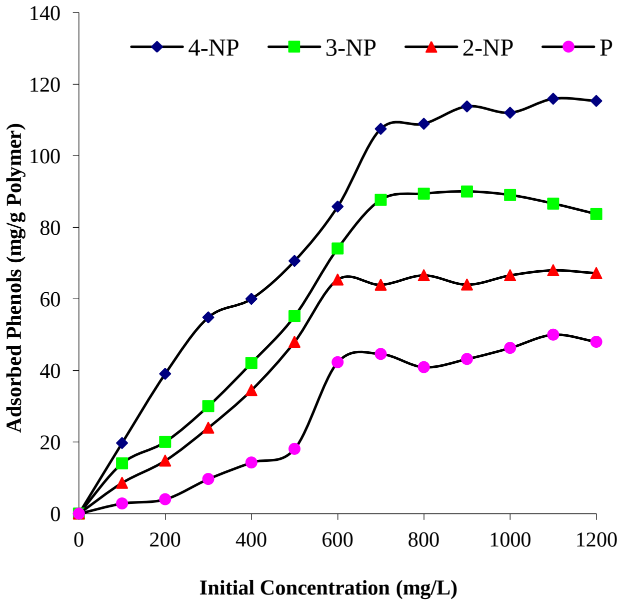


Figure 9. P and NPs adsorption capacity of the CB-F3GA@mPHEMA (T 25 °C, pH 2, agitation rate 400 rpm).

Yang et al have studied magnetic ZIF-67 substance to eliminate of 2-nitroresorcinol from wastewater [38]. Hammiche-bellal et al have investigated the utilization of magnetite Fe_3O_4 as a catalyst for the transformation of 4-NP to 4-aminophenol (4-AP). The higher the ratio of Fe^{3+}, the more active is the catalyst [39].

3.4.4. Effects of pH

As shown in Figure 10 pH versus adsorbed P and NPs are given. The adsorption reduced with escalating pH. Maximum adsorption of P and NPs happened at pH 2.00. But, in between 2.00 and 6.00 pH range, there is not important fallen in the adsorption. The adsorption was notably reduced above pH=6.5. The amount of adsorbed on the CB-F3GA@mPHEMA in pH=6.5 are maximum for 3.04 $mg.g^{-1}$ 4-NP, 1.88 $mg.g^{-1}$ 3-NP, 1.32 $mg.g^{-1}$ 2-NP, and 1.24 $mg.g^{-1}$ P. The order is as follows: 4-NP >3-NP >2-NP >P. The affinity of the NPs changes because of the chemical structure in CB-F3GA@mPHEMA. A distinction in geometric form is presumably for the immobilized CB-F3GA@mPHEMA ligand, following in a comparatively adsorption of 4-NP.

The intermolecular affinity between NPs and CB-F3GA@mPHEMA are low in the neutral pH. The falling in adsorption may be because of the competing OH^{-1} groups. This can be described to either the adsorption of OH^- ions onto the positive charge centers of CB-F3GA@mPHEMA or the deprotonation of surface OH^- groups.

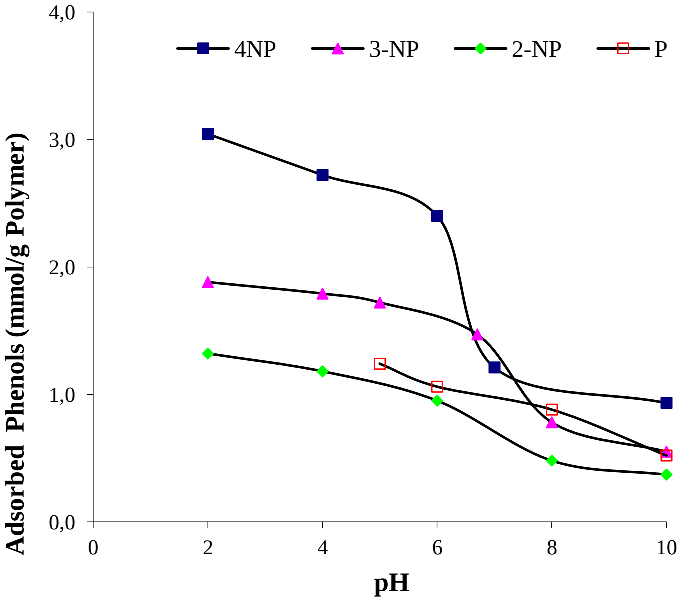


Figure 10. Effect of pH on adsorption of P and NPs on the CB-F3GA@mPHEMA. (initial concentration 25 mg/L, T 25°C, agitation rate 400 rpm).

3.4.5. Adsorption Kinetics

The experimental data obtained from the Ce/qe versus Ce straight shows that it fits the linear Langmuir equation. The values of parameters Q, KL, and R^2 were tabulated in Table 2, in which the values of R^2: 0.997, 0.997, 0.9985, and 0.994 respectively, indicated that the Langmuir model can be well used to fit the sorption data of 4-NP, 3-NP, 2-NP and P.

Table 2. Langmuir isotherm parameters for Ph and NPs adsorption on CB-F3GA@mPHEMA microbeads (initial concentration 25 mg/L, T 25°C, agitation rate 400 rpm).

Adsorbent	Langmuir Coef.	4-NP	3-NP	2-NP	Ph
CB-F3GA@mPHEMA	K_L	0.200	0.094	0.066	0.065
	Q^0	1.512	0.532	0.248	0.236
	R^2	0.997	0.997	0.985	0.994

3.4.6. Regeneration of CB-F3GA@mPHEMA

Desorption treatments were made with ethyl alcohol mixture (30%, v/v). The CB-F3GA@mPHEMA loaded P and NPs were located within the desorption medium, and then the amount of NPs desorbed in 30 minute was calculated.

4. Conclusions

Waters including phenolic pollutants pose an imported problem. CB-F3GA@mPHEMA was studied for adsorption/desorption of P and NPs from aquatic media.
The results of this study are presented below.

- The maximum adsorption capacities of CB-F3GA@mPHEMA from solution were 3.04 mg.g^{-1} for 4-NP, 1.88 mg.g^{-1} for 3-NP, 1.32 mg.g^{-1} for 2-NP, and 1.24 mg.g^{-1} for P.
- The affinity sequence was as follows: 4-NP>3-NP>2-NP>P.
- The adsorption capacity of P and NPs increased with decreasing pH. The adsorption of phenolic compounds reduced with increasing pH. The adsorption of NPs was high as compared to Ph, because NPs are more hydrophobic nature than P.
- Alternate adsorption and desorption cycles exhibited the usability of this CB-F3GA@mPHEMA for elimination of P and NPs from solutions.
- CB-F3GA@mPHEMA has shown to be an effective new type of adsorbents in water treatment area.
- CB-F3GA@mPHEMA could be repeatedly used 3 times without any noteworthy loss of adsorption capacity.

Finally, CB-F3GA@mPHEMA may have a great subscribe to the sustainable environment. Certainly, these adsorbents present many benefits for the wastewater treatment processes.

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