Design and characterization of phosphonic acid-functionalized grafted sepiolite nanohybrids and their adsorption studies for removal of copper ions from aqueous solution

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Abstract: Novel, economical and efficient phosphonic acid-functionalized grafted sepiolite nanohybrids were synthesized in present work, for selective elimination of copper ions from water. These nanohybrids were prepared by graft polymerization of glycidyl methacrylate onto sepiolite. We utilized free radical graft polymerization to graft glycidyl methacrylate (GMA) onto silanized sepiolite. The nanohybrids obtained showed 479% grafting percentage at 0.3 g of KPS initiator, 15% GMA monomer and after 4 h reaction. In the quest of the selective removal of metal ions from water, the maximum grafted nanohybrid i.e., (PGE₃) was chemically treated with phosphoric acid to introduce phosphonic acid groups on it. FTIR, XRD, SEM, CHO analysis, BET and TGA analysis were utilized to characterize the developed nanohybrids. We carried out batch adsorption studies using AAS process, examining the

impact of pH, adsorbent weight, contact time, adsorbate concentration, and temperature on the adsorption process. Due to the selectivity of phosphonic acid groups towards copper ions, phosphonic acid-functionalized grafted sepiolite nanohybrid (PGE₃-P) was used for copper ions removal from its aqueous solution. The maximum adsorption capacity of PGE₃-P adsorbents was 134.5 mg/g for copper ions. The data from kinetic studies suggests that the adsorption process of copper ions obeyed pseudo-second order model. Langmuir isotherm proved to be a more fitting model in equilibrium isothermal investigations. The thermodynamic analysis of the data indicates that the adsorption of copper ions by PGE₃-P is an endothermic and spontaneous process. The development of this phosphonic acid-functionalized grafted sepiolite nanohybrid adsorbent is a new contribution into the field of adsorption. The developed material can be utilized as selective adsorbent for elimination of other heavy metals from water.

Keywords: Nanohybrids, Sepiolite, glycidyl methacrylate, free radical graft polymerization, phosphonation, and adsorption.

1. Introduction

The rapid increase in industrialization has led to the contamination of clean water streams with hazardous metals like copper, cadmium, chromium, nickel, lead, and mercury [1]. Industrial processes often involve the use and release of these metals into water streams, either intentionally or as byproducts of manufacturing activities. For example, copper is commonly used in electronic and electrical components [2], while cadmium is found in batteries [3]. Chromium is used in metal plating and other industrial processes [4], and mercury is present in certain chemical applications [5]. As these metals find their way into water streams, they pose serious threats to the environment and human health above their permissible limit. They can accumulate in aquatic ecosystems, leading to the contamination of drinking water sources and negatively impacting aquatic life. The consequences of exposure to these metals include

various health issues in humans, ranging from gastrointestinal problems to more severe conditions like damage to the nervous system, liver, and kidneys [6]. The permissible limit of copper in industrial discharge is 1.3 mg/L as per U.S. Environmental Protection Agency (USEPA). Water resources polluted with copper can cause nausea, diarrhea, vomiting and gastrointestinal problems in humans [7]. Its excessive consumption can also cause hepatic necrosis, ultimately resulting in death [7]. To address these concerns, there is a need for effective water treatment and remediation strategies to remove or reduce the concentration of these hazardous metals in water, ensuring the protection of both the environment and public health.

GMA is a versatile monomer. Its versatility arises from its chemical structure, which includes both a reactive epoxy group and a methacrylate group. This dual functionality makes GMA highly adaptable for various polymerization reactions [8]. It is well-known in selective removal [9] and recovery of metals [10]. Its epoxy group can be converted into suitable functional groups for selective metal ion uptake [11]. Wang et al. prepared triethylene teramine (TETA) functionalized magnetic poly (glycidyl methacrylate) (PGMA) nanoadsorbents for effective adsorption of Hg (II) [12]. Zhao et al. prepared a novel adsorbent by functionalizing poly(glycidyl methacrylate) microspheres with pyromellitic acid and used it to adsorb Pd (II) from wastewater [13].

The process of graft polymerization is an attractive method for creating nanohybrids, involving the polymerization of various monomers on a compatible substrate [14]. In such a process, the polymer grafting percentage is crucial and depends on reaction parameters like initiator amount, monomer concentration, and reaction time etc. Therefore, the optimization of these parameters is essential to obtain an optimum polymer grafted product [15]. Moreso, the substrate modification/functionalization prior to polymer grafting is a unique strategy to increase the polymer grafting percentage on the substrate [16]. For instance, silanization of

substrate by silane coupling agents has been used to modify the surface chemistry of substrate and thereby to increase the quantity of grafted polymer [17]. Nasir et al. polymerized acrylonitrile and aniline on a silanized GO substrate and the grafting percentage was increased up to twice for polyacrylonitrile [18] and 1.5 times for polyaniline than pristine GO, respectively [19].

Herein, we have prepared a GMA grafted sepiolite nanohybrid by a free radical graft polymerization method. This nanohybrid serves as a precursor for the development of selective metal ion adsorbent. We have used a silanized sepiolite substrate to graft GMA and optimized the reaction conditions i.e., initiator amount, monomer concentration, and reaction time. The optimal grafted product was further converted into phosphonic acid-functionalized grafted sepiolite nanohybrid by treating it with phosphoric acid. The developed nanohybrids were characterized by spectroscopic techniques including FTIR spectroscopy, XRD analysis, TGA analysis, SEM, and BET analysis and phosphonic acid-functionalized grafted sepiolite nanohybrid was used in metal ion removal using Cu (II) as model pollutant.

2. Materials and methods

2.1. Materials

In present work, pristine sepiolite (PS) (with 99% pure mineral contents), vinyl trimethoxy silane (VTMS, 97%), tween-80 (98%), glycidyl methacrylate (GMA) (97%, d = 1.042 g/ml), acetone (99.5%), isopropanol (> 99.8%), methanol (99.7%), copper sulfate (99.9%), lead acetate trihydrate (99.9%), hydrochloric acid (37%), sulfuric acid and phosphoric acid were obtained from Sigma-Aldrich, Germany. Potassium persulphate (KPS) purchased from Daejung, Korea was used after recrystallization in water. All the chemicals were used as received.

2.2. Purification and Silanization of Sepiolite

The purification process for PS involved stirring it in deionized water for 24 hours. Following this, the resulting product was filtered and subjected to vacuum drying. The dried product was pulverized into fine powder and stored in a desiccator. This purified and dried PS was further used to react with VTMS [20]. In this study, VTMS has been used as vinyl-based silane coupling agent due to its highly reactive nature [21]. In short, an appropriate quantity of PS was introduced into isopropanol within a round bottom flask and blended with hydrolyzed VTMS at room temperature. Afterward, the temperature was raised to 60 °C \pm 2, and the system was maintained under persistent stirring for a period of 2 hours. The obtained product was filtered, washed with methanol, and then subjected to vacuum drying for 15 minutes. Subsequently, the dried product was pulverized, stored in a desiccator, and labelled as vinyl modified sepiolite (VMS).

2.3. Free radical graft polymerization PGMA onto VMS

In free radical graft polymerization of PGMA on VMS, appropriate quantity of VMS, tween-80 and distilled water were added into a glass reactor. A stable suspension was obtained after stirring for 15 minutes. GMA followed by KPS was put into this suspension and the temperature was elevated to 70 °C for a duration of 4 hours under an inert atmosphere. Subsequently, the obtained product was filtered, separated from homopolymer by soxhlet extraction in DMF, dried, and labelled as PGE. The chemical composition and codes of the prepared samples are shown in Table 1.

Sample code	GMA (w/v%)	KPS (g)	Reaction time (h)
PGE1	5.0	0.3	4.0
PGE ₂	10.0	0.3	4.0
PGE3	15.0	0.3	4.0
PGE4	20.0	0.3	4.0
PGE5	15.0	0.1	4.0
PGE6	15.0	0.2	4.0
PGE7	15.0	0.4	4.0
PGE8	15.0	0.3	3.0
PGE9	15.0	0.3	5.0
PGE10	15.0	0.3	6.0

Table 1. Chemical composition and codes of PGMA grafted nanohybrids

*Amount of VMS = 1.0% (w/v); Amount of tween-80 = 0.1% (w/v)

2.4. Grafting percentage

Grafting percentage is the amount of polymer that has been grafted on a base material. It is measured from the increment in weight of base material after grafting reactions. Mostly, it is calculated by using subsequent equation:

Grafting percent (%) =
$$\frac{W_g - W_o}{W_o} \times 100$$

Where, W_0 = Weight of PS before grafting, W_g = Weight of grafted product.

2.5. Phosphonation

Epoxide groups of PGE₃ were converted into phosphonated form. 1 g of PGE₃ was put into two necked round bottom flasks followed by addition of 10 ml concentrated H₃PO₄. The mixture was stirred for 6 h at 80 °C. The obtained product, PGE₃-P, was rinsed with distilled water for neutralization, followed by vacuum drying and storage in a desiccator for further use. Key steps involved in the synthesis phosphonic acid-functionalized grafted sepiolite nanohybrid are given in Figure 1.



Figure 1. Key steps involved in the synthesis phosphonic acid-functionalized grafted sepiolite nanohybrid

2.6. Characterization

The structural variations of nanohybrids were studied using a Nicolet 6700 FTIR spectrophotometer with a diamond crystal. The scanning of all samples was completed from

4000 to 400 cm⁻¹ at 6 cm⁻¹ resolution. XRD analysis of all samples was performed at room temperature using the D8 Discover X-ray diffractometer. The X-ray beam utilized for the analysis was generated by nickel-filtered Cu K α (λ ¹/₄ 1.542A°) radiation, operating at 30 kV and 30 mA. All the diffractograms were generated within a 2 θ ranging from 5° to 85° at a scanning rate of 1.1/min. Thermogravimetric measurements were conducted using the TGA/DSC1 model from Mettler Toledo, Switzerland, under an inert atmosphere, ranging from room temperature to 800°C. The heating rate was maintained at 20°C/min with a nitrogen flow rate of 100 mL/min. All samples underwent vacuum drying Before SEM analysis, and were subsequently coated with amorphous carbon to enhance surface conductivity.

2.7. Zeta potential measurements

The zeta potential measurements of PGE₃-P were conducted using a Zeta Meter 3.0 equipped with a microprocessor unit. The pH-dependent zeta potential variations were investigated. A 0.5 g sample of PGE₃-P in 100 mL distilled water, containing the desired electrolytes, was introduced into a thermostatic shaker bath and left to rinse for 24 hours at $25\pm1^{\circ}$ C. Afterward, the samples were allowed to settle for 1 minute to facilitate the settling of larger particles. Zeta potential was then measured using an aliquot taken from the supernatant.

2.8. Metal removal studies

Stock solution (1000 ppm) of analytical grade CuSO₄·5H₂O was prepared in distilled water. The required concentration of metal ions was attained by diluting its stock solutions in water. The mixtures containing adsorbent and Cu (II) solution were put in a shaker for a certain time, at 800 rpm. Electronic pH meter was used to examine the pH and pH of solutions was sustained with addition of 0.1 M HCl or 0.1 M NaOH solution. The Varian SpectrAA-300 atomic absorption spectrophotometer, was used to measure the amount of metal ions in liquid samples after adsorption experiments. Different parameters influencing adsorption process such as; pH, adsorbent weight, contact time, adsorbate concentration, and temperature were studied. Adsorption capacity (Q_e) of adsorbent was measured using following equation:

Adsorption Capacity =
$$Q_e = \frac{(C_o - C_e)}{m} \times V$$

Where $C_o =$ Initial concentration (mg/L) of metal, $C_e =$ Equilibrium concentration of metal, V = Volume (ml) of solution, and m = Mass (mg) of the adsorbent.

3. **Results and discussion**

3.1. Free radical graft polymerization

PGMA grafted sepiolite nanohybrids, synthesized by a free radical graft polymerization method, follows a free radical induced polymerization mechanism. This mechanism consists of initiation, propagation and termination reactions. The process begins with the dissociation of initiator $(S_2O_8^{-2})$ upon heating, which generates free radicals $(SO_4^{-\bullet} = R^{\bullet})$. These free radicals react with GMA monomer molecules (G) and vinyl groups present on VMS to start the graft polymerization reaction as well as homopolymerization of GMA [15]. The growing polymer chains propagate by the interaction of free radicals with other GMA molecules. Since both, the monomer radicals and the VMS, contain vinyl groups, active sites are generated and the grafting process follows "grafting onto" and "grafting from" mechanisms. The propagating polymer chains are terminated by self-reaction of "n" GMA free radicals (nG[•]), leading to homopolymerization, and PGMA grafted radicals (pG[•]-RVMS), which ultimately results in the formation of the grafted polymer product [22]. The chemical reactions involved in the mechanism of free radical graft polymerization of PGMA on VMS is illustrated in Figure 2.



Figure 2. Chemical reactions involved in synthesis of PGE by free radical free radical graft polymerization

3.2. Influence of reaction parameters

The polymerization reaction parameters, including the amount of initiator, monomer concentration and reaction time, play a significant role in determining the polymer grafting percentage [23]. These parameters were optimized to obtain the maximum grafting percentage of PGMA on VMS, and the obtained results are described below:

3.3.1 Effect of initiator amount

The effect of the initiator (KPS) on the polymer grafting percentage was thoroughly investigated. The amount of KPS was systematically varied from 0.1 to 0.4% w/v, and the

results are presented in Figure 3A. The figure shows that an increase in the grafting percentage was observed with the rise in amount of KPS. As the KPS amount increased, the grafting percentage also increases. This is because more KPS generates higher number of free radicals for reaction.

Notably, at 0.3% (w/v) initiator amount, an optimal balance was achieved, ensuring an adequate supply of free radicals for both GMA polymerization and grafting reactions and at this point, the maximum grafting percentage of 251% was achieved. However, when the initiator amount was increased beyond 0.3% (w/v), it led to a decrease in the grafting percentage. This decrease was primarily due to a significant increase in the formation of free radicals. The excessive presence of free radicals promoted the homopolymerization of GMA and utilization of larger proportion of the monomer in homopolymerization rather than participating in the grafting reaction, thereby reducing the grafting on the substrate [24].

Based on these results, 0.3% (w/v) KPS amount was fixed for further reactions, as it yielded the best results in terms of grafting efficiency and minimized unwanted homopolymerization.

3.3.2. Effect of monomer concentration

In Figure 3B, the impact of monomer concentration on the grafting percentage of PGMA is depicted. The monomer concentration was changed from 5 to 20% (w/v) and the amount of initiator and surfactant was kept constant. The grafting percentage exhibited a considerable increase with a rise in monomer concentration, reaching its maximum value i.e., 479% at 15% (w/v). However, beyond this point, a rise in the monomer concentration led to a decline in the grafting percentage. This suggests that there is an optimal concentration of monomer for achieving the highest grafting percentage, and exceeding this concentration hinders the grafting reaction which is 15% (w/v) in our case. At this optimal monomer concentration, maximum

number of GMA can participate in the grafting reaction. At higher monomer concentration (20% (w/v)), the grafting percentage experienced a decrease. This can be attributed to the presence of a huge amount of monomer, which led to excessive homopolymerization. The excessive homopolymer formed was physically adsorbed on the VMS surface creating a barrier that hindered the accessibility of GMA monomers and oligomers, thereby impeding the further grafting of PGMA onto VMS. As a result, the grafting process was restricted, leading to the observed decrease in grafting percentage at higher monomer concentrations [25]. Based on these results, GMA concentration of 15% (w/v) was fixed in further experiments.

3.3.3. Effect of reaction time

The impact of reaction duration on the polymer grafting percentage was examined, and the resulting findings are shown in Figure 3C. The reaction time was varied from 2 to 5 h for a specific concentration of reactants i.e., KPS and GMA. It was observed that as the reaction time increased, a higher grafting percentage was obtained. This rise in grafting percentage can be ascribed to the availability of more free radicals for the graft polymerization reaction, which increases the polymer chain propagation and growth on VMS. The maximum grafting percentage of 479% was achieved after 4 h. It can be concluded that 4 h was the sufficient time for the radicals to react and promote efficient polymerization and grafting on the substrate. Beyond 4 hours, the grafting percentage showed minimal change. This can be attributed to the consumption of all the reactants during the reaction, and no further alteration in the grafting percentage was observed even with an extended reaction time [26]. Using the optimized conditions and suitable quantities of reactants, a reasonable amount of grafted product was prepared for further studies. The photographs of PGE₃ and PGE₃-P i.e., synthesized nanohybrids are presented in Figure 3D.



Figure 3. (A) Effect of initiator amount on PGMA grafting percentage: reaction time = 3 h, GMA = 5% (w/v). (B) Effect of monomer concentration on PGMA grafting percentage: reaction time = 3 h, KPS = 0.3% (w/v). (C) Effect of reaction time on polymer grafting percentage: GMA = 15% (w/v), KPS = 0.3% (w/v); VMS = 1.0% (w/v), tween-80 = 0.1% (w/v), T = 70 °C for (A), (B) and (C). (D) Photographs of PGE₃ and PGE₃-P nanohybrids

3.4. FTIR analysis

FTIR spectroscopy was used to analyse the chemical changes occurring during the modification, grafting and phosphonation processes, and the corresponding results are presented in Figure 4. The FTIR spectrum of PS, as shown in Figure 4a exhibits bands within the 3690-3410 cm⁻¹ range, indicative of stretching vibrations attributed to OH groups. These hydroxyl groups are indicative of water molecules incorporated within the sepiolite structure. The peak detected at 1653 cm⁻¹ correspond to the OH bending of water molecules present in sepiolite, respectively [27]. Furthermore, peaks ascribed to the Si-O-Si groups of the tetrahedral sheets of sepiolite were detected at 1004 cm⁻¹ and 464 cm⁻¹ [28], along with Si-O vibrations at 974 cm⁻¹, 783 cm⁻¹, 685 cm⁻¹ and 644 cm⁻¹ [29].



Figure 4. FTIR spectra (a) PS (b) VMS (c) PGE₃ (d) PGE₃-P and (e) PGE₃-P-Cu

In the IR spectrum of VMS (Figure 4b), a new peaks emerged at 2932 cm⁻¹ and 2886 cm⁻¹, which can be ascribed to the asymmetric and symmetric stretch of the –C-H group of the vinyl group present in the sepiolite structure [29]. The peaks observed at 1714 cm⁻¹ and 1652 cm⁻¹ correspond to the C=C stretch of the vinyl group and the OH bending of water molecules present in sepiolite, respectively [27]. Moreover, the IR spectrum revealed the existence of peaks at 1392 cm⁻¹ and 1274 cm⁻¹, corresponding to the –C-H bending vibration of vinyl groups present in the sepiolite structure [30].

In the FTIR spectrum of PGE₃ nanohybrid (Figure 4c), peaks representative of both VMS and GMA are present. It revealed important peaks related to specific functional groups present in the grafted nanohybrid. The peaks at 2996 and 2936 cm⁻¹ can be attributed to the stretching vibrations of -CH groups, while their corresponding bending vibrations are observed at 1479 cm⁻¹ [31]. A noticeable peak at 1721 cm⁻¹ was detected, signaling the presence of the

carbonyl (-C=O) group in GMA. Additionally, peaks associated with epoxy groups were observed at 1250 cm⁻¹, 905 cm⁻¹, and 843 cm⁻¹ [32]. The presence of all peaks of GMA in PGE₃ spectrum, confirms the grafting of PGMA onto VMS. In the FTIR spectrum of PGE₃-P (Figure 4d), a distinct -OH band emerges in the range of 3500-3000 cm⁻¹. Additionally, the peak at 1163 cm⁻¹ and 769 cm⁻¹ emerged due to the presence of P=O and P-O-C stretches [33]. The presence of these peaks in spectrum of PGE₃-P confirms the successful phosphonation reaction. FTIR spectrum of PGE₃-P-Cu exhibited the peaks at 750 cm⁻¹ and 470 cm⁻¹ attributed to Cu-O bonds. The presence of these peaks confirms interaction of PGE₃-P with Cu (II) ions.

3.5. XRD analysis

The structural analysis of PS, VMS, PGE₃ and PGE₃-P was conducted using XRD analysis and the diffractograms are shown in Figure 5. The diffractogram of PS (Figure 5a) displayed all the characteristic peaks as specified in the standard XRD pattern for pristine sepiolite (JCPDS Card No.: 00-029-1492). These peaks were observed at the following angles: 16.6° (060), 19.8° (131), 20.4° (260), 24°, 27°, 34.8°, 37.3° and 40° [34]. In the diffractogram of VMS, presented in Figure 5b a small decrease in the peaks intensities was observed which suggest that the reaction of VMS with PS slightly affects its structure [29] and it maintained its structural integrity even after modification.



Figure 5. XRD diffractogram of (a) PS, (b) VMS, (c) PGE₃ (d) PGE₃-P and (e) PGE₃-P-Cu

The spectrum of PGE₃ (Figure 5c) displayed peaks at 16.6°, 24°, 27°, and 34.8°, which correspond to VMS. However, these peaks showed slight positional shifts compared to the standard VMS pattern [35]. The grafting of PGMA on VMS leads to a reduction in crystallinity, indicating a decrease in the overall degree of crystalline ordering. Characteristics peaks of PGMA were observed at $2\theta = 17.5^{\circ}$ and $2\theta = 29.0^{\circ}$. These reflections provide confirmation of the presence of grafted PGMA on VMS, indicating the successful grafting of PGMA chains onto VMS. A decrease in the height of peaks and the disappearance of peaks beyond $2\theta = 40^{\circ}$, indicates the dilution of the crystalline phase of VMS after grafting of amorphous PGMA. However, the average crystallite size increases after PGMA grafting, suggesting a growth or enlargement of individual crystalline domains [36]. The reduced crystallinity of PGE₃ promotes adsorption, due to increase in amorphous character. The diffractogram of PGE₃-P as shown in Figure 5d, depicts a reduced peak intensity as compared to PGE₃. The reduction in intrinsic crystallinity of PGE₃ was due to incorporation of amorphous organic (PO₃H) groups [37]. The diffractogram of PGE₃-P-Cu as given in Figure 5e shows complete disappearance of the peaks, demonstrating the formation of a chelate between copper ions and PGE₃-P. Table 2 presents crystallinity (%) and crystallite sizes of pristine sepiolite and its modified forms.

Table 2. Crystallinity	(%) and average	crystallite size	(nm) of	pristine sepi	iolite and its
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Sample Codes	PS	VMS	PGE3	PGE3-P	PGE3-P-Cu
Crystallinity (%)	83.2±1.07	78±3.07	62±2.07	47±1.01	46.1±1.21
Average crystallite size (nm)	106.2±9.07	108.2±9.07	113.2±8.07	153.5±9.05	155.1±7.04

modified forms

3.6. Morphological analysis

Figure 6 shows the SEM micrographs of PS, VMS, PGE₃ and PGE₃-P nanohybrids. The SEM micrograph of PS (Figure 6a) displays a smooth surface and long bundles of sepiolite fibers [20]. These bundles are formed due to van der Waals forces and hydrogen bonding between adjacent fibers [38]. Upon silanization, as depicted in Figure 6b, the sepiolite fibers become shorten. Their bundles are also disrupted. The interaction between the silanol groups on the sepiolite fibers' surface and the vinyl groups of VTMS is responsible for this transformation [29]. The introduction of non-polar vinyl groups through VTMS treatment also disrupts the electrostatic interactions between the sepiolite fibers [20].



Figure 6. SEM micrographs of (a) PS, (b) VMS, (c) PGE₃, (d) PGE₃-P and (e) PGE₃-P-Cu

In the SEM micrograph of PGE_3 (Figure 6c), the observed changes include appearance of new surfaces, providing evidence for the growth of PGMA chains on the surface of VMS. As a result of the grafting process, the PGMA chains have fully enveloped the individual fibers of

VMS, resulting in a distinct morphology [39]. In contrast to the well-defined surface of PS, PGE₃ possesses a rough surface with tightly attached embedded fibers. The results provide confirmation of the successful grafting of PGMA on VMS surface. The micrographs of VMS and PGE₃ are in agreement with the XRD analysis as the structural integrity of sepiolite was maintained in VMS and PGE₃ because functionalization occurred largely on the surface or by partial replacement of zeolitic water [29].

Phosphonation of PGE₃ resulted in a further increase in surface roughness and compactness, as depicted in Figure 6d. This effect can be attributed to the hydrophilic nature of the introduced phosphonic acid groups, as reported by previous studies [40]. FESEM micrographs of PGE₃-P also revealed the presence of globular and compact structures. Notably, the fibers of PS and VMS were entirely covered with PO₃H groups, indicating successful phosphonation of the surface [41]. Figure 6e displays the change in morphology of PGE₃-P after Cu (II) adsorption. The image indicates that after Cu (II) adsorption the size of globules further increases.

3.7. CHO analysis

CHO analysis was performed to examine the alterations in the composition of PS during its silanization and grafting process. Table 3 shows the results of elemental analysis of the sepiolite. The detection of carbon in the CHO analysis of VTMS provides evidence supporting the silanization and incorporation of vinyl groups onto the PS surface during this reaction. Moreover, decrease in the atomic percentage of oxygen occurred due to the silanization reaction between VTMS and sepiolite. In this reaction, silanol groups of sepiolite reacted by condensation reaction of silanol groups with VTMS and removal of water molecules occurs. Due to the removal of water molecules, oxygen content decreases in VMS.

The atomic percentage of carbon was further increased in PGE₃ which can be attributed to the PGMA grafting onto the PS. PGMA grafting introduces additional carbon atoms to the VMS structure [20]. Also, the oxygen atomic percentage increases in PGE₃, which is due the oxygen of epoxy and carbonyl groups of grafted PGMA, present in PGE₃ [33]. CHOP analysis of PGE₃-P shows increase in atomic percentages of oxygen and hydrogen as compared to PGE₃ and presence of P percentage confirms the successful incorporation of phosphonic acid group in the structure of PGE₃ and its conversion into PGE₃-P.

These results from the elemental analysis provide valuable insights into the compositional variations that occur during synthesis of PS nanohybrids.

Sample codes	Atomic percentage					
-	С	0	Н	Р		
PS	-	3.5	58.2	-		
VMS	55.3	40.8	52.1	-		
PGE ₃	67.3	52.7	78.5	-		
PGE ₃ -P	67.2	65.7	81.2	4.15		

Table 3. Comparison of elemental composition of pristine sepiolite and its modified forms

3.8. BET Analysis

The surface area, pore volume and pore size of a material are greatly affected by chemical changes. The influence of chemical treatments on PS and its modified forms was carried out using BET analysis. The findings of this analysis are presented in Table 4. It can be observed from this table that a noticeable decrease in the surface area, pore volume and pore size has been occurred in PS upon silanization reaction. This condensation reaction introduced new functionalities on sepiolite, which subsequently resulted in a significant decrease of

approximately 75.5% in its surface area. The grafted sample i.e., PGE₃ showed even more reduced surface area, pore volume and pore size. Grafting of PGMA chains, filled the pores on VMS surface [29]. This grafting reaction resulted in reduction of up to 64% in pore volume and approximately 40% in pore size. The BET analysis results indicated that the silanization and subsequent grafting reaction significantly influenced the surface area, pore size and pore volume of PS. To note that these are crucial factors in a material's property and its applications.

Surface area of PGE₃, decreased further after its phosphonation because of the incorporation of phosphonic acid groups on PGE₃. After phosphonation, also a decrease in pores volume and pores size was examined, because of the filling of empty pores with bulky polymeric chains having PO₃H groups at the surface. These filled pores can also be seen in SEM micrographs given in Figure 6.

Sample Codes	PS	VMS	PGE3	PGE3-P
BET Surface Area (m ² /g)	212.6	160.8	135.2	93±0.58
Pore volume (cm ³ /g)	59.3	57.1	24.2	19.5
Pore size (nm)	62.8	62.4	57.2	68.2

Table 4. BET surface area analysis of pristine sepiolite and its modified forms

3.9. Thermogravimetric analysis

Thermal stability analysis of the synthesized nanohybrids was conducted using TGA and the corresponding thermograms are presented in Figure 7. The thermogram of PS (Figure 7a) showed a three-step mass loss. In the first step (58-172 °C), 8% mass loss was detected because of the removal of adsorbed water on sepiolite [42]. Subsequently, from 172 to 395 °C, 4% mass loss was observed as a result of the loss of zeolitic and coordinated water [43]. A 2.5% mass loss was observed up to 580 °C in the third step and was attributed to the dehydroxylation of

sepiolite anhydride [44]. The thermogram of VMS (Figure 7b) demonstrated approximately 2.5% mass loss from 50 to125 °C due to loss of adsorbed water, a 2.5% mass loss occurred up to 125 to 240 °C due to removal of zeolitic and coordinated water [43] and decomposition of vinyl groups occurred from 240 to 550 with 10% mass loss [45].

The thermogram of PGE₃ (Figure 7c) showed a 14.5% mass loss up to 58.5-140 °C ascribed to the removal of adsorbed water [46]. In the next step, 12% mass loss was observed up to 140-240 °C, which could be attributed to the removal of physiosorbed water [47], or water adsorbed to the material's surface through van der Waals forces or hydrogen bonding [35]. The degradation of grafted PGMA chains starts from 240 °C and a 33.5% mass loss can be seen at 550 °C; such a decomposition could result in the depolymerization of PGMA [48] or formation of glycidyl, allyl alcohol, isobutene, CO, CO₂, acrolein and propene through ester degradation [49].



Figure 7. TGA thermogram of (a) PS, (b) VMS, (c) PGE₃, (d) PGE₃-P

Thermogram of PGE₃-P (Figure 7d) showed first step mass loss of 19.6% within the temperature range of 52 °C to 134 °C. This mass loss is due to the evaporation of water molecules linked to the hydrophilic PO₃H groups [50]. Another mass loss of 134-240 °C with 8.6% mass loss can be ascribed to the removal of coordinated water of sepiolite [47]. Mass loss of 8.1% from 240- 550 °C can be assigned to the degradation of the grafted PGMA chains [51]. PGE₃-P has higher thermal stability than its un-sulphonated form, this enhanced stability can be ascribed to the phosphonation process [52]. The remaining residues primarily comprise the char resulting from the carbonaceous polymeric material and clay silicates [53]. The residual mass of pristine sepiolite and its modified forms at 800 °C is included in Table 5.

Sample codes	Residue (%) at 800 °C
PS	83.8
VMS	82.97
PGE ₃	38.6
PGE ₃ -P	61.5

Table 5. The residual mass of pristine sepiolite and its modified forms at 800 °C

4. Post-polymerization modification of PGMA grafted sepiolite nanohybrids

GMA is a vinyl monomer characterized by the presence of an epoxide group. The distinctive reactivity of the epoxy group allows for a wide range of reaction pathways. For instance, when PGMA reacts with phosphoric acid or other acids, a ring-opening reaction takes place. The unique characteristic of epoxide polymers enables a broad spectrum of functionalization possibilities under mild reaction conditions. As a result, GMA and its derived polymers provide significant flexibility in tailoring the properties of polymer adsorbents to meet specific application requirements [54].

In present work, the maximum grafted product, PGE₃, was utilized as a precursor to create phosphonic acid-functionalized grafted sepiolite. This was achieved by reacting PGE₃ with H₃PO₄ through the ring opening reaction of the epoxy group present in PGMA [55].

4.1. Cu adsorption on phosphonic acid-functionalized grafted sepiolite nanohybrids

The phosphonic acid-functionalized grafted sepiolite nanohybrid (PGE₃-P) was used for Cu (II) ion adsorption from its aqueous solution. Cu (II) was selected as a model pollutant because PGE₃-P possesses -PO(OH)₂ groups, which exhibit a higher affinity for Cu (II) ions compared to other metal ions. The chemical nature of the phosphonic acid groups enables it to form stronger coordination bonds with Cu ions [56]. Below are the results of adsorption studies obtained by varying the pH, adsorbent weight, contact time, adsorbate concentration and temperature.

4.1.1. Effect of pH

To study the effect of pH on Cu (II) adsorption by PGE₃-P nanohybrid, pH of the aqueous solution was changed from 2 to 6. It is to be noted that pH is known to influence the adsorption process by changing the surface charge and speciation of metal ions. A linear upsurge in Cu (II) adsorption capacity was observed with rise in pH up to 4 in Figure 8. At low pH, the reduced adsorption of Cu (II) ions is attributed to the competition between hydrogen ions and metal ions for binding with the phosphonic acid groups. Additionally, the oxygen groups present in PGE₃-P become more protonated at low pH values, making them less accessible to effectively capture Cu (II) ions [57].

At 4 pH, maximum adsorption capacity was observed. The enhanced adsorption capability is ascribed to the existence of free lone pairs of electrons on deprotonated oxygen atoms within the PGE₃-P. These exposed lone pairs serve as appropriate ligands for

coordinating with the copper ions, facilitating stronger and more effective adsorption interactions [58]. At higher pH values, adsorption capacity decreases because at higher pH Cu (II) ions tend to precipitate as hydroxides. Based on the obtained results, pH of the aqueous solution was kept 4 in further experiments.



Figure 8. Effect of pH on Cu (II) ions uptake: adsorbent weight = 4 g/L, time = 1 h, $C_o = 20$ mg/L and T = 398 K

The pH dependence of the zeta potential in PGE₃ is also notable. As the pH increases from 2-6, the values of zeta potential decreases progressively from 18.1 to -17.9 mV. The pH of the zero-point charge (pH_{ZPC}) was observed at 3.7 Zeta potential of PGE₃-P at pH ranging from 2-6 is depicted in Figure 9.



Figure 9. Zeta potential of PGE₃-P at pH ranging from 2-6

4.1.2. Effect of adsorbent weight

The weight of the adsorbent is also a pivotal parameter in metal adsorption studies and it can significantly affect the efficiency of an adsorption process. If the adsorbent weight is too low, the active sites may not be available or limited and this would lead to incomplete capture of metal ions in the solution. Conversely, excessive or too high weight of the adsorbent can complicate the separation or recovery process of the nanohybrid from the solution thus escalating the cost [59]. Hence, optimizing the weight of the adsorbent is crucial to achieve optimal efficiency and cost-effectiveness. The adsorbent weight was varied from 1 to 6 g/L in a metal adsorption process to investigate its influence on the adsorption of Cu (II) from aqueous solutions and the results are shown in Figure 10. A rise in Cu (II) adsorption capacity can be observed, ranging from 30 mg/g to 46 mg/g, with an increase in adsorbent weight from 1 g/L

to 4 g/L. The increase in the weight of adsorbent can elevate the number of accessible adsorption sites. Also, with the increase in the adsorbent weight, chances for copper ions or molecules to interact and adhere to the adsorbent material enhances, resulting in increased adsorption capacity for Cu (II) [60].

After 4 g/L further increase in adsorbent weight does not notably affect the adsorption process. This can be attributed to the limited number of adsorbate molecules at this point. Although excess of adsorbent is available in the solution, but the adsorbate molecules are no more available at this stage [61]. Based on these results adsorbent weight of 4 g/L was fixed for further studies.



Figure 10. Effect of adsorbent weight on Cu (II) uptake: pH = 4, time = 1 h, C_o = 20 mg/L

and T = 398 K

4.1.3. Effect of contact time

In an adsorption process, an optimal contact time is also crucial to obtain the maximum adsorption capacity. Contact time is a vital parameter to investigate the kinetics of adsorption process. Figure 11 illustrates the impact of contact time intervals on the adsorption capacity of Cu (II). The adsorption capacity showed a gradual increase with extended contact time. This behaviour is attributed to the abundance of available adsorption sites on the surface of the adsorbent, enhancing the reaction rate [62]. After 50 minutes, no significant increase in adsorption capacity is observed. This is because at this stage, the adsorption sites on the adsorption sites on the adsorbent surface become saturated [63], and the adsorption capacity reaches its maximum point, where additional adsorbate molecules cannot be accommodated [64]. Based on these results contact time of 50 minutes was fixed for further studies.



Figure 11. Effect of contact time on Cu (II) uptake: pH = 4, adsorbent weight = 5 g/L, $C_o =$

20 mg/L and T = 398 K

 Table 6. Comparison of parameters obtained by pseudo-first order and pseudo-second

 order models for Cu (II) uptake

Pseudo-first order					Pseudo-seco	nd order	
R ²	K ₁	Qe (cal)	Q _e (exp)	R ²	K ₂	Q _e (cal)	Q _e (exp)
	(min ⁻¹)	(mg/g)	(mg/g)		(g.mg ⁻¹ .min ⁻¹)	(mg/g)	(mg/g)
0.0436	-0.00014	7.15	43.1	0.997	0.00919	44.64	43.1

In order to study the adsorption kinetics, pseudo-first order and pseudo-second order models were applied and the results are presented in Figure 12. The pseudo-second-order show showed a better fit to the experimental data, as evident by a higher R² values of 0.997 for PGE₃-P. The best fitting of pseudo-second order model suggest that the adsorption process involves the formation of chemical interactions between the adsorbent and adsorbate interface [65]. Table 6 summarizes the comparison of parameters obtained from the kinetic models.



Figure 12. (a) Pseudo-first order and (b) Pseudo-second order plots of Cu (II) adsorption kinetics on the PGE₃-P: pH = 4, adsorbent weight = 5 g/L, $C_o = 20$ mg/L and T = 398 K

4.1.4. Effect of adsorbate concentration

The concentration of adsorbate influences the adsorption capacity and therefore it is essential to optimize the adsorbate concentration. By finding the right balance in adsorbate concentration, we can achieve the maximum adsorption capacity, leading to potential cost optimization. Figure 13 shows the impact of adsorbate concentration on the adsorption capacity.



Figure 13. Effect of adsorbate concentration on the Cu (II) uptake: pH = 4, adsorbent weight = 5 g/L, contact time = 50 minutes and T = 398 K

As the initial concentration of Cu (II) ions rises, there is a corresponding increase in the adsorption capacity. Initially, this increase showed a linear trend (up to 100 mg/L) and then became gradual which may be due to limited amount of available adsorption sites existing at adsorbent's surface [66]. Maximum capacity was found at 250 mg/L, so it was fixed in next experiment.



Figure 14. (a) Freundlich and (b) Langmuir model fit for Cu (II) uptake by PGE₃-P adsorbent: pH = 4, adsorbent weight = 5 g/L, contact time = 50 minutes and T= 398 K

To study the adsorption mechanism, the isothermal data was fitted with Langmuir [67] and Freundlich [68] isothermal models and their equations are given below:

$$\frac{C_{e}}{Q_{e}} = \frac{1}{K_{L}Q_{m}} + \frac{C_{e}}{Q_{m}}$$
 (Langmuir equation)
$$\log Q_{e} = \log K_{F} + \frac{1}{n}\log C_{e}$$
 (Freundlich equation)

Where Q_e is the adsorption capacity (mg/g) at equilibrium and C_e is equilibrium concentration (mg/L) of metal in solution. K_L is the Langmuir constant (L/mg) associated with the adsorption free energy. K_F and 1/n are Freundlich and heterogeneity constants (L/g), where K_F indicates the extent of adsorption and 1/n indicates the adsorption intensity [69]. As can be seen in Figure 14 and Table 7, R^2 (correlation coefficient) was higher for Langmuir model and it indicates that the adsorbent PGE₃-P follows monolayer [70] adsorption phenomenon for Cu (II) uptake on a homogenous surface [71].

 Table 7. Comparison of parameters obtained by Langmuir and Freundlich models on adsorbents at 398 K

Freundlich isotherm constants			Langmuir isotherm constants			
1/n	K _F	R_F^2	R_L^2	K _L	Q _m (cal)	Q _m (exp)
	$(g/mg min^{-1})$			(L/mg)	(mg/g)	(mg/g)
0.613	2.0718	0.02102	0.02710	0.01015	134.228	132.50

4.1.5. Effect of temperature

In an adsorption process, temperature have a significant impact on the adsorption capacity kinetics, and thermodynamics of the process. Figure 15 depicts the results of adsorption studies carried out for Cu (II) uptake at different temperatures. Upon increasing the temperature from 25 to 45 °C, there is a rise in the adsorption capacity of Cu (II) up to 2%. With the increase in temperature, molecules gain kinetic energy, which promotes diffusion rates and transport of

metal ions from the solution to the adsorbent's adsorption sites. After 45 °C, adsorption capacity starts to decrease, this can be attributed to increase in rate of desorption. At higher temperatures, instead of adsorption, desorption becomes dominant phenomenon [72].



Figure 15. Effect of temperature on the Cu (II) uptake: contact time = 50 minutes, pH = 5, adsorbent weight = 5 g/ L, $C_o = 250 \text{ mg/L}$

The Thermodynamic studies gives information about the free energy, enthalpy and entropy of the system during an adsorption process. Below are the equations utilized to calculate the Gibbs free energy (ΔG°), enthalpy and entropy changes (ΔH° and ΔS°) [73].

$$\Delta G = -RT \ln k$$

$$\ln K = -\frac{\Delta H^{\circ}}{R} + \frac{\Delta S^{\circ}}{R}$$

Where, R is the universal gas constant (8.314 Jmol⁻¹ K⁻¹), T is the temperature in kelvin and K is the equilibrium rate constant. K can be calculated the following equation:

$$K = \frac{C_{ads}}{C_{eq}}$$

Here C_{ads} is the concentration of adsorbate (Cu (II) ions) in mg/L, adsorbed at surface per liter of the metal solution, C_{eq} is the concentration of metal ions (mg/L) at equilibrium.

As presented in Table 8, ΔG° values are found to be negative at all studied temperatures and it indicates the spontaneous nature and feasibility of Cu (II) ion adsorption on the adsorbents. ΔG° values in the range of -20 kJ gmol⁻¹ suggest electrostatic interactions between sorption sites and metal ions (indicative of physical adsorption), whereas ΔG° values more negative than -40 kJ gmol⁻¹ entail charge sharing or transfer from the adsorbent surface to the metal ion, forming a coordinate bond (reflective of chemical adsorption). In this study, the obtained ΔG° values are < -20 kJ gmol⁻¹ and it showed that the Cu (II) ion adsorption follows physical adsorption mechanism, at the given temperatures [74]. Moreover, the value of ΔH° obtained from the slope of plot of ln K values against 1/T (Figure 16) is positive and it verifies adsorption in this study as an endothermic process. Typically, when ΔH values range from 2 kJ/mol to 30 kJ/mol, it indicates physical adsorption. In contrast, for chemical adsorption ΔH° values ranges from 40 kJ mol⁻¹ to 200 kJ mol⁻¹ [75]. Hence, the estimated value of ΔH° (10.47 kJ mol⁻¹ for PGE₃-P) demonstrates the dominance of physisorption mechanism in adsorption process. The positive value of ΔS° (50.51 kJ/mol) indicate that some structural variations occurred at the solid-liquid boundary, leading to increased system randomness [76].



Figure 16. Plot of ln K vs 1/T for calculation of the adsorption thermodynamic parameters

Temperature	ΔG° at	ΔG° at	ΔG° at	ΔH°	ΔS
(K)	308	328	348	(kJ/mol)	(kJ/mol)
PGE ₃ -P	-5.0017	-5.9496	-7.0001	10.4737	50.51

Table 8. Thermodynamics parameters for adsorption of Cu (II) on PGE₃-P

4.1.6. Mechanism of Cu (II) adsorption

In Cu (II) adsorption a combination of ion exchange, chemical bonding, electrostatic interactions, complexation and physical adsorption are involved. Understanding the mechanisms is crucial for designing effective adsorbents for copper removal from polluted water. Often adsorption kinetic studies and infrared spectroscopic analyses are used to investigate the reaction mechanism in detail. In present study the best fit of pseudo- second order model suggest adsorption is chemisorption. While thermodynamics parameters support physisorption and electrostatic interactions between PGE₃-P adsorbent and Cu (II) ions. The presence of Cu-O peaks in infrared also supports chemisorption and formation of covalent
bonds between Cu and adsorbent molecules. So, from these results we can conclude that adsorption in present work is a physio-chemical process, not pure physisorption and chemisorption. Figure 17 illustrates the proposed mechanism of Cu (II) adsorption by PGE₃-P drawn on the basis of above-mentioned conclusions.



Figure 17. Proposed mechanism of Cu (II) adsorption by PGE₃-P

4.1.7. Selectivity and reusability studies

The selectivity of nanohybrid is demonstrated through adsorption tests conducted in the presence of other metal ions that may potentially interrupt the adsorption process. Here we have conducted selectivity tests for PGE₃-P in the presence of copper, lead, nickel and cobalt (100 ppm). The findings are presented in Table 9. The nanohybrid demonstrated distinct selectivity towards Cu (II) ions and effectively resisted interference from other coexisting metal ions.

The reusability assessments were conducted using 1 M NaCl as the desorption medium, and the outcomes are depicted in Figure 18. The nanohybrid exhibited 68% Cu (II) adsorption capacity over three consecutive adsorption-desorption cycles, relative to the first cycle.



Figure 18. Regeneration studies on PGE₃-P: Adsorbent weight = 5 g/ L, V = 20 ml, T = 398 K, desorption medium = NaCl

Element	Cu	Pb	Ni	Со
Adsorption capacity (mg/g)	84.3	24.2	15.2	10.4

Table 9. Effect of other metal ions on adsorption of Cu (II) on PGE₃-P

Below in Table 10, a comparison of the maximum adsorption capacity of different adsorbents for Cu (II) ions reported in literature has been included and the PGE₃-P has shown better adsorption capacity for lead adsorption as compared to other adsorbents.

Table 10. Comparison of adsorption capacities of different materials for Cu (II) ions removal

Adsorbents	Adsorption capacity (mg/g)	References
Chitosan composites with amidoxime grafted graphene oxide	115.3	[77]
Chitosan crosslinked with glutaraldehyde/methylene bisacrylamide	95.7	[78]
Poly acrylic acid/alginate	63.59	[79]
PGE ₃ -P	134.5	Present work

Conclusion

In present study novel and efficient phosphonic acid-functionalized grafted sepiolite nanohybrids were synthesized via free radical graft polymerization for the selective removal of copper ions from water. Free radical graft polymerization is a cost effective, easy to use and green process. Moreover, higher grafting percentages of grafted polymers can be obtained in the presence of very small amounts of initiators by using this process. Optimization of grafting parameters yielded a maximum grafting percentage of 479% at 15% GMA using 0.3 g initiator in a 4-hour reaction. The chosen nanohybrid, PGE₃, underwent further modification by transforming epoxy groups into phosphonic acid groups to enhance Cu (II) ion adsorption capacity. Confirmation of grafting and phosphonation was achieved through FTIR, XRD, and

TGA analyses. The presence of new vibrations and changes in crystallinity were observed, and FESEM provided insights into morphological alterations. The BET technique assessed surface area changes in the synthesized nanohybrids.

In adsorption studies, the batch adsorption system was used as a function of pH, adsorbent weight, adsorbate concentration, contact time and temperature. The maximum adsorption capacity of PGE₃-P adsorbent was found 134.5 mg/g for Cu (II) ions. In kinetics studies pseudo-second order model best fitted. In equilibrium isothermal studies, Langmuir isotherm model fitted best. The thermodynamic parameters indicated that the adsorption process is both endothermic and spontaneous in nature.

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References

- Jaishankar M, Tseten T, Anbalagan N, Mathew BB, Beeregowda KN. Toxicity, mechanism and health effects of some heavy metals. Interdisciplinary Toxicology 2014; 7 (2): 60. https://doi.org/10.2478%2Fintox-2014-0009.
- [2]. Singh B, Kumar R, Chohan J, Sharma S, Singh J et al. Investigation of copper reinforced Acrylonitrile Butadiene Styrene and Nylon 6 based thermoplastic polymer nanocomposite filaments for 3D printing of electronic components. High Performance Polymers 2023; 35 (2): 115-125. https://doi.org/10.1177/09540083221112307.
- [3]. Recknagel S, Radant H, Kohlmeyer R. Survey of mercury, cadmium and lead content of household batteries. Waste Management 2014; 34 (1): 156-161. https://doi.org/10.1016/j.wasman.2013.09.024.
- [4]. Khurshid H, Mustafa MRU, Isa MH, Adsorption of chromium, copper, lead and mercury ions from aqueous solution using bio and nano adsorbents: A review of recent trends in the application of AC, BC, nZVI and MXene. Environmental Research 2022; 212: 113138. http://dx.doi.org/10.1016/j.envres.2022.113138.
- [5]. Kumari S, Jamwal R, Mishra N, Singh DK, Recent developments in environmental mercury bioremediation and its toxicity: A review. Environmental Nanotechnology, Monitoring & Management 2020; 13: 100283.
- [6]. Dahiya V, Heavy metal toxicity of drinking water: A silent killer. GSC Biological and Pharmaceutical Sciences, 2022; 19 (1): 020-025. https://doi.org/10.30574/gscbps.2022.19.1.0107.
- [7]. Al-Saydeh SA, El-Naas MH, Zaidi SJ. Copper removal from industrial wastewater: A comprehensive review. Journal of Industrial and Engineering Chemistry 2017; 56: 35-44. https://doi.org/10.1016/j.jiec.2017.07.026.

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- [8]. Chauhan A, Islam A, Javed H, Kumar S. Facile fabrication of Amberlite XAD-16 with dipicolylamine for remediation of industrial wastewater containing lead and copper: Isotherm, kinetics, thermodynamics and selectivity studies. Microchemical Journal 2019; 146: 606-613. https://doi.org/10.1016/j.microc.2019.01.051.
- [9]. Seko N, Ninh NTY, Tamada M. Emulsion grafting of glycidyl methacrylate onto polyethylene fiber. Radiation Physics and Chemistry 2010; 79 (1): 22-26. https://doi.org/10.1016/j.radphyschem.2009.08.014.
- [10]. Sekine A, Seko N, Tamada M, Suzuki Y. Biodegradable metal adsorbent synthesized by graft polymerization onto nonwoven cotton fabric. Radiation Physics and Chemistry 2010; 79 (1): 16-21.

https://ui.adsabs.harvard.edu/link_gateway/2010RaPC...79...16S/doi:10.1016/j.radphyschem. 2009.08.007.

- [11]. Sokker HH, Badawy SM, Zayed EM, Nour Eldien FA, Farag AM. Radiation-induced grafting of glycidyl methacrylate onto cotton fabric waste and its modification for anchoring hazardous wastes from their solutions. Journal of Hazardous Materials 2009; 168 (1): 137-144. https://doi.org/10.1016/j.radphyschem.2023.110967.
- [12]. Jazani OM, Rastin H, Formela K, et al. An investigation on the role of GMA grafting degree on the efficiency of PET/PP-g-GMA reactive blending: Morphology and mechanical properties. Polymer Bulletin 2017; 74 (11): 4483-4497. https://doi.org/10.1007/s00289-017-1962-x.
- [13]. Wang Y, Zhang Y, Hou C, He X, Liu M. Preparation of a novel TETA functionalized magnetic PGMA nano-absorbent by ATRP method and used for highly effective adsorption of Hg(II). Journal of the Taiwan Institute of Chemical Engineers 2016; 58: 283-289. https://doi.org/10.1016/j.jtice.2015.05.044.

- [14]. Zhao J, Wang C, Wang S, Zhou Y, Zhang B. Experimental and DFT studies on the selective adsorption of Pd(II) from wastewater by pyromellitic-functionalized poly(glycidyl methacrylate) microsphere. Journal of Molecular Liquids 2020; 300. https://doi.org/10.1016/j.molliq.2019.112296.
- [15]. Taimur S, Hassan MI, Yasin T. Removal of copper using novel amidoxime based chelating nanohybrid adsorbent. European Polymer Journal 2017; 95: 93-104. https://doi.org/10.1016/j.eurpolymj.2017.08.004.
- [16]. Taimur S, Yasin T. Influence of the synthesis parameters on the properties of amidoxime grafted sepiolite nanocomposites. Applied Surface Science 2017; 422: 239-246. https://doi.org/10.1016/j.apsusc.2017.05.263.
- [17]. Beauger C, Lainé G, Burr A, Taguet A, Otazaghine B. Improvement of Nafion®-sepiolite composite membranes for PEMFC with sulfo-fluorinated sepiolite. Journal of Membrane Science 2015; 495: 392-403. https://dx.doi.org/10.1016/j.memsci.2015.08.014.
- [18]. Abali S, Aydin YA. Silanization of sepiolite with various silane coupling agents for enhancing oil uptake capacity. Separation Science and Technology (Philadelphia) 2023; 58 (3): 586-597. https://doi.org/10.1080/01496395.2022.2138434.
- [19]. Nasir A, Raza A, Tahir M, Yasin T. Free-radical graft polymerization of acrylonitrile on gamma irradiated graphene oxide: Synthesis and characterization. Materials Chemistry and Physics 2020; 246. https://doi.org/10.1016/j.matchemphys.2020.122807.
- [20]. Nasir A, Raza A, Tahir M, Yasin T, Nadeem M, Ahmad B. Synthesis and study of polyaniline grafted graphene oxide nanohybrids. Materials Research Bulletin 2023; 157. https://doi.org/10.1016/j.materresbull.2022.112006.
- [21]. Raza A, Nasir A, Tahir M, Taimur S, Yasin T, Nadeem M. Synthesis and EMI shielding studies of polyaniline grafted conducting nanohybrid. Journal of Applied Polymer Science. 2020; 138 (2): 49680. https://doi.org/10.1002/app.49680.

- [22]. JIA Di, LIU Jin-quan, YAO Xing-fang WY lin. Modification of sepiolite by treatment with methyl triethoxysilane. Journal of Wuhan University of Technology (Materials Science) 2004; 19 (1): 1-4. https://doi.org/10.1007/BF02838361.
- [23]. Nasir A, Raza A, Tahir M, Yasin T. Free-radical graft polymerization of acrylonitrile on gamma irradiated graphene oxide: Synthesis and characterization. Materials Chemistry and Physics 2020; 246. https://doi.org/10.1016/j.matchemphys.2020.122807.
- [24]. Hassan MI ul, Taimur S, Yasin T. Upcycling of polypropylene waste by surface modification using radiation-induced grafting. Applied Surface Science 2017; 422: 720-730. https://doi.org/10.1016/j.apsusc.2017.06.086.
- [25]. Gürdağ G, Güçlü G, Özgümüş S. Graft copolymerization of acrylic acid onto cellulose: Effects of pretreatments and crosslinking agent. Journal of Applied Polymer Science 2001; 80 (12): 2267-2272. https://doi.org/10.1002/app.1331.
- [26]. Abdullah Sani NS, Arsad A, Rahmat AR. Synthesis of a compatibilizer and the effects of monomer concentrations. Applied Mechanics and Materials. 2014; 554: 96-100. http://dx.doi.org/10.4028/www.scientific.net/AMM.554.96.
- [27]. Shafiq M, Yasin T, Saeed S. Synthesis and characterization of linear low-density polyethylene/sepiolite nanocomposites. Journal of applied polymer science 2010; 116 (5): 2658-2667. https://doi.org/10.1002/app.34633.
- [28]. Raji M, Mekhzoum M.E.M, Rodrigue D, Qaiss A el kacem, Bouhfid R. Effect of silane functionalization on properties of polypropylene/clay nanocomposites. Composites Part B: Engineering 2018; 146: 106-115. http://dx.doi.org/10.1016/j.compositesb.2018.04.013.
- [29]. Taimur S, Hassan MI, Yasin T. Removal of copper using novel amidoxime based chelating nanohybrid adsorbent. European Polymer Journal 2017; 95: 93-104. https://doi.org/10.1016/j.eurpolymj.2017.08.004.

- [30]. Abali S, Aydin YA. Silanization of sepiolite with various silane coupling agents for enhancing oil uptake capacity. Separation Science and Technology (Philadelphia) 2023; 58 (3): 586-597. https://doi.org/10.1080/01496395.2022.2138434.
- [31]. Cheng C, Ma L, Ren J, et al. Preparation of polyethersulfone-modified sepiolite hybrid particles for the removal of environmental toxins. Chemical Engineering Journal 2011; 171 (3): 1132-1142. https://doi.org/10.1016/j.cej.2011.05.011.
- [32]. Dian J, Konečný M, Broncová G, Kronďák M, Matolínová I. Electrochemical fabrication and characterization of porous silicon/polypyrrole composites and chemical sensing of organic vapors. International Journal of Electrochemical Science 2013; 8 (2): 1559-1572. https://doi.org/10.1016/S1452-3981(23)14247-7.
- [33]. Elkady MF, Abu-Saied MA, Abdel Rahman AM, Soliman EA, Elzatahry AA et al. Nano-sulphonated poly (glycidyl methacrylate) cations exchanger for cadmium ions removal: Effects of operating parameters. Desalination 2011; 279 (1-3): 152-162. https://doi.org/10.1016/j.desal.2011.06.002.
- [34]. Galhoum AA, Elshehy EA, Tolan DA, et al. Synthesis of polyaminophosphonic acidfunctionalized poly (glycidyl methacrylate) for the efficient sorption of La (III) and Y (III). Chemical Engineering Journal 2019; 375: 121932. https://doi.org/10.1016/j.cej.2019.121932.
- [35]. Raza A, Nasir A, Tahir M, Taimur S, Yasin T et al. Synthesis and EMI shielding studies of polyaniline grafted conducting nanohybrid. Journal of Applied Polymer Science 2021; 138 (2): 49680. https://doi.org/10.1002/app.49680.
- [36]. Asif R, Tahir M, Nasir A, Yasin T. Sepiolite grafted polypyrrole: Influence of degree of grafting on structural, thermal, and impedance properties of nanohybrid. Journal of Applied Polymer Science 2020; 137 (37): 49085. https://doi.org/10.1002/app.49085.

- [37]. Ashfaq A, Clochard MC, Coqueret X, Dispenza C, Driscoll MS et al. Polymerization reactions and modifications of polymers by ionizing radiation. Polymers 2020; 12 (12): 1-67. https://doi.org/10.3390/polym12122877.
- [38]. Taimur S, Yasin T. Influence of the synthesis parameters on the properties of amidoxime grafted sepiolite nanocomposites. Applied Surface Science 2017; 422: 239-246. https://doi.org/10.1016/j.apsusc.2017.05.263.
- [39]. Zhou F, Yan C, Zhang Y, Tan J, Wang H et al. Purification and defibering of a Chinese sepiolite. Applied Clay Science 2016; 124: 119-126. https://doi.org/10.1016/j.clay.2016.02.013.
- [40]. Khan IA, Hussain H, Yasin T, Inaam-ul-Hassan M. Surface modification of mesoporous silica by radiation induced graft polymerization of styrene and subsequent sulfonation for ionexchange applications. Journal of Applied Polymer Science 2019; 48835: 2-9. https://doi.org/10.1002/app.48835.
- [41]. Jiang P, Zhang S, Bourbigot S, Chen Z, Duquesne S, Casetta M. Surface grafting of sepiolite with a phosphaphenanthrene derivative and its flame-retardant mechanism on PLA nanocomposites. Polymer Degradation and Stability 2019; 165: 68-79. https://doi.org/10.1016/j.polymdegradstab.2019.04.012.
- [42]. Hassan MI ul, Taimur S, Khan IA, Yasin T, Ali SW. Surface modification of polypropylene waste by the radiation grafting of styrene and upcycling into a cation-exchange resin. Journal of Applied Polymer Science 2019; 136 (10). https://doi.org/10.1002/app.47145.
- [43]. Sotelo JL, Ovejero G, Rodríguez A, Álvarez S, García J. Study of natural clay adsorbent sepiolite for the removal of caffeine from aqueous solutions: Batch and fixed-bed column operation. Water Air and Soil Pollution 2013; 224 (3). https://doi.org/10.1007/s11270-013-1466-8.

- [44]. Tartaglione G, Tabuani D, Camino G. Thermal and morphological characterization of organically modified sepiolite. Microporous and Mesoporous Materials 2008; 107 (1-2): 161-168. https://doi.org/10.1016/j.micromeso.2007.04.020.
- [45]. Wu S, Cui H, Wang C, Hao F, Liu P, Xiong W. In situ self-assembled preparation of the hybrid nanopigment from raw sepiolite with excellent stability and optical performance. Applied Clay Science 2018; 163: 1-9. https://doi.org/10.1016/j.clay.2018.07.009.
- [46]. Shafiq M, Yasin T, Saeed S. Synthesis and characterization of linear low-density polyethylene/sepiolite nanocomposites. Journal of Applied Polymer Science 2012; 123 (3): 1718-1723. https://doi.org/10.1002/app.34633.
- [47]. Rehan KM, Basha K A, Safiullah SM. Synthesis of poly (glycidyl methacrylate) based hybrid materials and evaluation of methylene blue adsorption: Structural characterization and adsorption behavior. Journal of Inorganic and Organometallic Polymers and Materials 2023; 1-16. https://doi.org/10.1007/s10904-023-02671-3.
- [48]. Raza A, Tahir M, Nasir A, Yasin T, Nadeem M. Sepiolite grafted polypyrrole: Influence of degree of grafting on structural, thermal, and impedance properties of nanohybrid. Journal of Applied Polymer Science 2020; 137 (37). https://doi.org/10.1002/app.49085.
- [49]. Mohammed Safiullah S, Abdul Wasi K, Anver Basha K. Synthesis of poly(glycidyl methacrylate)-copper nanocomposite beads by in-situ suspension polymerization and deposition method A comparative study. Polymer 2015; 66: 29-37. https://doi.org/10.1016/j.polymer.2015.04.018.
- [50]. Cherifi Z, Boukoussa B. Structural, morphological and thermal properties of nanocomposites poly (GMA)/clay prepared by ultrasound and in-situ polymerization. Ultrasonics Sonochemistry. 2018; 48: 188-198. https://doi.org/10.1016/j.ultsonch.2018.05.027.

- [51]. Hassan MI ul, Taimur S, Khan IA, Yasin T, Ali SW. Surface modification of polypropylene waste by the radiation grafting of styrene and upcycling into a cation-exchange resin. Journal of Applied Polymer Science 2019; 136 (10). https://doi.org/10.1002/app.47145.
- [52]. Hassan MI ul, Taimur S, Khan IA, Yasin T, Ali SW. Surface modification of polypropylene waste by the radiation grafting of styrene and upcycling into a cation-exchange resin. Journal of Applied Polymer Science 2019; 136 (10). https://doi.org/10.1002/app.47145.
- [53]. Chen T, Sun N, Zhao Y, Gao J, Hu G et al. Removal of La(III) by amino-phosphonic acid functionalized polystyrene microspheres prepared via electron beam irradiation. Journal of Saudi Chemical Society 2022; 26 (6). https://doi.org/10.1016/j.jscs.2022.101564.
- [54]. Elkady MF, Abu-Saied MA, Abdel Rahman AM, Soliman EA, Elzatahry AA et al. Nano-sulphonated poly (glycidyl methacrylate) cations exchanger for cadmium ions removal: Effects of operating parameters. Desalination. 2011; 279 (1-3): 152-162. https://doi.org/10.1016/j.desal.2011.06.002.
- [55]. Qassim MI, Khalill MM, Hamed Mohamed A, Gizawy AA, El-Hag Ali A. Synthesis and evaluation of a novel polycarbonate grafted poly (glycidyl methacrylate) resin for sorption of 131I. 2023; 110774. https://dx.doi.org/10.2139/ssrn.4181445.
- [56]. Abu-Saied MA, Fontananova E, Drioli E, Mohy Eldin MS. Sulphonated poly (glycidyl methacrylate) grafted cellophane membranes: Novel application in polyelectrolyte membrane fuel cell (PEMFC). Journal of Polymer Research. 2013; 20 (7). http://dx.doi.org/10.1007/s10965-013-0187-4.
- [57]. Wang X, Liang X, Wang Y, et al. Adsorption of Copper (II) onto activated carbons from sewage sludge by microwave-induced phosphoric acid and zinc chloride activation. Desalination. 2011; 278 (1-3): 231-237. http://dx.doi.org/10.1016/j.desal.2011.05.033.

- [58]. Ferrah N, Abderrahim O, Didi MA, Villemin D. Removal of copper ions from aqueous solutions by a new sorbent: Polyethyleneiminemethylene phosphonic acid. Desalination. 2011; 269 (1-3):17-24. https://doi.org/10.1016/j.desal.2010.11.035.
- [59]. Denizli A, Gu¨gu¨leren O¨Zkan G, Arica MY. Preparation and characterization of magnetic polymethylmethacrylate microbeads carrying ethylene diamine for removal of Cu(II), Cd(II), Pb(II), and Hg(II) from aqueous solutions. 2000. http://dx.doi.org/10.1002/1097-4628.
- [60]. Liu X, You Y, Zhang T, Li M, Qin Z, Wang J and Yin X. Pb²⁺-imprinted thermosensitive antibacterial adsorbent derived from sodium alginate and PNIPAM for Pb²⁺ recovery. International Journal of Biological Macromolecules, 2023; 225: 207-218. https://doi.org/10.1016/j.ijbiomac.2022.10.250.
- [61]. Gürses A, Hassani A, Kranşan M, Açşl Ö, Karaca S. Removal of methylene blue from aqueous solution using by untreated lignite as potential low-cost adsorbent: Kinetic, thermodynamic and equilibrium approach. Journal of Water Process Engineering. 2014; 2: 10-21. http://dx.doi.org/10.1016/j.jwpe.2014.03.002.
- [62]. Soliman NK, Moustafa AF. Industrial solid waste for heavy metals adsorption features and challenges; a review. Journal of Materials Research and Technology. 2020; 9 (5): 10235-10253. https://doi.org/10.1016/j.jmrt.2020.07.045.
- [63]. Singh S, N P, Naik TSSK, et al. Removal of Pb ions using green Co₃O₄ nanoparticles: Simulation, modeling, adsorption, and biological studies. Environmental Research 2023; 222. https://doi.org/10.1016/j.envres.2023.115335.
- [64]. Genç-Fuhrman H, Mikkelsen PS, Ledin A. Simultaneous removal of As, Cd, Cr, Cu, Ni and Zn from stormwater using high-efficiency industrial sorbents: Effect of pH, contact time and humic acid. Science of the Total Environment. 2016; 566-567: 76-85. https://doi.org/10.1016/j.scitotenv.2016.04.210.

- [65]. Nishikida K, Coates J. Infrared and Raman Analysis of Polymers. Plastics Engineering-New York- 2003; 68: 201-340. https://doi.org/10.1201/9780203911983.
- [66]. Musah M, Azeh Y, Mathew JT, Umar MT, Abdulhamid Z and Muhammad AI. Adsorption kinetics and isotherm models: a review. CaJoST 2022; 4 (1): 20-26. https://dx.doi.org/10.4314/cajost.v4i1.3.
- [67]. Zenasni MA, Benfarhi S, Merlin A, Molina S, George B, Meroufel B. Adsorption of Cu(II) on maghnite from aqueous solution: Effects of pH, initial concentration, interaction time and temperature. Natural Science 2012; 04 (11): 856-868. http://dx.doi.org/10.4236/ns.2012.411114.
- [68]. Nasir A, Inaam-ul-Hassan M, Raza A, Tahir M, Yasin T. Removal of copper using chitosan beads embedded with amidoxime grafted graphene oxide nanohybrids. International Journal of Biological Macromolecules 2022; 222: 750-758. https://doi.org/10.1016/j.ijbiomac.2022.09.188.
- [69]. Ayawei N, Ebelegi AN, Wankasi D. Modelling and interpretation of adsorption isotherms. Journal of Chemistry 2017. https://doi.org/10.1155/2017/3039817.
- [70]. Dada AO, Olalekan AP, Oluwasogo D. Langmuir, Freundlich, Temkin and Dubinin– Radushkevich isotherms studies of equilibrium sorption of Zn²⁺ unto phosphoric acid modified rice husk. IOSR Journal of Applied Chemistry 2012; 3 (1): 38-45. http://dx.doi.org/10.9790/5736-0313845.
- [71]. Muthana Alasadi A, Fawwaz Izzat K, Akl Mohammad A. Adsorption of Cu(II), Ni(II) and Zn(II) ions by nano kaolinite: Thermodynamics and kinetics studies. Chemistry International 2019; 5 (4): 258-268. https://doi.org/10.5281/zenodo.2644985.
- [72]. Awwad AM, Mohammad WA and, M. Al-aqarbeh M. TiO₂-kaolinite nanocomposite prepared from the jordanian kaolin clay: Adsorption and thermodynamics of Pb(II) and Cd(II) ions in

aqueous solution. Chemistry International 2020; 4 (4): 168-178. https://doi.org/10.5281/zenodo.3597558.

- [73]. Li J, Dong X, Liu X, Xu X, Duan W et al. Comparative study on the adsorption characteristics of heavy metal ions by activated carbon and selected natural adsorbents. Sustainability 2022; 14 (23). https://doi.org/10.3390/su142315579.
- [74]. Di J, Ruan Z, Zhang S, Xu X, Duan W, et al. Adsorption behaviors and mechanisms of Cu²⁺,
 Zn²⁺ and Pb²⁺ by magnetically modified lignite. Scientific Reports 2022; 12 (1): 1394.
 https://doi.org/10.1038/s41598-022-05453-y.
- [75]. Gürses A, Hassani A, Kıranşan M, Açışlı Ö, Karaca S. Removal of methylene blue from aqueous solution using by untreated lignite as potential low-cost adsorbent: Kinetic, thermodynamic and equilibrium approach, Journal of Water Process Engineering 2014; 2: 10-21. https://doi.org/10.1016/j.jwpe.2014.03.002.
- [76]. Chen YG, Ye WM, Yang XM, Deng FY, He Y, Effect of contact time, pH, and ionic strength on Cd(II) adsorption from aqueous solution onto bentonite from Gaomiaozi, China. Environmental Earth Sciences 2011; 64 (2): 329-336. https://doi.org/10.1007/s12665-010-0850-6.
- [77]. Ferreira BCS, Teodoro FS, Mageste AB, Gil LF, Freitas RP, Gurgel LVA, Application of a new carboxylate-functionalized sugarcane bagasse for adsorptive removal of crystal violet from aqueous solution: kinetic, equilibrium and thermodynamic studies. Industrial Crops and Products 2015; 65: 521-534. https://doi.org/10.1016/j.indcrop.2014.10.020.
- [78]. Nasir A, Inaam-ul-Hassan M, Raza A, Tahir M, Yasin T. Removal of copper using chitosan beads embedded with amidoxime grafted graphene oxide nanohybids. International Journal of Biological Macromolecules 2022; 222: 750-758. https://doi.org/10.1016/j.ijbiomac.2022.09.188.

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- [79]. Abdel-Raouf MES, Farag RK, et al. Chitosan-Based Architectures as an Effective Approach for the Removal of Some Toxic Species from Aqueous Media. ACS omega 2023; 8(11), 10086-10099. https://doi.org/10.1021/acsomega.2c07264.
- [80]. AL Samman MT, Sánchez, J. Adsorption of copper and arsenic from water using a semiinterpenetrating polymer network based on alginate and chitosan. Polymers 2023; 15 (9): 2192. doi.org/10.3390/polym15092192.

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Figure 1. Key steps involved in the synthesis phosphonic acid-functionalized grafted

sepiolite nanohybrid



Figure 2. Chemical reactions involved in synthesis of PGE by free radical free radical graft

polymerization



Figure 3. (A) Effect of initiator amount on PGMA grafting percentage: reaction time = 3 h, GMA = 5% (w/v). (B) Effect of monomer concentration on PGMA grafting percentage: reaction time = 3 h, KPS = 0.3% (w/v). (C) Effect of reaction time on polymer grafting percentage: GMA = 15% (w/v), KPS = 0.3% (w/v); VMS = 1.0% (w/v), tween-80 = 0.1%(w/v), T = 70 °C for (A), (B) and (C). (D) Photographs of PGE₃ and PGE₃-P nanohybrids



Figure 4. FTIR spectra (a) PS (b) VMS (c) PGE₃ (d) PGE₃-P and (e) PGE₃-P-Cu



Figure 5. XRD diffractogram of (a) PS, (b) VMS, (c) PGE₃ (d) PGE₃-P and (e) PGE₃-P-Cu



Figure 6. SEM micrographs of (a) PS, (b) VMS, (c) PGE₃, (d) PGE₃-P and (e) PGE₃-P-Cu



Figure 7. TGA thermogram of (a) PS, (b) VMS, (c) PGE₃, (d) PGE₃-P



Figure 8. Effect of pH on Cu (II) ions uptake: adsorbent weight = 4 g/L, time = 1 h, $C_o = 20$ mg/L and T = 398 K



Figure 9. Zeta potential of PGE₃-P at pH ranging from 2-6



Figure 10. Effect of adsorbent weight on Cu (II) uptake: pH = 4, time = 1 h, $C_o = 20 \text{ mg/L}$

and T = 398 K



Figure 11. Effect of contact time on Cu (II) uptake: pH = 4, adsorbent weight = 5 g/ L, $C_o = 20 \text{ mg/L}$ and T = 398 K



Figure 12. (a) Pseudo-first order and (b) Pseudo-second order plots of Cu (II) adsorption kinetics on the PGE₃-P: pH = 4, adsorbent weight = 5 g/L, $C_o = 20$ mg/L and T = 398 K



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Figure 15. Effect of temperature on the Cu (II) uptake: contact time = 50 minutes, pH = 5, adsorbent weight = 5 g/ L, $C_o = 250 \text{ mg/L}$



Figure 16. Plot of ln K vs 1/T for calculation of the adsorption thermodynamic parameters



Figure 17. Proposed mechanism of Cu (II) adsorption by PGE₃-P



Figure 18. Regeneration studies on PGE₃-P: Adsorbent weight = 5 g/ L, V = 20 ml, T = 398 K, desorption medium = NaCl

Sample code	GMA (w/v %)	KPS (g)	Reaction time (h)
PGE1	5.0	0.3	4.0
PGE ₂	10.0	0.3	4.0
PGE3	15.0	0.3	4.0
PGE4	20.0	0.3	4.0
PGE5	15.0	0.1	4.0
PGE6	15.0	0.2	4.0
PGE7	15.0	0.4	4.0
PGE8	15.0	0.3	3.0
PGE9	15.0	0.3	5.0
PGE10	15.0	0.3	6.0

Table 6. Chemical composition and codes of PGMA grafted nanohybrids

*Amount of VMS = 1.0% (w/v); Amount of tween-80 = 0.1% (w/v)

Table 7. Crystallinity (%) and average crystallite size (nm) of pristine sepiolite and its

modified forms

Sample Codes	PS	VMS	PGE3	PGE3-P	PGE3-P-Cu
Crystallinity (%)	83.2±1.07	78±3.07	62±2.07	47±1.01	46.1±1.21
Average crystallite size (nm)	106.2±9.07	108.2±9.07	113.2±8.07	153.5±9.05	155.1±7.04

Sample codes	Atomic percentage				
F-2 00 a 00	С	0	Н	Р	
PS	-	3.5	58.2	-	
VMS	55.3	40.8	52.1	-	
PGE ₃	67.3	52.7	78.5	-	
PGE ₃ -P	67.2	65.7	81.2	4.15	

Table 8. Comparison of elemental composition of pristine sepiolite and its modified forms

Table 9. BET surface area analysis of pristine sepiolite and its modified forms

Sample Codes	PS	VMS	PGE3	PGE3-P
BET Surface Area (m ² /g)	212.6	160.8	135.2	93±0.58
Pore volume (cm ³ /g)	59.3	57.1	24.2	19.5
Pore size (nm)	62.8	62.4	57.2	68.2

Table 10. The residual mass of pristine sepiolite and its modified forms at 800 °C

Sample codes	Residue (%) at 800 °C
PS	83.8
VMS	82.97
PGE ₃	38.6
PGE ₃ -P	61.5
Table 6. Comparison of parameters obtained by pseudo-first order and pseudo-second

 order models for Cu (II) uptake

Pseudo-first order				Pseudo-second order			
R ²	K ₁	Qe (cal)	Q _e (exp)	R ²	K_2	Qe (cal)	Q _e (exp)
	(min ⁻¹)	(mg/g)	(mg/g)		(g.mg ⁻¹ .min ⁻¹)	(mg/g)	(mg/g)
0.0436	-0.00014	7.15	43.1	0.997	0.00919	44.64	43.1

Table 7. Comparison of parameters obtained by Langmuir and Freundlich models on

adsorbents at 398 K

Freundlich isotherm constants			Langmuir isotherm constants			
1/n	K _F	R_F^2	R_L^2	K _L	Q _m (cal)	Q _m (exp)
	$(g/mg min^{-1})$			(L/mg)	(mg/g)	(mg/g)
0.613	2.0718	0.02102	0.02710	0.01015	134.228	132.50

Table 8. Thermodynamics parameters for adsorption of Cu (II) on PGE₃-P

Temperature	ΔG° at	ΔG° at	ΔG° at	ΔH°	ΔS
(K)	308	328	348	(kJ/mol)	(kJ/mol)
PGE ₃ -P	-5.0017	-5.9496	-7.0001	10.4737	50.51

Table 9. Effect of other metal ions on adsorption of Cu (II) on PGE₃-P

Element	Cu	Pb	Ni	Со
Adsorption capacity (mg/g)	84.3	24.2	15.2	10.4

Table 10. Comparison of adsorption capacities of different materials for Cu (II) ions removal

Adsorbents	Adsorption capacity (mg/g)	References
Chitosan composites with amidoxime grafted graphene oxide	115.3	[77]
Chitosan crosslinked with glutaraldehyde/methylene bisacrylamide	95.7	[78]
Poly acrylic acid/alginate	63.59	[79]
PGE ₃ -P	134.5	Present work