


Adsorption of Phosphate from Aqueous Solution onto Iron-coated Waste Mussel Shell: Physicochemical Characteristics, Kinetic, and Isotherm Studies

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Abstract: High amounts of phosphate (PO_4^{3-}) discharged in receiving water can lead to eutrophication, which endangers life below water and human health. This study elucidates the removal of PO_4^{3-} from synthetic solution by iron-coated waste mussel shell (ICWMS). The PO_4^{3-} adsorption by ICWMS was determined at different process parameters, such as initial PO_4^{3-} concentration (7 mg L^{-1}), solution volume (0.2 L), adsorbent dosage (4, 8, 12, 16, and 20 g), and contact time. The highest efficiency of PO_4^{3-} removal can reach 96.9% with an adsorption capacity of 0.30 mg g^{-1} could be obtained after a contact time of 48 h for the use of 20 g of ICWMS. Batch experimental data can be well described by the pseudo-second-order kinetic model ($R^2 = 0.999$) and Freundlich isotherm model ($R^2 = 0.996$), suggesting that chemisorption and multilayer adsorption occurred. The efficiency of PO_4^{3-} removal from aqueous solution by ICWMS was verified to contribute to applying a new low-cost adsorbent obtained from waste mussel shell in the field of wastewater treatment.

Keywords: adsorption; eutrophication; iron-coated waste mussel shell; isotherm model; kinetic model; phosphate.

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1. Introduction

Phosphorus (P) is a key nutrient that stimulates the development of biological organisms and algae. However, the discharge of an excessive amount of P into surface water strongly accelerates eutrophication [1,2]. Over-enrichment of P in water bodies expedites plant growth and causing algal blooms [3]. The water body may also lose its important functions and cause negative effects on the environment and human health [4]. The principal forms of P in water are orthophosphate, polyphosphate, and organically bound phosphate. The most common P compound in wastewater is orthophosphate [5,6]. The effects of P to surface water release have led to legislation such as those by the United State Environmental Protection Agency

(USEPA) and the European Union (EU). The USEPA permits the effluent limit of total phosphorus (TP) of less than 0.8 mg L⁻¹. Meanwhile, the EU allows the discharge limit of 2 mg P L⁻¹ for 10,000 – 100,000 population equivalents [7].

The excessive amounts of P can be treated with various methods such as adsorption technique, biological process, and chemical process. The biological process to treat wastewater can be highly variable due to operational difficulties [8,9], while the chemical treatment entails high chemical costs [10]. From all these removal methods, adsorption is the potential technologies that could be employed to remove P from water given its simple reaction and low cost of the materials [11,12]. Several studies have shown that some waste materials such as sand and eggshell coated with iron could be favorable and inexpensive adsorbent for PO₄³⁻ removal [13–15]. Mussel shells are waste products from food processing areas and are usually dumped in foreshores. It can also be used as a low-cost adsorbent material to eliminate PO₄³⁻ from water [16].

This study aimed to delve into the feasibility of utilizing ICWMS for PO₄³⁻ removal from synthetic solution. The influence of the initial PO₄³⁻ concentration (C_i), adsorbent dosage (m), and contact time (t) on the PO₄³⁻ removal was scrutinized. Freundlich and Langmuir isotherm models were employed to understand the adsorption mechanism.

1.1. Adsorption kinetics and isotherms

1.1.1. Kinetics adsorption models.

The adsorption kinetic is of interest for many aspects of surface chemistry to elucidate the mechanisms and potential rate-controlling step of the adsorption process [17,18]. The mechanism of the adsorption process was described by using two different types of adsorption kinetic models, namely pseudo-first-order (PFO) and pseudo-second-order (PSO) (Table 1). PFO equation can be expressed as given in Eq. (1) [19]–[21]:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \tag{1}$$

PSO equation can be expressed as [22]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

Table 1. List of kinetic and isotherm adsorption models.

Models	Linear form	Plot	Parameters
<u>Kinetic</u>			
PFO	$\ln(q_e - q_t) = \ln(q_e) - k_1 t_i$	$\ln(q_e - q_t)$ vs. t_i	q_e k_1
PSO	$\frac{t_i}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t_i}{q_e}$	$\frac{t_i}{q_t}$ vs. t_i	q_e k_2
<u>Isotherm</u>			
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	$\ln q_e$ vs. $\ln C_e$	K_F n
Langmuir	$\frac{1}{q_e} = \frac{1}{K_L q_{max} C_e} + \frac{1}{q_{max}}$	$\frac{1}{q_e}$ vs. $\frac{1}{C_e}$	q_{max} K_L
<u>Nomenclature</u>			
k_1	PFO constant (min ⁻¹)		
k_2	PFO constant (g mg ⁻¹ min ⁻¹)		
K_F	Freundlich constant (mg g ⁻¹)		
K_L	adsorption energy coefficient (L mg ⁻¹)		
n	heterogeneity factor (dimensionless)		
C_e	concentration of the adsorbate at equilibrium (mg L ⁻¹)		
q_e	adsorption capacity at equilibrium (mg g ⁻¹)		
q_t	adsorption capacity at time t (mg g ⁻¹)		
q_{max}	maximum adsorption capacity (mg g ⁻¹)		
t_i	adsorption time (min)		

1.2. Isotherm adsorption models.

The Freundlich and Langmuir equations are the equations commonly used to describe adsorption isotherms. The Freundlich model describes that the adsorbates' heterogeneous surface is formed on the surface of adsorbent with multilayer sorption of different energies of adsorption [23]. The Langmuir model assumes that the adsorbent is being saturated when the monolayer adsorbate coverage of the adsorbent is attached with a homogenous surface without interactions between the adsorbed molecules [24]. The linear form of the Freundlich isotherm can be written as [25]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (3)$$

The Freundlich isotherm suggests that a plot $\ln q_e$ against $\ln C_e$ of the Eq. (3) should give a straight-line intercept at K_F with $1/n$ as the slope (Table 1). The adsorption coefficient K_F may indicate the affinity of the adsorbate-adsorbent. The exponent n is related to the energetic heterogeneity of the adsorbent surface and determines either the favorable or unfavorable curve [12].

The linear form of the Langmuir isotherm can be expressed as [26]:

$$\frac{1}{q_e} = \frac{1}{K_L q_{max} C_e} + \frac{1}{q_{max}} \quad (4)$$

The value of K_L and q_{max} represents the Langmuir bonding term related to interaction energies and the maximum adsorption capacity, respectively.

2. Materials and Methods

2.1. Adsorbents.

Waste mussel shell (WMS) was used as an adsorbent in this study. The WMS was collected from riverbank areas in Pasir Gudang, Johor, Malaysia. The sample was washed several times with tap water, and the cleaned sample was naturally dried in the open air for 48 h. The sample was crushed and finally sieved to particle sizes with a range of 0.60–1.18 mm.

For the preparation of ICWMS, a solution of 0.5 M Fe (III) was prepared by dissolving $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in deionized water (DW). A 5.0 N NaOH base solution was added using dropper into 0.5 M 100 mL of Fe (III) solution until it reached a pH of 9.5 ± 0.1 . About 200 g sample of WMS was added to 100 mL of 0.5 M Fe (III). The mixture was agitated on a shaker at room temperature with a constant speed of 160 rpm for 24 h. Then, the ICWMS was washed with DW until the run-off reached a pH of 7 and dried at 100°C for 8 h [27]. The dried ICWMS was used as an adsorbent for removing PO_4^{3-} from the synthetic solution.

2.2. Synthetic solutions.

Synthetic solutions (i.e., 100 mg P L^{-1}) was prepared by dissolving anhydrous potassium dihydrogen phosphate (KH_2PO_4) (analytic grade) into 1 L of DW. The synthetic solution was diluted with DW to get the desired concentration, and the solution was set up at pH 7.

2.3. Analytical methods.

The measurements of PO_4^{3-} were determined using an amino acid method (UV–Vis Spectrophotometer, HACH DR 6000, United States) [28]. The portable pH meter (Jenway Model 350 pH meter) was used to measure pH. A scanning electron microscope (SEM) (Model

TM3000, Hitachi, Japan) was used to characterize the surface morphology of the unmodified adsorbents. Types of mineral phases in the ICWMS were identified using a Bruker D8 advance high-resolution X-Ray Diffractometer (XRD). The chemical composition (in %) of ICWMS was analyzed using Energy Dispersive X-Ray Fluorescence (EDXRF) Spectrometer (Rigaku, Japan). The functional groups of the ICWMS were investigated using Fourier Transform Infrared (FTIR) Spectroscopy (IRTracer-100, Shimadzu, Japan). The measurement of the specific surface area of ICWMS was performed by the multiple-point method according to the Brunauer, Emmett, and Teller (BET) theory, using a surfer analyzer (Surface Analyzer, Thermo Scientific Technologies, Italy).

2.4. Batch experiments.

In batch experiments, the equilibrium adsorption kinetics were investigated by adding 4, 12, and 20 g of the ICWMS. The equilibrium adsorption isotherm experiments were determined by adding 4, 8, 12, 16, and 20 g of the ICWMS into different Erlenmeyer flask containing 0.2 L of 7 mg L⁻¹ PO₄³⁻ solution. Each sample was shaken at 160 rpm. Afterward, the concentrations of PO₄³⁻ in each flask were determined at certain time intervals until reaching the equilibrium stage. The sample solutions were centrifuged. The HACH DR 6000 UV–Vis Spectrophotometer was used to evaluate supernatant concentrations of PO₄³⁻ present in each Erlenmeyer flask. The PFO and PSO models were applied to understand the adsorption kinetics. The adsorption isotherms of PO₄³⁻ onto ICWMS were explored by using Freundlich and Langmuir isotherm models. Each batch adsorption experiment was conducted twice, and the data obtained are the average values. The adsorption capacity (*q*) and the *E* were calculated using Eq. (5) and Eq. (6), respectively.

$$q = \frac{(C_i - C_f) \times V}{m} \tag{5}$$

$$E = \frac{C_i - C_f}{C_i} \times 100\% \tag{6}$$

3. Results and Discussion

3.1. Physicochemical characteristics of the ICWMS.

As depicted in Table 2, the major chemical compositions of ICWMS discovered in this study are CaO (87.90%) and Fe₂O₃ (5.93%), while the minor compositions are SrO (0.37%), MgO (0.10%), and Al₂O₃ (0.06%).

Table 2. Composition of the ICWMS and WMS (wt.%) by EDXRF.

CaO	Fe ₂ O ₃	SrO	MgO	Al ₂ O ₃	K ₂ O	Na ₂ O	P ₂ O ₅
87.90	5.93	0.37	0.10	0.06	ND	ND	ND

Remarks that ND is not detected.

The SEM micrograph images with 1500, 6000, and 10000 times are shown in Figure 1. As shown in Figs. 1a and b, the surface feature of ICWMS were relatively rough. The ICWMS surfaces were occupied by iron oxides formed during the coating process [14]. The SEM image with 10000 times magnification exhibits small pores at the surface of the ICWMS (Figure 1c).

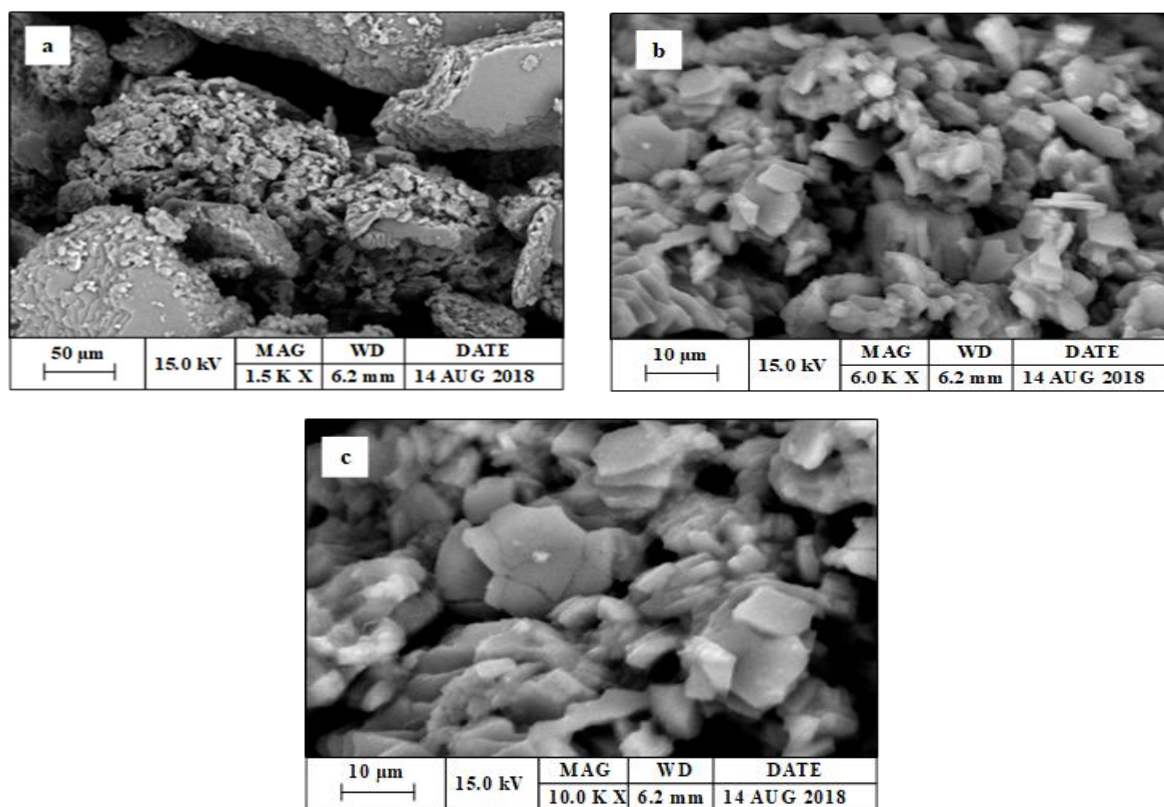


Figure 1. The SEM photomicrograph of ICWMS: (a) SEM images of 1500× (b) 6000× and (c) 10000× magnifications.

The XRD pattern (Figure 2) of the ICWMS sample indicates that calcium carbonate (CaCO_3), calcium oxide (CaO), and iron oxide (Fe_2O_3) are the major component of the ICWMS of Skudai. The other components listed on the XRD pattern are strontium oxide (SrO), magnesium oxide (MgO), and aluminum oxide (Al_2O_3). Several researchers have reported that CaCO_3 and CaO have good adsorption ability for PO_4^{3-} ions. The work of Torit *et al.* [29] affirmed that a high calcium material content could increase PO_4^{3-} adsorption associated with the ability for calcium to form $\text{HCO}_3\text{-Ca-HPO}_4$ at the carbonate sites. Nam *et al.* [30] proved that PO_4^{3-} was effectively adsorb by a material containing a high calcium element. Besides that, iron-based materials have been reported as an effective adsorbent for removing PO_4^{3-} in an aqueous solution; PO_4^{3-} reacts with two singly coordinated Fe-OH groups to form $(\text{Fe-O})_2\text{-PO}_2\text{H}$ [10].

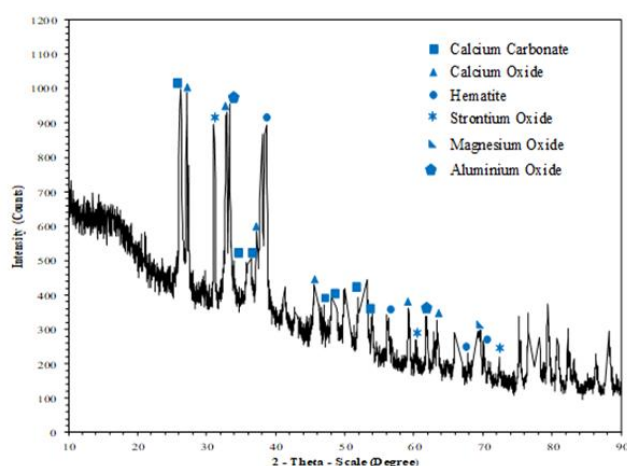


Figure 2. X-ray diffraction patterns of ICWMS.

The FTIR spectra (see Figure 3) of natural and PO_4^{3-} adsorbed ICWMS were carried out over the range from 600 to 4000 cm^{-1} and were compared with each other to obtain information on the modifications and surface functional groups [31]–[33]. The FTIR spectral characteristics of ICWMS before and after adsorption of PO_4^{3-} ions are listed in Table 3. The position and shape of the PO_4^{3-} stretching band in the FTIR spectra of the ICWMS are influenced by the nature and position of the surface functional groups. The tetrahedral PO_4^{3-} molecules are coordinated [34].

Before the adsorption of PO_4^{3-} , the FTIR spectral results with two bands observed at 860 and 712 cm^{-1} would confirm the presence of iron oxide [35,36]. After the adsorption of PO_4^{3-} solute from synthetic solution onto the ICWMS, a new peak located at 1,467 cm^{-1} was observed and could be associated to the vibrational modes of the H_2PO_4^- and HPO_4^{2-} substituted at the CO_3^{2-} on the surface of ICWMS; the inner-sphere surface complexes were formed through Lewis acid-base interactions between PO_4^{3-} and $\equiv\text{Ca-CO}_3$ [37]. The peak shifted from 3,446 to 3,393 cm^{-1} is due to O-H stretching bands at the surface of ICWMS are affected by asymmetric stretching mode of vibration for PO_4^{3-} group [38]. The band near 2,365 cm^{-1} was obtained for PO-H stretching [39]. The peak at 1,083 cm^{-1} was corresponded to the PO_4^{3-} bending [39,40]. The influence of the PO_4^{3-} molecules adsorbed onto the surface of ICWMS on Fe-O-H bending may increase a 2 cm^{-1} (714 – 712 cm^{-1}) and (862 – 860 cm^{-1}) frequency spectrum due to ion exchange between PO_4^{3-} and Fe-O-H functional group can affect the stretching because of the vibrations [35,36]. The peak at 1,384 cm^{-1} could be assigned as synthesis residue associated with NO_3^- group disappears during the adsorption process [41].

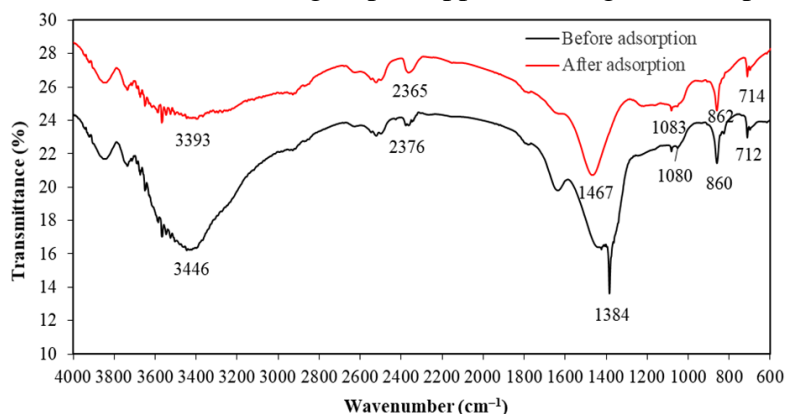


Figure 3. The FTIR spectra of ICWMS of before and after PO_4^{3-} adsorption.

Table 3. FTIR spectral characteristics of ICWMS before and after adsorption of PO_4^{3-} ions.

Frequency spectrum (cm^{-1})			Detection of functional group	Reference
Before adsorption	After adsorption	Differences		
3446	3393	-53	OH^- stretching bands	[40]
2376	2365	-11	PO-H stretching	[39]
-	1467	-	OH^- stretching bands	[39]
1384	-	-	N-O stretching band	[41]
1080	1083	3	P-O bending	[39,40]
860	862	2	Fe-O-H bending	[35,36]
712	714	2	Fe-O-H bending	[35,36]

3.2. Variations of PO_4^{3-} removal efficiency and adsorption capacity.

As shown in Figure 4, the efficiency of PO_4^{3-} removal can reach 86.1, 94.8, and 96.9% for removing PO_4^{3-} after a contact time of 48 h with the amounts of ICWMS 4, 12, and 20 g, respectively. PO_4^{3-} removal efficiency promptly increases for the period of 1, 2.5, and 3.5 h. It

then slowly increases until it reaches a constant value (see Figure 4). The rapid removal of PO_4^{3-} from aqueous solution by ICWMS during the first 3.5 h of the experimental run may be due to the availability of many free binding sites on the surface of the ICWMS [43]. According to the results of a batch experiment, the ability of ICWMS as an adsorbent can attract PO_4^{3-} because the affinity between Fe_2O_3 on the surface of ICWMS and PO_4^{3-} is quite strong due to the reaction of these two compounds with the presence of guest components containing hydroxyl groups (-OH), which can form hydrogen bonds, the complex of iron-hydroxy-phosphate can be significantly stabilized in the forms of amorphous or crystalline [44].

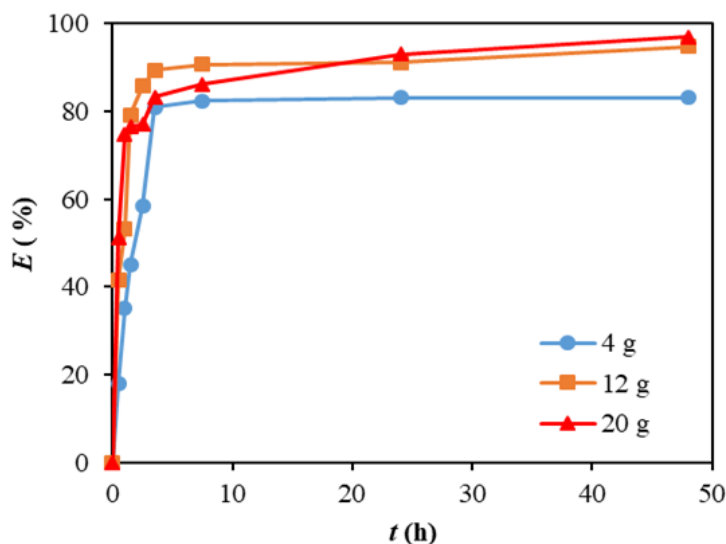


Figure 4. The efficiency of PO_4^{3-} removal from synthetic solution.

The relationship of E against m and q against m for the adsorption of PO_4^{3-} onto ICWMS is depicted in Figure 5. E gradually increases from 86.1 to 96.9%; however, q gradually decreases from 0.30 to 0.07 mg g^{-1} when m increasing from 4 to 20 g as illustrated in Figure 5. More adsorbents used in a batch experiment could have more active sites available to adsorb PO_4^{3-} from a synthetic solution. Thus, the E increases [45]. The q decreases as m increases because at high ICWMS adsorbent dosages, the available number of PO_4^{3-} solute in aqueous solution is insufficient to completely bind with all available surface binding sites on the ICWMS adsorbent [46].

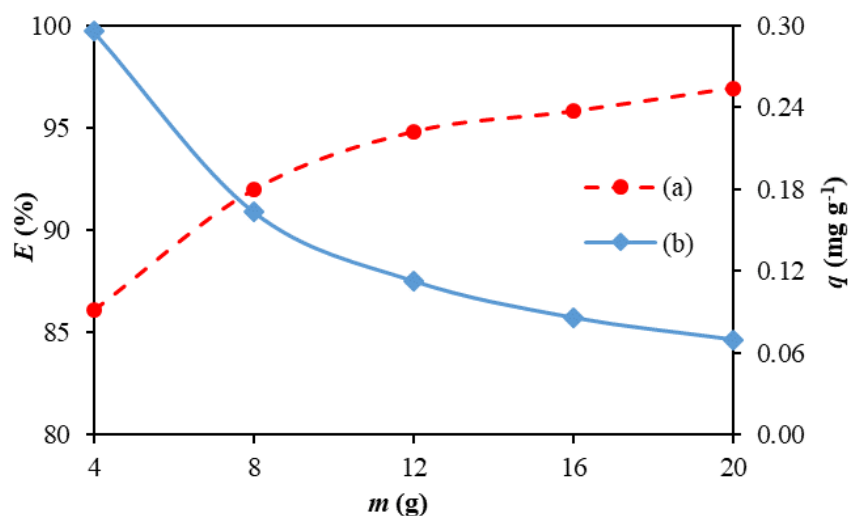


Figure 5. Relationship of: (a) E against m and (b) q against m for the adsorption of PO_4^{3-} onto ICWMS.

3.3. Adsorption kinetics of PO_4^{3-} onto the ICWMS.

The value of F_e can be calculated according to the following equation [47]. The most appropriate model, either PFO or PSO should have the highest R^2 and smallest F_e value.

$$F_e = \sqrt{\left(\frac{1}{n-p}\right) \sum_i^n (q_{t(exp)} - q_{t(theo)})^2} \tag{7}$$

where n is the number of measurements, p is the number of kinetic parameters, $q_{t(exp)}$ is the experimental q value, and $q_{t(theo)}$ is the theoretical q value ($mg\ g^{-1}$).

The kinetic parameters obtained from the PFO and PSO models are shown in Table 4. The ($R^2 = 0.999$) for PSO model was higher than that ($R^2 > 0.698$) for PFO model, as shown in Table 4. This study verifies that the PSO model could be more suitable than PFO model due to the lower value of F_e and the higher value of R^2 have been evaluated (Table 4). According to the results of this study, the adsorption of PO_4^{3-} onto ICWMS can be categorized as chemical adsorption; $H_2PO_4^-$ and HPO_4^{2-} react with some oxides present on the surface of ICWMS (i.e., Ca–O–H and Fe–O–H) via hydrogen bonding [48]. The value of k_2 increases from 0.052 to 0.297 and to 0.392 $g\ mg^{-1}\ min^{-1}$ with an increasing amount of the ICWMS from 4 to 12 and to 20 g, meaning that the rate of PO_4^{3-} adsorption onto ICWMS can be increased by increasing the amount of ICWMS [49,50].

Table 4. The kinetic parameters were obtained from the PFO and PSO models.

Sample	Amount (g)	PFO model			F_e	q_e (exp) ($mg\ g^{-1}$)
		q_e (theo) ($mg\ g^{-1}$)	k_1 (min^{-1})	R^2		
Synthetic solution	4	0.30	0.012	0.881	0.033	0.30
	12	0.04	0.006	0.721	0.081	0.11
	20	0.02	0.003	0.698	0.057	0.07
Sample	Amount (g)	PSO model			F_e	q_e (exp) ($mg\ g^{-1}$)
		q_e (theo) ($mg\ g^{-1}$)	k_2 ($g\ mg^{-1}\ min^{-1}$)	R^2		
Synthetic solution	4	0.30	0.052	0.999	0.031	0.30
	12	0.11	0.297	0.999	0.152	0.11
	20	0.07	0.392	0.999	0.005	0.07

3.4. Adsorption isotherms of PO_4^{3-} onto the ICWMS.

The experimental data were analyzed using the linearized forms of the Freundlich and Langmuir isotherm models. The results (see Table 5) represent the parameters obtained from the Freundlich and Langmuir models. This study suggested that the experimental data agreed with the Freundlich model ($R^2 = 0.996$; see Table 5). The adsorption of PO_4^{3-} occurred on the heterogeneous site of ICWMS progression with multilayer adsorption, meaning that the adsorbed PO_4^{3-} on the surface of ICWMS can capture more PO_4^{3-} from bulk water. The surfaces of the ICWMS are heterogeneous, and sorption of PO_4^{3-} onto ICWMS occurs in the form of multilayers [51,52]. The n value of 1.16 was verified (see Table 5). It indicates favorable adsorption, active sites with the highest binding energies would be used first for less heterogeneous surfaces and then pursued by weaker sites for more heterogeneous surfaces [53,54].

Table 5. The adsorption isotherm parameters.

Sample	n	Freundlich model		Langmuir model		
		K_F ($mg\ g^{-1}$)	R^2	q_{max} ($mg\ g^{-1}$)	K_L ($L\ mg^{-1}$)	R^2
Synthetic solution	1.16	0.26	0.996	1.08	0.31	0.992

3.5. Comparison of the adsorption capacities.

The comparison of the PO_4^{3-} adsorption capacities for PO_4^{3-} adsorption onto various adsorbents, as had been done by previous researchers, is shown in Table 6. The adsorption capacity of coarse mussel shell and mussel shell with their particle sizes of less than 3.0 mm as high as 1.00 mg g^{-1} and 0.10 mg g^{-1} , respectively, has been verified [7]. The use of ICWMS with its adsorption capacity of 0.30 mg g^{-1} is better than that of raw mussel shell with its adsorption capacity of 0.05 mg g^{-1} for removing PO_4^{3-} from aqueous solution [16]. Another study by Chen *et al.* [55] reported that the adsorption capacity of 0.119 mg g^{-1} was obtained to remove PO_4^{3-} from wastewater by an oyster shell.

Table 6. Comparison of the PO_4^{3-} adsorption capacities of the various adsorbent.

Adsorbent	C_i (mg L^{-1})	Dosage (g L^{-1})	Duration (h)	$q_{e(\text{exp})}$ (mg g^{-1})	Size of particles (mm)	pH	References
Mussel shell	5	2	50	0.10	0.60 to 1.18	7	[7]
Mussel shell	15	13	72	0.05	1.5	9.2	[16]
Coarse Mussel shell	0.5	100	n/a	1.00	0.5 to 3.0	9.1	[56]
Fine Mussel Shell	0.5	100	n/a	<0.43	< 1	9.3	[56]
Oyster Shell	3	25	48	0.119	<200	7	[56]
Zeolite Clinoptilolite	3	0.075	24	0	n/a	5.9	[57]
Hardwood	24	5	24	0.24	<2	8.5	[58]
Shale	25	80	24	0.23	1 to 2	11	[59]
ICWMS	7	20	48	0.30	0.60 to 1.18	7	This study

Remarks that n/a is not available.

4. Conclusions

The feasibility of using ICWMS as an adsorbent for the removal of PO_4^{3-} in an aqueous solution was explored. The adsorption kinetic data agreed with the PSO model ($R^2 = 0.999$), suggesting that the adsorption phenomena between ICWMS and PO_4^{3-} could be leading to chemisorption. The adsorption isotherm data were well fitted to the Freundlich model ($R^2 = 0.996$), implying that the adsorption of PO_4^{3-} onto ICWMS from synthetic solution would occur as a multilayer. The results findings can help solve the excessive amounts of PO_4^{3-} problem using ICWMS as an adsorbent and thus potentially improve environmental quality.

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Conflicts of Interest

The authors declare no conflict of interest.

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