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Municipal Solid Waste Incineration (MSWI) Fly Ash as a Potential Adsorbent for Phosphate Removal

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Abstract: Phosphorus, in the form of phosphate, is an essential nutrient used in agriculture, but in excess, it becomes harmful to the environment by promoting the eutrophication of aquatic ecosystems, leading to oxygen depletion and phytoplankton overgrowth. This study aims to repurpose municipal solid waste incineration (MSWI) fly ash for phosphate removal by adsorption and develop sustainable, cost-effective MSWI fly ash-based mitigation strategies for phosphorus pollution. Batch experiments were conducted to examine the effects of contact time, phosphate concentration, MSWI fly ash dosage, and pH on phosphate removal efficiency. The results indicate that the phosphate removal efficiency significantly improved with a longer contact time, pH of 2, increased MSWI fly ash dosage, and higher initial phosphate concentrations. These findings highlight the potential of repurposing MSWI fly ash as an economical and sustainable adsorbent to mitigate the impacts of phosphate pollution on aquatic ecosystems, a strategy that promotes not only waste reduction and the circular economy but also environmental protection and conservation.

Keywords: phosphate; eutrophication; wastewater treatment; adsorption; fly ash

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1. Introduction

Urbanization, rapid population growth, and sustained economic development have significantly contributed to the excessive generation of municipal solid waste (MSW), a major global challenge exacerbated by changing lifestyles like easier access to fast foods and more convenient food delivery services, both of which extensively use disposable plastics and single-use packaging materials. A World Bank report, for example, estimated that by 2050, 3.4 billion tonnes of MSW will be generated annually worldwide [1]. Aside from the large amounts of MSW generated, the complex composition of this solid waste stream makes its management difficult. Developed countries with well-developed waste management infrastructures have regulations for waste segregation and sorting at the source, a strategy that not only improves the predictability of waste composition but also promotes recycling and repurposing. Unfortunately, such policies are either non-existent or only weakly implemented in low- and middle-income countries, making MSW management more challenging because of its unpredictable composition [2]. Changing lifestyles, as noted previously, have also substantially impacted MSW composition. The proliferation of take-outs and delivery services, for example, has increased the relative abundance of various types of plastics in MSW, which are hazardous to the environment and human health because they can generate microplastics and eluate harmful organic

compounds like Bisphenol A (BPA), as well as ferrying heavy metals and other hazardous organic compounds [3–5].

In the waste management hierarchy, priority is given to waste prevention and in order of decreasing preference, this is followed by reuse, recycling, recovery, and disposal. Conventional MSW management practices are typically composed of four stages: (1) collection, (2) transportation, (3) treatment, and (4) disposal. In the final stage, technologies like incineration, landfilling, or thermal/chemical decomposition are employed to reduce its volume, recover energy, generate gas for fuel (e.g., methane), reduce environmental impacts, and recover valuable resources [2]. Among these methods, sanitary landfills are the most commonly used strategy for MSW disposal because of their simplicity of operation and low maintenance; however, landfills have serious drawbacks, including the need for large parcels of land, contaminated leachate formation, and greenhouse gas (GHG) emissions [2]. When land area is scarce, building and maintaining landfills is costly, so incineration becomes a viable alternative. Incineration is a thermal process that destroys organic compounds at high temperatures, and it is ideal when wastes contain a large portion of combustible materials like food scraps, organic matter, and many types of plastics [1,2,6–9].

One of the main advantages of incineration is its ability to not only effectively reduce waste volumes but also transform reactive waste into more benign materials, both of which mitigate the strain on landfills [10]. Despite this advantage, however, the gaseous emissions of pollutants (e.g., dioxins, furans, heavy metals, and particulate matter) and fly ash generation remain major drawbacks of incineration [11]. Particulate matter (PM) produced from waste incineration is typically composed of fine particles categorized as PM 10 (<10 μm in size) and PM 2.5 (<2.5 μm in size). Fly ash, a subset of PM, is the fine, unburned residue that goes with flue gases during incineration, which is subsequently captured by pollution control devices like fabric filters or electrostatic precipitators (ESP). The compositions of fly ashes and PM depend on not only waste composition but also incineration conditions. Environmentally regulated pollutants like heavy metals (e.g., lead, cadmium, and mercury), dioxins, furans, polycyclic aromatic hydrocarbons (PAHs), and other organic and inorganic compounds are among the most prevalent constituents of waste streams from incineration [12].

Fly ash has substantial economic, health, and environmental impacts, and if not appropriately managed, presents serious environmental and health hazards. The direct inhalation of fly ash particulates can cause respiratory problems and severe health issues due to the presence of fine silica particles and accompanying hazardous heavy metals [13]. Moreover, the exposure of fly ashes to the environment could induce the release of their associated hazardous inorganic pollutants like arsenic, boron, lead, and mercury and contaminate the soil, groundwater, and surrounding ecosystems [14–16]. Because of the potential human health and environmental impacts of fly ashes, their management and disposal are subject to stringent regulations to reduce their risks [17].

For example, fly ashes are conventionally disposed of in special landfills, which are designed with a leachate collection system and impermeable barriers to limit discharge into the environment [18]. However, there are drawbacks to this conventional method, including the long-term maintenance of landfills and the high costs related to leachate management and treatment [19]. Another approach is to stabilize heavy metals and other toxic substances in fly ashes by stabilization/solidification. This method treats contaminated media like fly ashes by mixing them with binding reagents like cement and geopolymers [20]. More recently, circular economy strategies championed by the United Nations in its Sustainable Development Goals (UN-SDGs), like the repurposing of industrial wastes and by-products (e.g., MSWI fly ashes, mining wastes, and metallurgical slags) into construction and pollution control materials, have become more popular and widespread [20]. This approach has notable socio-environmental benefits over traditional landfilling and burial, including reduced hazards and risks associated with toxic pollutant release and the potential for carbon dioxide sequestration [20].

From the perspective of economics, the repurposing of fly ashes reduces the burden on landfills, improves the durability and mechanical properties of construction materials, and lowers construction costs [21]. It also reduces the demand for basic materials such as limestone and clay, thereby conserving natural resources [14]. Moreover, fly ash repurposing offers a valuable opportunity to implement "Responsible Consumption and Production" in accordance with SDG #12, helping the waste management, construction, and resources sectors not only reduce their environmental footprint and improve their social license to operate but also raise their profitability by converting waste and byproducts into valuable resources. Among the various repurposing applications for fly ashes, significant attention has been given to their utilization as adsorbents for the removal of ions from effluents. According to Ahmaruzzaman (2010) [14], fly ash effectively adsorbs heavy metals such as chromium, cadmium, and lead from solutions through ion exchange and chemisorption. These processes are likely promoted because fly ash contains unreacted lime, which induces alkaline conditions and promotes heavy metal removal by precipitation. Moreover, their small particle size, large surface area, high porosity, and abundance of silica, alumina, and iron oxides make fly ashes effective adsorbents of hazardous dyes and environmentally persistent anions like phosphate [22,23].

Phosphorus is an essential nutrient for the normal growth and metabolism of plants and animals and is generally added in farming and crop production as fertilizer. In solution, it predominantly exists as phosphate (PO_4^{3-}) but can transform into other chemical forms like orthophosphate, polyphosphate, and particulate phosphorus depending on the prevailing geochemical conditions. At high concentrations, however, PO_4^{3-} is a serious environmental hazard, especially in aquatic ecosystems, because it promotes eutrophication. Eutrophication is the process by which water bodies become oversaturated with nutrients, resulting in the excessive growth of algae and other aquatic vegetation [24]. The excessive growth of algae and aquatic vegetation rapidly depletes oxygen levels in the water and blocks sunlight, resulting in the death of aquatic life. Over time, this can lead to the formation of dead zones in water bodies where aquatic life is unable to survive [25].

Traditional approaches to PO_4^{3-} removal from effluent include chemical precipitation, biological treatment, and membrane filtration, all of which are costly, require specialized knowledge, and have complex operational and maintenance protocols. In comparison, adsorption is a more cost-effective alternative for the removal of PO_4^{3-} because it is easy to implement, simple to maintain and operate, and has a high efficiency [25]. For example, adsorbents like activated carbon, clay minerals, metal oxides, and sulfide minerals have been shown to capture PO_4^{3-} effectively and reduce its concentration in solution and actual wastewaters [26]. Adsorption, in contrast to chemical methods, generates less residue and permits the regeneration and recycling of adsorbents, thereby promoting sustainability [27]. Moreover, adsorbents can be modified and optimized to improve their adaptability, applicability, and effectiveness for a wide range of target pollutants in various wastewater types [28]. Zhang et al. (2024) also highlighted that carbon-based adsorbents, such as wood-based carbon materials, are effective in water treatment due to their high adsorption capacity and reusability, further supporting the sustainable potential of adsorption in various applications [29,30].

Among the various types of industrial fly ashes, coal fly ash (CFA) is one of the most studied byproducts because it is used in geopolymers and contains critical elements like lithium and rare earth elements [31]. As an adsorbent, CFA has been reported as a potentially good adsorbent of PO_4^{3-} [32]. However, research on the application of MSWI fly ash as an adsorbent of environmentally regulated compounds like PO_4^{3-} remains limited. Therefore, this study focuses on the repurposing of MSWI fly ash to eliminate PO_4^{3-} from wastewater. Our goal is two-fold: first, to elucidate the factors and processes that influence PO_4^{3-} adsorption to MSWI fly ash using batch tests, and second, to contribute to the body of knowledge regarding environmentally sustainable, cost-effective, and effective solutions to PO_4^{3-} pollution.

2. Materials and Methods

2.1. Sample Characterization

The MSWI fly ash samples used in this study were provided by an MSW incineration plant in Thailand. The sample was oven-dried at 105 °C for 24 h, then sieved to obtain a particle size fraction of 106–150 μm. The chemical composition of the samples was determined using X-ray fluorescence spectroscopy (XRF, Epsilon 4, Malvern Panalytical Ltd., Malvern, UK).

2.2. Adsorption Experiments

2.2.1. Preparation of Stock Solution

All reagents employed in this study were of analytical grade. Phosphate (PO_4^{3-}) stock solution was prepared by dissolving potassium dihydrogen phosphate (KH_2PO_4; KemAus, New South Wales, Australia) in deionized water to obtain a phosphorus (P) concentration of 300 mg/L (i.e., 800 mg/L PO_4^{3-}). The initial pH of this synthetic phosphorus effluent was adjusted using hydrochloric acid (HCl; KemAus, New South Wales, Australia) or sodium hydroxide (NaOH; KemAus, New South Wales, Australia) to obtain pH values between 2 and 8.

2.2.2. Batch Experiments

Batch experiments were conducted to assess the adsorption capacity of MSWI fly ash for PO_4^{3-}. The effects of variables such as initial PO_4^{3-} concentrations (i.e., 50–400 mg/L), adsorbent dosages (i.e., 0.1–1.5 g), contact time (i.e., 0–48 h), and pH (i.e., pH 2–8) were investigated in these tests. Predetermined amounts of MSWI fly ash were mixed with 500 mL of PO_4^{3-} solutions at room temperature. After the specified contact times, the suspensions were filtered through 0.45 μm membrane filters (Whatman, Hangzhou, China), and the filtrates were collected in 10 mL volumetric flasks. The PO_4^{3-} concentration in the solutions was determined based on the total P measured using inductively coupled plasma optical emission spectroscopy (ICP-OES, Model plasma quant 9100 elite, Analytik Jena, Jena, Germany). For the mass balance calculations, total P concentrations of stock solutions before the adsorption were also measured by ICP-OES.

2.3. Equilibrium Studies

Understanding the connection between the amount of adsorbate on the adsorbent and its concentration in solution at equilibrium is essential because it helps to establish isotherm models like Langmuir, Freundlich, and Temkin isotherms.

In these tests, MSWI fly ash (0.2 g) was added to a specific volume of PO_4^{3-} solution at varying concentrations (i.e., 50, 100, 200, and 400 mg/L), and the suspension was stirred at 200 rpm. The total P concentration was determined using ICP-OES. To ensure that all experiments reached apparent equilibrium, the duration for the isotherm tests was set to 48 h.

2.3.1. Langmuir Isotherm Model

The Langmuir isotherm model describes the adsorption of molecules on a solid surface and is employed to gain insights into a variety of physical and chemical processes. Several fundamental assumptions underpin the Langmuir isotherm model, including the following: (i) adsorption begins at specific homogeneous sites within the adsorbent, (ii) each site has the ability of accommodating only one adsorbate molecule, (iii) the adsorption energy is constant and unaffected by the degree of coverage, and (iv) there is no interaction between adsorbed molecules [33]. The Langmuir isotherm can be expressed as follows:

$$q_e = (q_m K C_e)/(1 + K C_e) \quad (1)$$

where q_e is the equilibrium amount of adsorbate adsorbed per unit mass of adsorbent, q_m is the maximum adsorption capacity, K is the Langmuir adsorption constant that is correlated

with the binding sites' affinity, and C_e is the equilibrium concentration of the adsorbate. Equation (1) can be linearized by plotting the equilibrium concentration of phosphate (C_e, in mg/L) as, the horizontal axis (x-axis), while the vertical axis (y-axis) is represented by the ratio of the equilibrium concentration of PO_4^{3-} to the amount of PO_4^{3-} adsorbed per unit mass of adsorbent (C_e/q_e).

2.3.2. Freundlich Isotherm Model

The Freundlich isotherm model is an empirical equation employed to characterize adsorption in heterogeneous systems [34]. It is based on the observation that the adsorption capacity fluctuates in accordance with the concentration of the adsorbate in the solution. In contrast to the Langmuir isotherm, which assumes a uniform surface with identical sites and a single layer of adsorption, the Freundlich isotherm considers the heterogeneous character of adsorbent surface and potential for multilayer adsorption [35]. The equation describing the Freundlich isotherm model is as follows:

$$q_e = K_F C_e^{1/n} \quad (2)$$

where K_F is the adsorption capacity indicated by the Freundlich constant and 1/n is a dimensionless parameter associated with the intensity of adsorption.

In this graph, the x-axis is the logarithm of the amount of PO_4^{3-} adsorbed per unit mass of adsorbent ($\log(q_e)$), and the y-axis is the logarithm of the equilibrium concentration of phosphate ($\log(C_e)$). This graph is used for illustrating the Freundlich isotherm.

2.3.3. Temkin Isotherm Model

The Temkin isotherm model is particularly useful for systems in which the heat of adsorption decreases linearly as the coverage increases [36]. The model suggests that the adsorption heat decreases linearly with coverage because of adsorbate–adsorbate interactions. This contrasts with the Langmuir isotherm, which assumes a consistent heat of adsorption for all sites [37]. The Temkin model is mathematically represented as

$$q_e = B \ln(AC_e) \quad (3)$$

where B is related to the heat of adsorption and A is the Temkin isotherm constant.

For the Temkin isotherm, the x-axis represents the amount of PO_4^{3-} adsorbed per unit mass of adsorbent (q_e, in mg/g), and the y-axis is the natural logarithm of the equilibrium concentration of PO_4^{3-} ($\ln(C_e)$).

3. Results and Discussion

3.1. Chemical Composition of Municipal Solid Waste Incineration Fly Ash

The chemical composition of MSWI fly ash based on the XRF analysis is illustrated in Figure 1, which shows significant amounts of SiO_2, CaO, Al_2O_3, and Fe_2O_3, among other elements. Notably, CaO accounted for 29% of the sample, which is predominantly from the lime (CaO) or slaked lime ($Ca(OH)_2$) added in the process to treat incineration gasses. The presence of CaO in MSWI fly ash plays a critical role in PO_4^{3-} removal, because when CaO reacts with PO_4^{3-} in water, this reaction leads to PO_4^{3-} immobilization via adsorption, surface precipitation, and/or bulk precipitation as insoluble calcium phosphate compounds if the critical solute concentrations of Ca^{2+} and PO_4^{3-} are reached. These reactions not only facilitate adsorption but also enhance P removal from aqueous solutions. Previous studies have demonstrated the effectiveness of calcium-based materials, including CaO, for PO_4^{3-} removal via adsorption and precipitation [38].

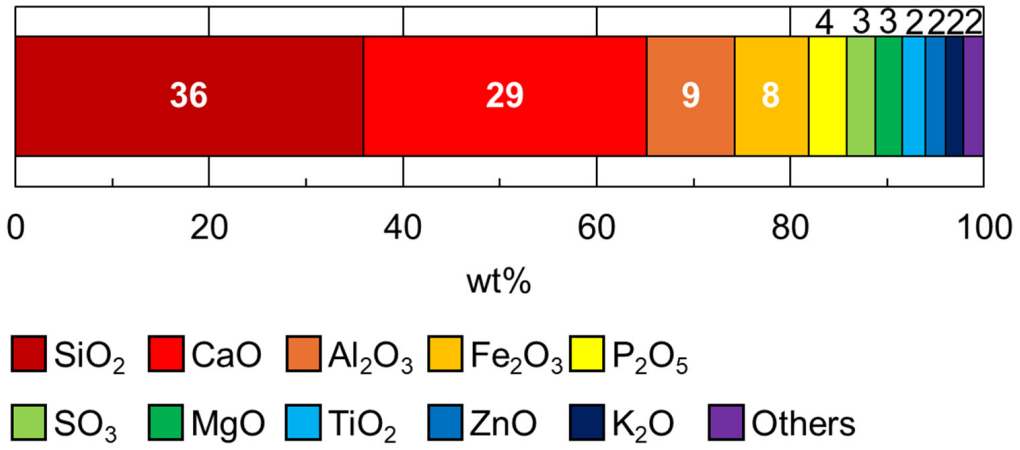

Figure 1. Chemical composition of the MSWI fly ash sample by XRF analysis.

The 29% CaO present in the MSWI fly ash sample is within the optimal range for PO_4^{3-} removal, as reported in several previous studies. Fly ash samples containing between 20% and 40% CaO have been shown to achieve high PO_4^{3-} removal rates. Specifically, fly ashes with 20−30% CaO content have been effective at adsorbing and precipitating PO_4^{3-}. The efficiency of PO_4^{3-} removal is closely linked to CaO content and other treatment conditions, making it a key component of the removal process. This aligns with the findings of Adam et al. [39] and Wu et al. [40], who emphasized the importance of CaO in achieving effective PO_4^{3-} removal from wastewater [39,40].

3.2. Effects of Contact Time on Phosphate Removal

The removal of PO_4^{3-} using MSWI fly ash was influenced by various factors. The relationship between contact time and PO_4^{3-} adsorption is evident in Figure 2a, which shows that adsorption exceeded 80% after 2 h. The concept of adsorption equilibrium is central to understanding why increased contact time results in increased PO_4^{3-} removal. A significant quantity of free adsorption sites is initially available, supporting an increased PO_4^{3-} adsorption rate. As these sites are gradually occupied, the rate of adsorption decreases until equilibrium is reached, wherein no additional adsorption takes place. The time necessary to achieve equilibrium is dependent on the properties of the adsorbents and the PO_4^{3-} concentration in the solution [41]. According to Li et al. [42], there exists an optimal contact time for a given quantity of adsorbent that optimizes PO_4^{3-} removal efficiency. These authors reported that increasing the contact time from 30 min to 4 h substantially improved PO_4^{3-} removal from 60% to 90%. Sharma and Bhattacharya [41] performed batch experiments and demonstrated that an increase in contact time resulted in a corresponding limit in PO_4^{3-} removal efficiency beyond a particular level. Additionally, the initial concentration of PO_4^{3-} is correlated with contact time. To reach similar removal efficiencies, a longer contact time may be necessary for higher initial concentrations of PO_4^{3-}, as these contain more adsorbates that require adsorption [43,44]. Once adsorption equilibrium is reached, extending the contact time will have negligible effects on the overall removal of PO_4^{3-}.

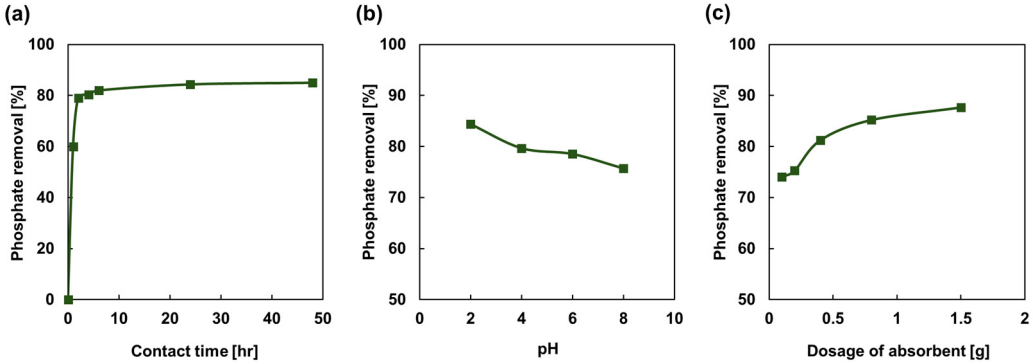

Figure 2. Influence of (**a**) contact time, (**b**) pH, and (**c**) dosage of adsorbent on PO_4^{3-} removal.

3.3. Effects of pH on Phosphate Removal

The PO_4^{3-} removal mechanism of MSWI fly ash involved PO_4^{3-} adsorption onto the ash particle surface. The surface charge of the adsorbent, which is significantly affected by the pH of the solution, is essential to this process [45]. A comprehensive knowledge of the impact of pH on PO_4^{3-} removal is essential due to the substantial influence that the pH of the solution has on the surface properties of fly ash, including its adsorption capacity [46].

The adsorption experiments were conducted at room temperature using 0.2 g of MSWI fly ash in 300 mg/L of PO_4^{3-} concentration, with a contact time of 24 h and pH values ranging from 2 to 8. The relationship between pH and PO_4^{3-} removal is illustrated in Figure 2b, showing a clear trend in PO_4^{3-} removal efficiency as the pH changes. At pH 2, PO_4^{3-} removal is highest at 84.4%, and it gradually decreases to 75.7% at pH 8. This decrease in PO_4^{3-} removal with increasing pH suggests that acidic conditions enhance PO_4^{3-} removal. The higher removal efficiency at lower pH levels is likely due to the decreased solubility of calcium phosphate in acidic environments, promoting its precipitation. In contrast, as the pH rises, the solubility of calcium phosphate increases, reducing the PO_4^{3-} removal efficiency.

Additionally, the dissolution of calcium (Ca) from the MSWI fly ash shows the opposite trend. At pH 2, only 50.7% of the calcium is dissolved, while at pH 8, almost all the calcium (99.6%) is dissolved. This indicates that calcium becomes more soluble in alkaline conditions, which could theoretically promote the formation of calcium phosphate precipitates. However, under the experimental conditions, the increase in calcium dissolution did not correspond to a significant improvement in PO_4^{3-} removal. The results suggest that while calcium dissolution increased with the pH, the efficiency of PO_4^{3-} removal declined, likely due to reduced precipitation at higher pH levels. The observed trend, where PO_4^{3-} removal decreased with increasing pH, was consistent across all evaluated contact times. This can be explained by two distinct mechanisms: adsorption and precipitation. While MSWI fly ash contains active elements such as silica (SiO_2) and alumina (Al_2O_3) that contribute to the physical adsorption of phosphate, their role in phosphate removal is limited compared to the chemical precipitation driven by calcium-based compounds like calcium oxide (CaO) [47]. At a low pH, adsorption dominates because the surface of the fly ash becomes positively charged due to protonation, enhancing the attraction of negatively charged phosphate ions [48]. However, as the pH increases, the surface becomes more negatively charged, leading to electrostatic repulsion between the surface and phosphate ions, thereby reducing adsorption efficiency.

Calcium is the primary active element in MSWI fly ash that facilitated the removal of PO_4^{3-} through chemical precipitation. Studies have shown that the CaO content in fly ash plays a critical role in this process, with calcium ions (Ca^{2+}) reacting with PO_4^{3-} to form insoluble calcium phosphate precipitates [47]. This chemical precipitation becomes more significant at higher pH levels, where calcium solubility increases, promoting the formation of calcium phosphate. However, the extent of this precipitation depends on factors such as the availability of Ca^{2+} and the specific pH conditions. In cases where calcium phosphate

precipitation is not significant under the experimental conditions, overall PO_4^{3-} removal will continue to decline with increasing pH.

Thus, it is crucial to consider both adsorption and precipitation mechanisms when interpreting the results, as calcium-based precipitation tends to dominate at higher pH levels, while silica and alumina contribute primarily to adsorption at lower pH levels. The balance between these mechanisms can significantly influence the observed trends in phosphate removal [48].

By modifying the pH of the effluent prior to treatment, the efficiency of PO_4^{3-} removal by MSWI fly ash can be increased. However, to prevent secondary contamination and ensure economic viability, the addition of acid or alkali to modify the pH must be meticulously managed [49].

3.4. Effects of Dosage of Municipal Solid Waste Incineration Fly Ash on Phosphate Removal

The efficiency of PO_4^{3-} removal was significantly influenced by the dosage of fly ash utilized. Previous works have demonstrated the existence of a dosage range that maximizes the efficiency of PO_4^{3-} removal. PO_4^{3-} in solution may precipitate as metal phosphates after the addition of MSWI fly ash due to more alkaline pH levels. The efficiency of the removal mechanism is influenced by the amount of MSWI fly ash utilized. In general, increased PO_4^{3-} removal occurs at higher concentrations because of a greater number of adsorption sites and precipitating agents.

Figure 2c shows the relationship between PO_4^{3-} removal and MSWI dosage, which varies from 0.1 g to 1.5 g. The results indicate that at a PO_4^{3-} concentration of 800 mg/L, PO_4^{3-} removal started leveling off after 0.5 g, a trend consistent with reaching apparent equilibrium, and at 1.5 g of adsorbent, the removal rate reached 88%.

These observed results are similar to those reported by Park et al. [49]. These authors also found that increasing the fly ash dosage from 1 g/L to 20 g/L led to a significant improvement in PO_4^{3-} removal efficiency, from 20% to almost 100%; however, a further increase in the dosage of fly ash failed to proportionately enhance the removal efficiency. This suggests a saturation limit, observed in this study at around 88% PO_4^{3-} removal, beyond which there is only a limited improvement in PO_4^{3-} removal even with large additions of the adsorbent. Factors such as variations in experimental conditions could also play a role in the decreased PO_4^{3-} removal efficiency at high MSWI fly ash dosages. For instance, while adding fly ash raises alkalinity and aids in PO_4^{3-} precipitation, excessively high pH levels may decrease removal efficiency due to competing reactions. Moreover, higher fly ash dosages may cause particle aggregation, reducing the effective surface area for adsorption. Differences in the initial PO_4^{3-} concentration or fly ash characteristics could also contribute to the lower removal efficiency observed. Together, these factors likely explain the observed differences in efficiency [49].

3.5. Isotherm Models

Phosphate removal efficiency by MSWI fly ash was significantly influenced by its concentration, the adsorption capacity of the adsorbent, and the saturation point. The PO_4^{3-} concentration ranged from 50 mg/L to 400 mg/L while the fly ash dosage was maintained at 0.2 g. An increase in PO_4^{3-} concentration resulted in an 80% removal, as shown in Figure 3.

The kinetic control of the adsorption process is generally observed at lower concentrations, where the rate at which PO_4^{3-} interacts with the adsorbent surface acts as the limiting variable. The probability of PO_4^{3-} adsorption increases close to the surface of the adsorbent as the concentration rises [50].

When the dosage of MSWI fly ash exceeds a particular limit, the adsorption sites become saturated, resulting in the leveling off of adsorption [51]. Determining the optimal operational conditions for the treatment process, particularly when designing systems for waters with varying PO_4^{3-} concentrations, is dependent on this saturation point.

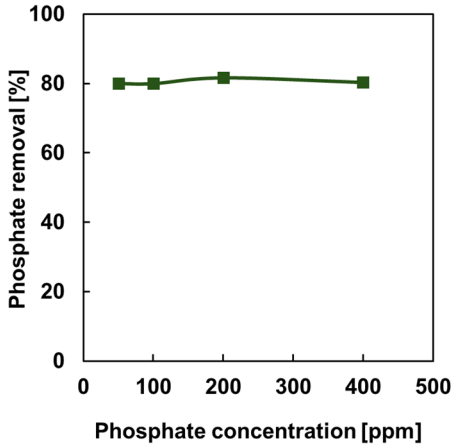

Figure 3. Influence of initial PO_4^{3-} concentrations on PO_4^{3-} removal by MSWI fly ash.

As illustrated in Figure 4, adsorption isotherms such as the Langmuir, Freundlich, and Temkin models were investigated. Table 1 summarizes the fitted parameters for these three isotherms. The Freundlich isotherm had the best fit of the experimental data correlation coefficient, higher than 0.99.

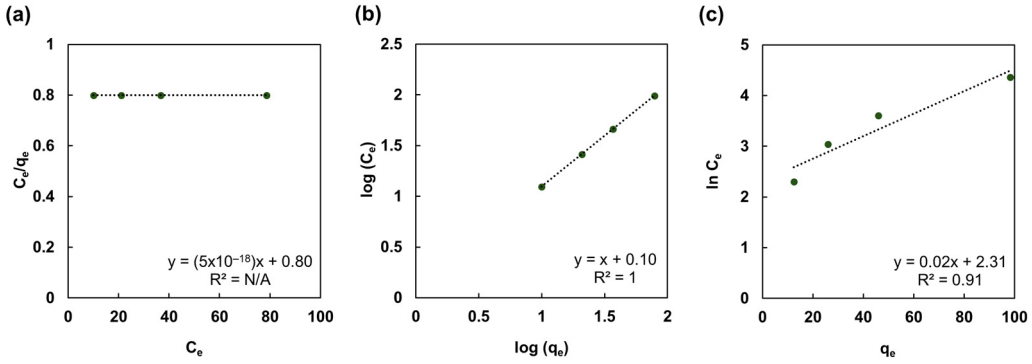

Figure 4. Adsorption data fitted with (**a**) Langmuir, (**b**) Freundlich, and (**c**) Temkin isotherm models.

Table 1. Fitted parameters for the adsorption isotherm models.

Isotherm Models	Isotherm Parameters	Values	R^2
Langmuir Model	q_m	0.00	N/A
	k_L	0.80	
Freundlich Model	1/n	0.10	1.00
	k_F	1.00	
Temkin Model	B_1	0.02	0.91
	k_T	2.31	

Note: q_m, Maximum adsorption capacity; k_L, Langmuir constant; 1/n, Heterogeneity factor; k_F, Freundlich constant; B_1, Temkin constant related to adsorption energy; k_T, Temkin isotherm constant.

The Freundlich isotherm assumes a heterogeneous surface with sites that exhibit varied affinities for the adsorbate. The model does not impose the same restrictions as other isotherms, such as Langmuir, which assumes monolayer adsorption on a homogeneous surface. This adaptability enables the model to effectively explain experimental data across a variety of adsorbent types and adsorbate concentrations [52].

Based on the results of this work and those from previously published studies, several key similarities between MSWI fly ash and CFA can be highlighted. Both types of fly ashes possess promising adsorbent properties due to their porous structures and the presence of metal oxides, which aid in PO_4^{3-} removal. The removal efficiency improves with an

increasing adsorbent dosage for both materials, as an additional dosage offers more surface sites for adsorption. Moreover, the pH of the solution plays a crucial role in determining PO_4^{3-} removal efficiency. In both cases, lower pH levels enhanced adsorption due to the protonation of adsorption sites and favorable interactions with PO_4^{3-}. Furthermore, the adsorption behaviors of both MSWI and CFA aligned well with isotherm models like Freundlich and Langmuir, which describe adsorption effectively under various conditions.

Despite these similarities, significant differences exist between the two types of fly ashes. MSWI fly ash contains higher levels of metal oxides, such as calcium, aluminum, and iron, which could facilitate PO_4^{3-} removal, primarily through calcium-mediated precipitation. In contrast, CFA tends to rely more on adsorption for PO_4^{3-} removal. The best pH range for PO_4^{3-} removal may also differ between the two fly ashes due to variations in their zeta potential and chemical compositions. Additionally, MSWI fly ash poses a higher risk of leaching heavy metals, such as lead or cadmium, compared to CFA, which generally contains fewer hazardous metals.

4. Conclusions

This study investigated the effects of contact time, PO_4^{3-} concentration, adsorbent dosage, and pH on PO_4^{3-} removal using MSWI fly ash. The main findings are summarized as follows:

- A longer contact time promoted PO_4^{3-} removal up to 82% until apparent equilibrium;
- The PO_4^{3-} removal capacity of 85% of MSWI fly ash was substantially influenced by the surface charge of the adsorbent, which in turn was determined by the pH of the solution. At pH 2, PO_4^{3-} removal by adsorption was more efficient;
- A higher MSWI fly ash dosage increased the PO_4^{3-} removal efficiency to 88% because of the greater number of PO_4^{3-} precipitating agents and adsorption sites;
- The adsorption experimental results fitted well with the Freundlich isotherm model;
- A strong correlation between PO_4^{3-} concentration and adsorption efficiency was observed, demonstrating that an increase in PO_4^{3-} concentration in the solution resulted in a corresponding rise in the rate of PO_4^{3-} removal.

These findings emphasize the necessity of optimizing operational parameters such as contact time, pH, adsorbent dosage, and the initial PO_4^{3-} concentration to attain optimal efficiency for the removal of PO_4^{3-} in wastewaters.

Future research should focus on scaling up the adsorption-based strategy to evaluate the real-world feasibility of using MSWI fly ash in large-scale wastewater treatment systems, emphasizing the impact of varying concentrations and operational conditions on efficiency. Additionally, comparative studies of different types of fly ashes from various sources or processes are necessary to determine the most effective type for PO_4^{3-} removal and whether specific treatments can enhance performance. Furthermore, long-term studies on the stability and regeneration of MSWI fly ash are crucial to assess its sustainability and cost-effectiveness in extended use. These research directions are essential for optimizing the practical application and overall efficiency of MSWI fly ash as a sustainable adsorbent for phosphate removal in wastewater treatment.

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