Red Mud as Adsorbent to Recover Phosphorous from Wastewater Streams

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Abstract: Background: Phosphorous (P) is an essential nutrient with finite and non-renewable resources; however, it can cause eutrophication in freshwater. The use or storage of red mud (RM), a by-product of alumina production with high iron and aluminium content, poses another environmental issue. Objective: This paper examines the possibility of P recovery from various wastewaters and landfill leachate with RM. Methods: Pulverized, on-site pre-treated red mud was used. Synthetic P solution, poultry wastewater effluent, the spiked effluent of a municipal wastewater treatment plant and landfill leachate were examined. Results and conclusions: Removal efficiencies of 0.41–1.24 mg P/mg RM for the wastewater effluents and 0.10–0.13 mg P/g RM for the leachate resulted in a decreased phosphorous concentration (0.02–0.57 mg P/L) for each liquid. Despite the doses being substantially higher than the stoichiometric value (103 mg P/g RM), the dosage increase did not result in a considerable cost increase. Further investigation is in progress to insert this solution into existing wastewater treatment technologies to facilitate excellent effluent quality and utilize the nutrient content of red mud.

Keywords: red mud; wastewater; landfill leachate; phosphorous recovery; adsorbent; secondary raw material

1. Introduction

Phosphorous (P) is an essential and non-substitutable nutrient for all the organisms on Earth [1], but its resources are finite, non-renewable and geographically restricted [2], which poses sustainability challenges to the global food chain. On the other hand, a major anthropogenic source of P is wastewater, mainly due to human excrement (3.17 Tg/year in 2010), but detergents also play a substantial role in the global nutrient emission of 1.7 Tg/year from households in 2010 [3]. Landfill leachate containing 0.07–148.7 mg P/L [4,5] represents another special environmental issue. P discharge from wastewater treatment plants (WWTPs) and landfills must be and is controlled to prevent high nutrient concentrations of natural waters [6,7] that would cause algal blooms, eutrophication and the deterioration of water quality [8]. While in Hungary, the lowest threshold for P is 0.7 mg/L [9], which is stricter than the value given in the Urban Wastewater Treatment Directive [10], in Sweden, the limit value is 0.3 mg P/L [11]. Following the Water Framework Directive (WFD) requirements, the EU countries defined total phosphorus and soluble reactive phosphorus threshold values for the different types of water bodies in the range of 9–400 µg/L [12].

The currently established wastewater treatment technologies focus primarily on removing P, but the possibility of recovery is gaining more attention. The two most widespread methods are chemical precipitation and enhanced biological phosphorous removal (EBPR) [13]. Both have their advantages and disadvantages [7,14], but the bioavailability of P in chemically treated sludge is much worse than in EBPR sludge [15].

Shaddel et al. [16] made an inventory of the different P recovery methodologies distinguishing commercial and emerging technologies. The most applied approach is the side-stream formation of struvite (MgNH₄PO₄·6H₂O), which can be used as fertilizer to
replenish soil nutrient content [17]. Vermicomposting could aid the methods that result in lower P bioavailability based on the findings of Turp et al. [18], although they mixed biomass ash (BA) with biowaste. Another option is to apply reusable adsorbents [19]. Lately, nanoparticles [20], duck eggshell [21] and two industrial residues, calcium silicate hydrate [22] and red mud (RM) [23], were examined as adsorbents, and studies on electro-chemical processes are also in progress [24]. Due to its composition, RM could serve as raw material to produce coagulants that have comparable removal efficiency to polyaluminium chloride (PACl) [25,26], but the P bioavailability in the precipitate was not explored.

Red mud in its treated or raw form can sequester different pollutants from wastewater due to two main characteristics. One is its extreme alkalinity, which facilitates the precipitation of metal-hydroxides, carbonates and phosphates [23]. The other is having a high concentration of iron, aluminium and titanium-oxides that provide surface sites for sorption reactions of metals and metalloids [27]. Nonetheless, two benefits of RM make it a good candidate for the amelioration of sandy soils. First, it has a high retention capacity of phosphorous at lower alkalinity (pH 8), which can be achieved by acidic treatment of the substance [28], and its trace element content which can improve soil [29]. In addition, its alkalic nature may be advantageous in reducing the mobility of toxic metals in acidic soils [30]. Therefore, if RM were used as an adsorbent to increase its P content and then as a soil amelioration medium, that would meet the criteria of a comprehensive utilization method [31]. However, existing limit values for toxic metals and metalloids in soils must also be considered.

Most of the scientific papers used synthetic phosphate solutions to test the adsorption of P on various RM-containing adsorbents; e.g., Guo et al. [32] studied the adsorption capacity of different types of RM, Tangde et al. [33] used hydrochloric acid, Cusack et al. [34] treated RM with seawater and gypsum, Lin et al. [35] tested thermally treated RM, and Yin et al. [36] used polypyrrole to modify RM. However, real wastewater was used only in a few cases: Despland et al. [37] carried out long-term experiments with Bauxsol™, the only RM-derived trademarked adsorbent, and Hu et al. [38] prepared and tested an adsorbent from boron mud and RM with the use of secondary effluent.

The current study adds to the list of research that tested the applicability of red mud for the removal of phosphorous from various real wastewater types. This paper only discusses the P removal stage, but the P-enriched adsorbent can be used as a soil amelioration medium based on the findings of the authors [39]. The ultimate goal of the research is to achieve complex, waste-free use of the red mud together with the coagulated sludge without additional recovery or modification steps.

2. Materials and Methods

2.1. Red Mud

The RM came from the tailings near Ajka, Hungary. Its composition is Fe₂O₃ (37.0% ± 2.6%); SiO₂ (20.0% ± 2.7%); Al₂O₃ (14.3% ± 1.6%); CaO (7.7% ± 2.5%); Na₂O (4.8% ± 1.3%); TiO₂ (3.8% ± 0.5%); MgO (0.53% ± 0.21%) [40]. It is highly alkaline; the pH is between 11–12, and the sodium ion concentration is 101.4 ± 81.6 mmol Na/L. XRF results of trace element content showed vanadium (~800 ppm), zirconium (~700 ppm), chromium (~600 ppm) and nickel (~280 ppm) [41]. The red mud used in this experiment was treated on-site with gypsum and carbon dioxide to reduce pH and was tempered at 800 °C for 2 h to manage its thixotropic characteristics. The treatment is carried out as a part of the normal operation in order to avoid the disposal of RM as a hazardous material. A large batch of the end product was transported to the laboratory. XRF measurement showed 34% Fe₂O₃ and 12% Al₂O₃ content. The RM had an average grain size of less than 10 µm, with 90% of the particles below 75 µm. Before starting each experiment, a small amount of material was pulverized and homogenized with a pestle and mortar.

The theoretical dose of RM was calculated based on the Fe and Al content and the stoichiometric equations (Equations (1) and (2)) of the reactions between iron, aluminium and phosphorous. According to this, 1.0 g of the red mud should be able to remove
102.8 mg P (the Fe content of the red mud is theoretically capable of reacting with 71.8 mg P, and the Al is capable of removing 31.0 mg P).

\[
\text{Fe}^{3+} + \text{PO}_4^{3-} = \text{FePO}_4 \quad (1)
\]

\[
\text{Al}^{3+} + \text{PO}_4^{3-} = \text{AlPO}_4 \quad (2)
\]

### 2.2. Experiments with Model Wastewater

Synthetic P solution (10 mg P/L) was diluted from a 50 mg P/L KH$_2$PO$_4$ stock solution prepared from KH$_2$PO$_4$ powder. The treatments were performed in a 200 mL liquid volume. First, the calculated amounts of red mud powder were measured into beakers, and then the P solution was added, which was then mixed by a magnetic stirrer. The pH was adjusted to the required value by 1 M HCl solution. The samples were taken at a given time from the stirred solution and filtered over Millipore S-Pak MCE membrane Filters (0.45 µm Ø 47 mm) before measuring P content. The phosphorous concentration of the samples was measured according to the standard MSZ EN 1189: “Water quality. Determination of phosphorous. Ammonium molybdate spectrometric method”. The pH was measured by a WTW Multi 3420 instrument, SenTix® 940 pH electrode in the filtered sample. The synthetic P solution was used in the experiments to test the effect of mixing time, control of pH with HCl and the combined effect of the dosages of red mud and HCl on the final pH, conductivity and P removal degree.

### 2.3. Experiments with Real Wastewater

The P removal was also investigated with three different effluent wastewater (ww) streams: wastewater from a Hungarian poultry processing plant (Sárvár) that was treated in a laboratory-scale sequencing batch reactor (SBR); wastewater effluent from a small municipal WWTP in Hungary (200 m$^3$/d); and landfill leachate from the Királyszentistván Waste Management Center. Since the P concentration of the municipal wastewater was much lower than anticipated based on previous experience, it was spiked with synthetic P solution. The main parameters of the wastewater streams were measured and are shown in Table 1. The pH was set with 1 M HCl solution for the poultry and municipal wastewater, and concentrated HCl was used for the leachate. All experiments and measurements were carried out in triplicates using the same methods as stated in Section 2.2.

**Table 1.** Measured parameters in real wastewater streams.

| Parameter          | pH  | COD  | TN   | NH$_4$-$N$ | NO$_3$-$N$ | NO$_2$-$N$ | OP    | TP  |
|--------------------|-----|------|------|------------|------------|------------|-------|-----|
|                    |     | mg/L | mg/L | mg/L       | mg/L       | mg/L       | mg/L  | mg/L|
| SBR effluent       | 7.20| 33   | 25   | 0.10       | 22.22      | 0.01       | 7.23  | 7.62|
| Municipal effluent | 7.71| 44   | 7    | 0.02       | 5.87       | 0.48       | 0.04/4.98* | 0.52|
| Landfill leachate  | 9.08| 5420 | 212  | 17.66      | 16.03      | 0.71       | 11.89 | 17.58|

* the original/spiked P concentration

### 3. Results

#### 3.1. Experiments with Synthetic Phosphorous Solution

Based on the composition of the red mud, the stoichiometric amount for coagulation was calculated to precipitate P from a synthetic solution. The model solution was 200 mL in volume and had a concentration of 10 mg P/L. Five different RM doses were tried (Table 2, column: factor of 2), and the stoichiometric value with a safety factor of two was taken as the middle, third dose. A safety factor is commonly used in wastewater treatment for liquid coagulants; therefore, it was applied automatically.
Table 2. Calculated dosage of red mud based on stoichiometry and experiments.

| Dose № | Multiplier | Factor of 2 | Factor of 60 |
|--------|------------|-------------|--------------|
| 1      | 1/3        | 13.0        | 389.0        |
| 2      | 1/2        | 19.5        | 583.5        |
| 3      | 1          | 38.9        | 1167.1       |
| 4      | 2          | 77.8        | 2334.1       |
| 5      | 3          | 116.7       | 3501.2       |

As expected, and confirmed by preliminary experiments, RM added to the solution in the stoichiometric ratio was not enough to reduce the P concentration. Therefore, the original dosage had to be increased by a factor of 30 (Table 2, column: factor of 60).

Further on, the middle dose was used to test the appropriate mixing time (Figure 1) with different hydrochloric acid dosing (0.85 mmol, 1.0 mmol and 1.5 mmol to 5.836 g RM in 200 mL 10 mg P/L solution) to compensate for the alkalinity of the bauxite residue. During the mixing time, the pH gradually increased, showing logarithmic growth ($R^2 > 0.95$ for all cases), indicating a caustic substance’s gradual release. It is assumed that the bound-soda (Na$_2$O, approx. 4.8 w/w% of the RM) content of the red mud comes into reaction with water, and sodium hydroxide (NaOH) is formed. The increase of pH, as time passed, was experienced when the red mud was mixed with distilled water as well. Therefore, the change of pH solely due to the reaction between the RM and phosphate was ruled out, though clarifying the mechanism of the reactions needs further research.

![Figure 1. Change in pH and phosphorous removal as a function of mixing time with different doses of hydrochloric acid (values indicated in the legend), initial TP$_{avg}$ = 10.17 mg/L.](image)

The RM dosages seemed to be appropriate for the given phosphate concentration, and a minimum of 90% removal efficiency was achieved when the solution was the most alkaline (pH 8.89 with 0.85 mL 1 M HCl at 120 min). As the solubility of aluminium phosphates and iron salts are the lowest at pH 5.7–7.5 and 7.0–9.0, respectively, the aim was to keep the pH below 8.5.
Based on these results, the mixing time was 20 min for the other experiments. Between 20 and 120 min, the pH increased by 9.4–21.9% and peaked at 8.82, 9.45 and 9.28 after 24 h, respectively. Tests with mixing time shorter than 20 min showed that the filtered solutions were acidic (pH~4), while homogenous samples were in the alkaline range (pH~10). Twenty minutes was considered a compromise between achieving high P removal efficiency, complete mixing of substances and the time requirement of the experiment.

After the mixing time was established, the dosages of RM and HCl respective to each other were determined by setting the pH level of the filtered samples to neutral. As Figure 2 shows, a small amount of acid could compensate for the alkalinity of the red mud in the synthetic solution.

![Figure 2. Correlation of empiric red mud and hydrochloric concentrations.](image)

Since phosphorous removal depends on the pH level and the adsorbent concentration, experiments were conducted to determine the co-dependency of these factors. Results for pH are shown in Figure 3. Logarithmic functions can be fitted onto the individual measurement series (fixed acid and adsorbent doses). Following this logic, a two-unknown logarithmic equation was set up and solved by Solver™ in Excel.

![Figure 3. Measured values for identifying the relationship between the red mud, hydrochloric acid and resulting pH in a 10 mg P/L model solution of 200 mL. Colouring is only used for visualization.](image)
The equation was transformed to determine the HCl molarity ($c_{HCl}$, $m_{RM}$) that would be required to achieve a certain level of pH at a given amount of RM ($m_{RM}$) (Equation (3)). Parameters of the solution are shown in Table 3 for the measurement results after 20 min and 24 h, along with the calculated sums of square residuals (SSR). The surface fitted to the 20 min data can be seen in Figure 4.

$$c_{HCl} = 10^{(pH - b - d - c \log(m_{RM}))}$$  \hspace{1cm} (3)

Table 3. Parameters of Equation (3) for pulverized RM calculated using Solver™.

| Parameters | 20 min | 24 h |
|------------|--------|------|
| a          | 3.1075 | 3.3592 |
| b          | -0.3617 | 0.0458 |
| c          | -3.7672 | -4.3354 |
| d          | -4.8007 | -4.7560 |
| SSR        | 1.72   | 11.50 |

Figure 4. Relationship between pulverized red mud, hydrochloric acid and pH after 20 min of mixing based on Equation (3).

Judging from the higher sum of square residuals of the 24 h values and the slightly different values for the two datasets, one can assume that other factors influence the pH in time than those included in the equation. The effect of aggregation of small particles and their subsequent settling is thought to be one of the influencing phenomena not taken into account. The other is that pH continues to change even after several hours, as seen earlier.

Results slightly overestimate actual values in the higher dose ranges. For example, according to the calculation, the maximum dosage of RM and HCl would result in a pH of 5.55, while the actual measured value was 6.0. In general, the required HCl volume is underestimated if calculated by Equation (3). Thus, further experiments were carried out with the initial empiric dosing.
Figures 5 and 6 show the measured values for conductivity and residual orthophosphate (OP) in the solution as a function of RM dosage and HCl after 20 min of mixing. The conductivity and pH of the synthetic P solution were originally 40 μS/cm and 5.93, respectively. While the conductivity increases with the amount of each chemical in a linear fashion, the phosphorous concentration cannot be described only by the combined dosage of the two additives, underlining the importance of pH adjustment. Nonetheless, the higher doses of RM were more efficient in precipitating/adsorbing the orthophosphate from the solution (Figure 6).

![Figure 5](image1.png)

**Figure 5.** Relationship between red mud, HCl and conductivity after 20 min of mixing in a 10 mg P/L model solution of 200 mL. For visual purposes, the HCl values are in reverse order. Colouring is only used for visualization.

![Figure 6](image2.png)

**Figure 6.** Relationship between red mud, hydrochloric acid and remaining orthophosphate after 20 min of mixing in a 10 mg P/L model solution of 200 mL. Colouring is only used for visualization.

The pH increased when the mixed solutions were left to settle for a day between 0.22–2.37 with an average of 1.39, which can substantially modify the metal-salts precipi-
tates’ solubility. The changes can neither be linked to the red mud’s dosing nor the amount of HCl added. It is assumed that despite the homogenization efforts, the RM’s material characteristics slightly vary from sample to sample.

On the other hand, after 24 h, in most cases, the OP concentration was close to or equal to zero, and there were only two experiments with values above one. One extreme value (7.21 mg P/L) was measured using minimal RM and maximal HCl dosages. In this case, the pH was 3.65 after 24 h, the lowest value in the entire experimental set-up. Except for this highly acidic solution, the results suggest that aggregates are formed in time that will slowly settle and (or) can be separated with a 0.45 µm membrane filter. It has to be mentioned, though, that there were thin rings of reddish residues near the surface of the liquids, even when cationic flocculant was added. The opacity of the solution decreased successfully with the addition of polymers, but further investigation is required to determine their exact effects.

3.2. Experiments with Real Wastewater

After getting a better insight into how bauxite residue reacts with orthophosphate in synthetic solutions, two types of wastewater effluents and a high-strength liquid (landfill leachate) were used in the following coagulation experiments. The first batch was the effluent of a laboratory scale SBR treating poultry ww originating from a Hungarian poultry processing plant. Due to the suboptimal nutrient ratio in the influent, there was a period when the P content of the treated water was higher than acceptable. These samples were collected and stored at 4 °C until used for this study.

Because of the imposed regulation on discharged wastewater quality, municipal ww effluent has high P content only if there are operational issues at the plant and effort is taken to reduce the concentration below the limit value. The group was provided with 20 L of effluent ww from a small municipal wastewater plant that usually has a high concentration of total phosphorus. Earlier, the TP concentration had been around 5 mg P/L, but that specific batch had 0.5 mg P/L. For technical reasons, the authors decided to use that effluent but spike it with synthetic P solution so that the final OP concentration would be 5 mg P/L. This batch of effluent is called spiked municipal ww.

Landfill leachate is another liquid with high P content, albeit not considered wastewater in the traditional sense. Adsorption or precipitation of P tends to happen simultaneously with the removal of organic matter and nitrate (NO$_3^-$-N), but since the ww effluents had a lower initial concentration of these compounds, the reduction was not that apparent. Therefore, landfill leachate was used for the tests to understand how the RM would react in a high-strength ww stream. The water quality parameters of the liquids used were measured before use and are shown in Table 1 in Section 2.

3.2.1. Treatment of SBR Effluent

For this experiment, the effluent from a laboratory scale SBR reactor treating poultry processing wastewater was used (SBR effluent in Table 1). Table 4 shows the results of the experiments.

| Doses | Results after 20 min |
|-------|---------------------|
| RM mg | HCl mmol | pH | OP mg/L | Conductivity µS/cm |
| 0.0 | 0.00 | 7.54 | 7.26 | 1597 |
| 389.5 | 0.13 | 7.12 | 4.30 | 1853 |
| 583.9 | 0.20 | 7.15 | 0.82 | 2035 |
| 1167.4 | 0.40 | 7.15 | 0.05 | 2530 |
| 2334.4 | 0.70 | 7.24 | 0.02 | 3355 |
| 3501.6 | 1.20 | 7.41 | 0.10 | 4325 |
Since the P concentration was relatively high and it was anticipated that the organic content of the effluent would reduce the efficiency of P removal, the same doses were opted for as in the case of the synthetic solutions. It is a well-known phenomenon in wastewater treatment plants that the coagulant reacts with the organic matter and the orthophosphate; therefore, higher doses of chemicals are needed to achieve the desired P precipitation efficiency. In addition, the higher initial conductivity indicates a degree of buffering capacity that would not allow large deviations in pH. The OP concentration was below 0.4 mg/L with RM doses No. 3–5, which was the target based on the highest threshold value determined for recipient water bodies in compliance with the WFD. The P concentration decreased with time in the case of the first two doses, and for current regulations, the second dose could also be sufficient.

3.2.2. Treatment of Spiked Municipal Wastewater

Because of the lower P concentration, RM and their respective HCl doses were halved (Table 5). As an undesired result, the pH was slightly more alkaline than optimal. The target P concentration was only met with the highest dose, which shows the importance of using safety factors in coagulant dosing in real wastewaters. The lower removal efficiencies for the first four cases are partly due to the higher pH than the SBR effluent.

| Doses | Results after 20 min | Conductivity µS/cm |
|-------|----------------------|--------------------|
| RM mg | HCl mmol | pH | OP mg/L |
| 0 | 0 | 7.79 | 4.98 | 1405 |
| 195.6 | 0.065 | 7.61 | 4.40 | 1485 |
| 293.3 | 0.100 | 7.52 | 3.84 | 1525 |
| 582.9 | 0.200 | 7.41 | 2.57 | 1706 |
| 1168.2 | 0.350 | 7.53 | 0.91 | 2075 |
| 1751.7 | 0.600 | 7.01 | 0.05 | 2635 |

3.2.3. Treatment of Landfill Leachate

Since the leachate was in the alkaline region and had a high concentration of organic matter besides a substantial amount of nitrogen (N), the RM and acid doses had to be increased (Table 6). A clear indicator of the strength of the wastewater stream is the tenfold increase in conductivity compared to the effluents. Therefore, the same RM doses were used as in the case of the SBR effluent, but the second dose was skipped, and a new maximum was chosen (4668.24 mg).

| Doses | After 20 min Mixing | Conductivity mS/cm |
|-------|----------------------|--------------------|
| RM mg | HCl mmol | pH | OP mg/L |
| 0 | 0 | 9.08 | 11.89 | 17.83 |
| 389.02 | 18 | 8.20 | 10.41 | 24.33 |
| 1167.06 | 18 | 8.09 | 4.36 | 25.20 |
| 2334.13 | 18 | 8.14 | 1.64 | 26.33 |
| 3501.19 | 18 | 8.12 | 0.57 | 27.50 |
| 4668.24 | 18 | 8.00 | 0.46 | 28.13 |

This time, due to the high buffer capacity of the solution, the acid dose was kept constant, and even with increasing the amount by four magnitudes, the pH could not be lowered below 8. Therefore, even with the new highest dose, only an average OP concentration of 0.46 mg/L could be achieved with triplicates. Parallel to the lower P
removal efficiency, a decrease in the chemical oxygen demand (COD) and NO$_3^-$-N concentration was experienced (Figure 7). From 5467 mg/L, the COD decreased to 4068 mg/L with the highest dose, while the nitrate went down from 16.93 to 5.64 mg N/L. A similar effect was seen with nitrite-nitrogen (NO$_2^-$-N), but the ammonium concentration did not change significantly. All concentrations were successfully lowered in other adsorption experiments [42] using low-cost adsorbents to remove ammonium, nitrate and phosphate.

![Figure 7. Decrease of COD and nitrate concentration as a factor of RM dose.](image_url)

4. Discussion

Red mud has been proven to remove the excess phosphorous from wastewater streams for a long time [43]. However, an issue with the research on using bauxite residue as an adsorbent is that the various treatment techniques and the type of red mud and wastewater are not always elaborated. This makes the comparison and assessment of the environmental effects of different solutions complicated [44]. The technology itself did not become widespread, and only one product engineered from bauxite residue (Bauxsol™, [https://virotec.com/our-technologies/] accessed on 29 September 2022)) is available on the market.

There are several possible reasons for that. Indeed, the case of Bauxsol™ shows that RM has the potential to be utilized as an adsorbent commercially, but one of the most determining barriers to large-scale use of RM is the cost implications of transport and processing, hampering the upscaling of promising technologies. Virotec, the company that owns the trademark, is based in Australia, and the product gained regulatory approval in only a few European countries when the paper was published. On the other hand, there is an abundance of RM in Europe that requires safe management and reuse, and the soils in Eastern Europe have the highest P depletion rates [45]. Utilizing local resources to resolve regional issues serves the notion of sustainability and the circular economy.

Another limitation for upscaling is that RM must be used in abundance to achieve the same removal efficiency as liquid coagulants containing iron, aluminium or both type of salts. Depending on the type of wastewater and the desired effluent quality, the multiplier might be 10–90. Simultaneous P removal in the biological tanks would be excluded due to the abrasive nature of the RM; its high density would impede mixing. Even without considering these factors, pumping costs would increase, and toxicological risks would occur due to the possible leaching of metals from the red mud. If the adsorbent is added after the separation of treated water and biomass to be recirculated, the issue of phase
separation occurs, raising additional costs of settling and disposal, that is if the red mud is not used after the treatment.

This paper is a part of ongoing research on the effects of red mud as a soil amendment combined with other components that would typically be disposed of. In their previous paper, the authors showed that the use of RM in 15% and 30% (of the same origin as this article) in a soil amelioration medium can act as a catalyst for plant growth, but the P content of the media was below the optimal percentage [39]. Therefore, by using RM to adsorb P from wastewater and subsequently for soil amelioration, the issues mentioned above can be counterbalanced.

Based on the measurements, the P removal efficiency of red mud was between 0.41–2.21 mg P/ g RM for the real wastewater effluents and 0.10–0.26 mg P/ g RM for the leachate. Lower efficiency values correspond mainly to the extremely low residual P values, indicating what could be considered an overdose of the adsorbent. On the other hand, if full recovery of phosphorous is the goal, using a cheap material that is available in large quantities and facilitates the reclamation of the nutrient afterwards, ‘overdosing’ could be a viable option.

Langmuir and Freundlich isotherms were applied to compare the adsorption capacity of the pulverized RM to other research results (Table 7). In two instances (spiked municipal ww and leachate), the first data points were omitted because including them resulted in negative adsorption constant (K_L) values for the Langmuir isotherm. While in some studies, the Freundlich isotherm gives a better fit [32], in this case, the Langmuir isotherm model was in better agreement with the results, similar to Li et al. [46] and Yousif et al. [47]. The maximum adsorbency (q_s) values in Table 7 are comparable with results by Cusack et al. [34] (0.35–2.73 mg P/g RM with synthetic water using untreated and treated RM), considering that the initial OP concentration was between 5–12 mg P/L. Akhurst et al. [48] achieved 8.37 mg P/g RM at pH 7.2 with an initial OP concentration of 15.5–190 mg P/L. Their results also suggest that the higher the initial P concentration, the better the adsorption capacity.

Table 7. Freundlich isotherm parameters and their significance level.

|                  | Langmuir       | Freundlich   |
|------------------|----------------|--------------|
|                  | R²  | q_s | K_L | α | R²  | n  | K_F | α  |
| Synthetic P solution | 0.995 | 4.155 | 1.931 | 0.0002 | 0.977 | 2.070 | 2.307 | 0.0015 |
| Spiked municipal ww * | 0.997 | 0.800 | 21.639 | 0.0017 | 0.938 | 11.794 | 0.720 | 0.0316 |
| SBR effluent     | 0.990 | 1.546 | 35.383 | 0.0004 | 0.399 | 5.275 | 1.385 | 0.2530 |
| Landfill leachate * | 0.988 | 0.313 | 0.992 | 0.0060 | 0.964 | 2.544 | 0.145 | 0.0184 |

* the first datapoint was omitted.

The adsorption constant is related to the enthalpy of adsorption: if the logarithm of 1/K_L is negative, the adsorption is considered spontaneous, which is mostly the case for phosphorous [49], but in the case of the landfill leachate, the value is positive. A possible reason is competition with other substances, such as organic matter and nitrate, besides other anionic compounds [50]. These compounds can react with the metal content of the bauxite residue resulting in lower P removal efficiency. Thus, higher dosages are required to precipitate the desired amount of phosphorous. Considering the wastewater effluents, with the initial COD values being between 30–40 mg O_2/L, 10–12 mg/L organic suspended solids content and 5–22 mg N/L nitrate competed for the charged particles of the adsorbent with the phosphorous. Regarding the leachate, the initial organic content was substantial, along with approximately 17 mg N/L nitrate; both were reduced during the experiment. The COD reduction could be described with neither the Langmuir nor the Freundlich isotherm, but the nitrate followed the Freundlich model, resulting in a 0.09 ± 0.02 mg N/g RM removal rate, irrespective of the RM dose.
Figure 8 shows the change in phosphorous removal efficiency for the wastewater streams from another aspect. The P removal efficiency is plotted against the RM amount used per unit of initial P content. According to this, 0.8 g RM/mg P is enough to remove more than 99% of the P from the SBR effluent and 63% of the spiked municipal wastewater. Considering the former, a simple comparison with commercial coagulants was conducted.

![Phosphorous removal efficiency as a factor of specific red mud dose in the wastewater samples.](image)

For the sake of simplicity, RM was considered to be transported from a 50 km distance to a wastewater treatment plant of 1000 m³/d capacity. The P removal requirement is 5 kg/d. Six tons of wet RM is needed per day to achieve that. Considering a 27 t truck, the transport cost would add up to EUR 88, which results in 19.35 EUR/d. To achieve a close to neutral pH, 2 mmol/L HCl would be needed (175 EUR/m³), adding up to a total daily cost of EUR 53.87. Using a 1:1 ratio of NaAlO₂ and FeCl₃ with a price of 205 EUR/m³, the daily cost would be EUR 17.53. There are various other aspects and costs to consider for both cases, but the safety factor of 30 used for the RM doses would only result in a 50% increase in the prices, considering the RM transportation costs and a threefold multiplier if the pH setting is necessary (this highly depends on the wastewater pH and buffer capacity). Neutralization agents would also be required if the liquid coagulants were used alone, increasing the cost on that side of the equation. It also has to be mentioned that a commercial practice is compared to the results of a laboratory batch experiment. The P removal capacity of RM can be improved further, as other studies have already shown (e.g., [48]); therefore, the difference can be reduced and maybe even turned around when circularity aspects are also considered.

The main limitations of the large-scale use of RM for P removal of wastewater are described in the first part of this section. These are cost, transportation, amount of RM needed compared with commercially available metal salts, the abrasive nature of RM, which makes it difficult to be inserted into a conventional WWTP, and the possible dissolution of toxic metals from the RM. In addition, there are some particular limitations of this study. For example, the RM used was pre-treated on-site to meet the disposal requirements; thus, the results cannot be compared to untreated RM from other sources. Additionally, a certain kind of wastewater has only been examined once; accordingly, there is limited information on the dosage requirements for a dynamically changing concentration. Further research is planned and carried out to overcome these constraints and to utilize the P-enriched RM in soil remediation on a large scale.
5. Conclusions

This manuscript discusses the results of using red mud as an adsorbent to reclaim phosphorous. Preliminary experiments with synthetic P solution showed the importance of finding the right amount of alkaline adsorbent and neutralization agent (hydrochloric acid) to achieve the optimal pH for phosphorous removal. Using red mud in pulverized form meant that the doses had to be increased by a factor of thirty in comparison with liquid, commercially available coagulants. Nevertheless, the applied dosages were sufficient to entirely remove the soluble P from the effluent in the synthetic and real wastewater streams; too, thus, it can be stated that stricter limit values to meet the environmental standards of WFD for sensitive water bodies can be achieved even with this waste material. Furthermore, the dosage increase did not result in an equally massive cost increase. Based on a simplified example, the costs would be only 50% more if RM was used instead of commercial coagulants, while the pH setting would triple the expenses. On top of that, the resulting sludge might be a promising additive for soil amelioration. Further investigation is in progress to insert this solution into the existing technology to facilitate excellent effluent quality and utilise the nutrient content of the red mud.

Author Contributions: Conceptualization, V.S., K.M.B. and R.K.; Formal analysis, V.S.; Funding acquisition, R.K.; Investigation, V.P. and K.M.B.; Methodology, V.P.; Resources, R.K.; Visualization, V.S.; Writing—original draft, V.S., V.P. and K.M.B.; Writing—review & editing, V.S. and V.P. All authors have read and agreed to the published version of the manuscript.

Funding: This work has been implemented by the TKP2021-NKTA-21 project with the support provided by the Ministry of Culture and Innovation of Hungary from the National Research, Development and Innovation Fund, financed under the 2021 Thematic Excellence Programme funding scheme.

Institutional Review Board Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The precise and committed laboratory work support of Rajmund Német is gratefully acknowledged.

Conflicts of Interest: The authors declare no conflict of interest.

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