# UTILISATION OF CHEMICALLY ACTIVATED MAIZE TASSEL FOR REMEDIATION OF EUTROPHIC PHOSPHORUS

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**Abstract-** Chemical precipitation with lime, the technology of choice for phosphate removal from contaminated waters, is expensive. In this study the feasibility of utilizing low-cost chemically activated maize tassel for the adsorptive removal of phosphate was assessed. $H_3PO_4$ was added to maize tassel powder in the impregnation ratio 2:1(w/w $H_3PO_4$: tassel) and activated at 600°C under an inert atmosphere of $N_2$. The activated product was characterized by BET. Activation resulted in an increase in specific surface area from $S_{BET}$ 2.54 to 803.8 $m^2/g$. Batch experiments were performed to study the removal of phosphate from simulated samples; the optimal parameters were found to be: contact time of 90 min, pH 7 and adsorbent dosage of 1.5 g per 100 mL solution. The adsorption data were fitted to the Langmuir isotherm model ($R^2 > 0.99$), yielding an estimated adsorption capacity of 15.41 mg $PO_4^{3-}$ (as P) per g adsorbent. The activated product was successfully applied for the remediation of phosphate in selected sewage samples.

**Keywords-** Maize tassel, chemical activation, eutrophication, phosphate removal.

## I. INTRODUCTION

The increase in agricultural and industrial activities in developing countries has led to the use of phosphorus as an essential resource and material. However, elevated levels of phosphates in surface and underground water from industrial and agricultural activities stimulate the growth of micro and macro organisms in water bodies, leading to eutrophication [1].

Hence, the total phosphate (as P) concentration in treated effluents from municipal and industrial sources should be less than 2.0 mg/L [2] before discharging them into water bodies. Various methods are available for phosphate removal including chemical precipitation, biological treatment and adsorption. Chemical precipitation uses lime, alum or ferric chloride as the common precipitants for efficient phosphate removal. However, problems such as the cost of the process and production of large amounts of sludge during the treatment of the wastewater arise [1].

As an alternative option, adsorption technology for removal of phosphate from aqueous solutions using cheap, easily available materials such as red mud [3], modified wheat residue [4] and fly ash [5] have been reported. Adsorption processes have merits; such as low-cost, fast operation and favourable performance, and have drawn considerable attention in recent years. Maize tassel is the male part of the maize plant which is usually discarded after harvesting. It is a lignocellulosic material possessing several desirable characteristics for an adsorbent; a low cost material, mesoporous with a high adsorption capacity for trace metal ions [6] and organics [7].
In order to enhance phosphate adsorption we attempted to activate maize tassel with phosphoric acid and use it to remove phosphate from simulated aqueous solutions as well as real environmental samples in batch experiments.

## II. MATERIALS AND METHODS

### Preparation and BET characterisation of raw and activated maize tassel adsorbents

Maize tassel was plucked off the woody parts of the maize plant, washed, air-dried and then milled using Laboratory Mill 3 (Stockholm, Sweden). $H_3PO_4$ (85% w/w) from Sigma (Pretoria, South Africa) were added as an activating agent to 20 g of raw maize tassel powder to produce a 2:1 (w/w $H_3PO_4$: tassel) impregnated material which was dried at 110 °C for 12 h and then activated at 600 °C under an inert atmosphere of nitrogen at a flow rate of 200 $cm^3$/min. The BET surface area ($S_{BET}$) and pore structural parameters were determined from the adsorption-desorption isotherms of nitrogen at 77 K (-196 °C) using a Micrometrics (TriStar 3000) Surface Area and Porosity Analyser.

### Batch adsorption studies

Batch adsorption studies were performed to study the effects of some experimental parameters known to influence the efficiency and rate of adsorption from aqueous solution. To study the effect of contact time, 1 g portions of adsorbent were added to 100 mL of 80 mg $L^{-1}$ $PO_4^{3-}$ solution in ten (10) 250 mL flasks. The mixtures were agitated using a thermostatic Labcon platform shaker (Labotech, Johannesburg) at 120 rpm for 60 min at 25 °C. A flask was removed after 10-100 min, the contents were filtered through 0.45 μm membranes and the concentration of phosphate in the filtrates was determined by UV/VIS molecular absorption spectrophotometry using a modified standard yellow (λ= 470 nm) vanadomolybdate-phosphoric acid method [8]. The effect of pH was studied by conducting equilibrium adsorption studies at pH 1.0-10.0 using the optimized contact time. The effect of adsorbent dosage was studied for 0.25-2.5 g adsorbent per 100 mL solutions using the optimized contact time and pH.

### Application of activated maize tassel

The potential of activated maize tassel for phosphate remediation in real environmental samples was assessed by applying the adsorbent to samples taken from three sewage treatment plants in Pretoria sited at Daarsport (domestic and industrial), Medunsa (domestic and hospital) and Sandspruit (domestic).

## III. RESULTS AND DISCUSSION

### BET characterization of the adsorbents

The BET isotherms exhibited a type IV isotherm with a hysteresis loop which indicates the mesoporous nature of the adsorbent. Values for the specific surface area and pore structural properties are given in Table 1.

**Table 1 – BET surface area and pore structural properties of the adsorbents.**

| Adsorbent | $S_{BET}$ ($m^2/g$) | Pore volume ($cm^3/g$) | Pore size (nm) |
|---|---|---|---|
| Raw tassel | 2.54 | 0.006 | 8.61 |
| Activated tassel | 803.8 | 0.447 | 2.22 |

The values of the pore sizes corroborate the isotherm shape indication of mesoporosity, as they all fall in the range 2 to 50 nm. The specific surface area of activated maize tassel powder (804 $m^2/g$) is greater than those reported for some other low cost adsorbents such as cassava peel (270 $m^2/g$) [9].

### Batch adsorption studies

The variation of percent phosphate removal with time for the different adsorbents is illustrated in Figure 1. It can be seen that activated maize tassel removed phosphate at a faster rate and with higher efficiency than raw maize tassel. The uptake of phosphate by activated maize tassel virtually ceased after a contact time of about 70 min, compared to about 90 min for raw maize tassel, with 85% and 66% phosphate removal at equilibrium, respectively. Similar trends using different adsorbents for phosphate removal have been reported [5, 10]. A contact time of 90 minutes was used in further experiments to study the effects of pH and adsorbent dosage, yielding optimised parameters of pH 7 and 1.5 g adsorbent per 100 ml solution.

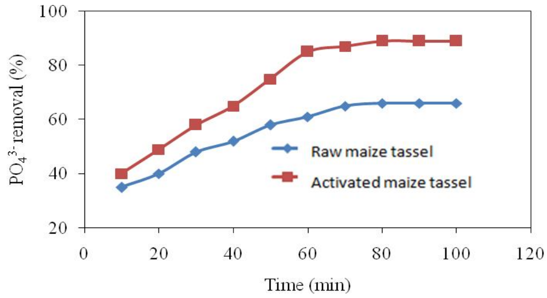


**FIGURE 1- Effect of contact time on the efficiency and rate of phosphate removal (Conditions: 100 mL of 80 mg/L $PO_4^{3-}$; 1.0 g adsorbent; 25°C).**

### Adsorption Isotherms

Adsorption equilibrium is established when the amount of solute being adsorbed onto the adsorbent is equal to the amount being desorbed. An equilibrium adsorption isotherm is predicted when the solid phase concentration is plotted against liquid phase concentration graphically. In the present study, two models, namely Langmuir and Freundlich were used to interpret the equilibrium data [11, 12].

A summary of the parameters for Langmuir isotherm plots are shown in Table 2. Based on the coefficients of determination ($R^2$) it can be concluded that phosphate adsorption followed the Langmuir rather than Freundlich isotherm ($R^2$ values 0.938 and 0.9772 for raw and activated maize tassel, respectively). This suggests that the adsorption occurs on a homogeneous surface by monosorption without significant interaction between adsorbed molecules. The Langmuir constant, $q_{max}$ [11] was 15.31 mg/g for activated maize tassel, which was greater than the $q_{max}$ of 10.46 mg/g for raw maize tassel, as expected.

**TABLE 2 - Langmuir parameters for phosphate adsorption using raw and activated maize tassel.**

| Isotherm | Parameter | Raw tassel | Activated tassel |
|---|---|---|---|
| Langmuir | Equation | y= 0.6109x-0.0956 | y= 1.0788x-0.0653 |
| | $R^2$ | 0.9934 | 0.9976 |
| | $q_{max}$ (mg/g) | 10.46 | 15.31 |

Application of the activated maize tassel for phosphate remediation from environmental wastewaters

Based on the promising results obtained in the batch studies of phosphate removal from aqueous solutions by activated maize tassel, the adsorbent capability was evaluated using real wastewater samples at the optimized conditions. Samples from three selected sewage treatment plants in Northern Pretoria, South Africa were used. The results are shown in Table 3. The levels of phosphate found in the raw sewage samples (18-43 mg/L) were very high, an indication of the vital importance of treatment before discharge into local rivers to prevent possible eutrophication in dams downstream. Evidently the microbiological treatment processes used at these plants are quite efficient for nutrients; bringing phosphate levels in the effluent down to below 5 mg/L. Significantly, batch treatment with activated maize tassel produced an even greater reduction to values below 1 mg/L, which meets widely accepted environmental requirements [2]. Chemical oxygen demand (COD) which is a measure of the amount of decaying matter (usually organics) that consume dissolved oxygen is an important water quality parameter; it was also found to decrease significantly after batch treatment of the sewage samples with chemically activated maize tassel. This is hardly surprising, as the removal of organics such as methylene blue from aqueous medium with activated tassel was recently reported [7].

**TABLE 3 - $PO_4^{3-}$ remediation in sewage samples.**

| Sampling site | Analyte | Raw sewage (mg/L) | After MB treatment[b] (mg/L) | After AMT treatment[c] (mg/L) |
|---|---|---|---|---|
| Medunsa | $PO_4^{3-}$(as P) | 28.0 ± 0.47 | 4.2 ± 0.21 | 0.32 ± 0.03 |
| | COD | 510 ± 28 | *NM* | 110 ± 6.8 |
| Sandspruit | $PO_4^{3-}$(as P) | 18 ± 1.25 | 2.9 ± 0.16 | 0.45 ± 0.044 |
| | COD | 239 ± 14 | *NM* | 86 ± 5.2 |
| Daarsport | $PO_4^{3-}$(as P) | 43 ± 0.82 | 3.7 ± 0.15 | 0.60 ± 0.037 |
| | COD | 602 ± 24 | *NM* | 118 ± 9.2 |

[a]Mean values ± SD (n = 3)
[b]Microbiological treatment by the sewage treatment plants.
[c]Activated maize tassel batch treatment (Conditions: 100 mL sample solution, 1.5 g adsorbent; pH 7; 25°C; 90 min contact time)
NM (Not measured)

## CONCLUSIONS

In this study chemically activated maize tassel was prepared, characterized and used for the removal of phosphate from aqueous solutions. Activation yields a product with higher specific surface area and total pore volume- characteristics of a good candidate for consideration as an adsorbent. Process parameters for optimal rate and efficiency of phosphate removal were established. The experimental adsorption data was best-fitted to the Langmuir isotherm model. The adsorbent was successfully applied to real environmental samples. The results from this study have shown the potential of activated maize tassel to be used as a low-cost and effective biosorbent for the removal of phosphate from environmental wastewaters.

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