UTILISATION OF CHEMICALLY ACTIVATED MAIZE TASSEL FOR REMEDIATION OF EUTROPHIC PHOSPHORUS

[1]NANA M. AGYEI, [2]ADEBAYO M. SHOFOLAHAN, [3]JONATHAN O. OKONKWO

[1,2]Chemistry Department, Sefako Makgatho Health Sciences University, Garankuwa 0208, South Africa.
[3]Environmental Sciences Department, Tshwane University of Technology, Pretoria 0001, South Africa.

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 ^oC. 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.

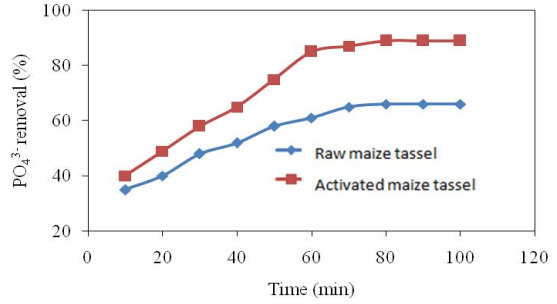


FIGURE 1- Effect of contact time on the efficiency and rate of phosphate removal (Conditions: 100 mL of 80 mg/L PO_4^{3-}; 1.0 g adsorbent; 25°C).

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.

REFERENCES

[1] Xu, K., Deng, T., Liu, J. and Peng, W. (2010) "Study on the phosphate removal from aqueous solution using modified fly ash." Fuel 89.12: 3668-3674.

[2] Eckenfelder, RL. (1980) Principles of Water Quality Management. CBI Publishing Company, Inc, Boston, Massachusetts.

[3] Zhao, Y., Wang, J., Luan, Z., Peng, X., Liang, Z. and Shi, L. (2009) "Removal of phosphate from aqueous solution by red mud using a factorial design." Journal of Hazardous Materials 165.1: 1193-1199.

[4] Wang, Y., Gao, B.Y., Yue, W.W. and Yue, Q.Y. (2007) Adsorption kinetics of nitrate from aqueous solutions onto modified wheat residue. Colloids and Surfaces A: Physicochemical and Engineering Asapects 308.1: 1-5.

[5] Agyei, N.M., Strydom, C.A., and Potgieter, J.H. (2002) The removal of phosphate ions from aqueous solution by fly ash, slag, ordinary Portland cement and related blends. Cement and Concrete Research 32: 1889-1897.

[6] Moyo, M., Chikazaza, L., Nyamunda, B.C. and Guyo, U. (2013) Adsorption batch studies on the removal of Pb(II) using maize tassel based activated carbon. Journal of Chemistry, 2013.5: 1–8.

[7] Olorundare, O.F., Msagati, T.A.M., Krause, R.W.M., Okonkwo,J.O. and Mamba,B.B. (2014) Steam activation, characterisation and adsorption studies of activated carbon from maize tassels. Chemistry and Ecology, 30: 473-490.

[8] Arnold, E. (1985) Phosphorus. In: Standard Methods for the Examination of Water and Wastewater, American Public Health Association.

[9] Rajeshwari, S., Sivakumar, S., Senthilkumar, P. and Subburam, V. (2001) Carbon from cassava peel, an agricultural waste, as an adsorbent in the removal of dyes and metal ions from aqueous solution. Bioresource Technology. 80.3: 233-235.

[10] Agyei, N.M. (2009) The mechanism of phosphate removal from aqueous solution by fly ash and slag. Fresenius Environmental Bulletin 18: 1614-1617.

[11] Langmuir, I. (1916) The constitution and fundamental properties of solids and liquids. Part I: Solids, Journal of the American Chemical Society 38: 2221–2295.

[12] Freundlich, H.M.F. (1907) Over the adsorption in solution, Journal of Physical Chemistry 57: 384–470.

★★★