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Valorization of banana waste by optimizing nitrocellulose production, yield, and solubility via nitrating acid mixtures and reaction time

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ORIGINAL ARTICLE

Abstract

The current research investigated the conversion of banana stem waste into cellulose nitrate, a potential bioplastic precursor. The research is of prime importance in terms of environmental pollution and sustainable development goals. The study aimed to isolate cellulose from banana stems, synthesize nitrocellulose, and assess its stability. Two different methods, that is, Method A, comprising HNO_3 and H_2SO_4, and Method B, comprising HNO_3 and P_2O_5, were applied to synthesize nitrocellulose, each using different acidic mixtures. Method A resulted in high nitrocellulose yield and higher nitrogen content but lower cellulose content. On the other hand, method B yielded nitrocellulose with a lower nitrogen content but higher cellulose content. It was found that composition of nitrating acid mixture, nitrating time, and ratio of nitrating acid–cellulose material influenced the yield and solubility of nitrocellulose. The highest yield of nitrocellulose was obtained using a 60:1 ratio of nitrating acid–cellulose material in method A and a 100:1 ratio of the same in method B after 90-min nitration time. It was also observed that nitrocellulose A was soluble in acetone and pyridine whereas nitrocellulose B was soluble in 1,4-dioxane, esters, and pyridine. Overall, the study demonstrated the feasibility of converting banana stem waste into a bioplastic precursor.

Keywords: agro-waste; banana waste; bioplastic; nitrocellulose; nitrating mixture

Introduction

Since last two decades, there is a dire need of sustainable and renewable resources to be used for in the society as well as industrial production. In recent times, "green polymers" has become a trending topic. Green polymers are produced from sustainable and renewable resources and in the future would be commonly used in industrial processes (Aziz *et al.*, 2024; Shouket *et al.*, 2023). Globally, agricultural waste, because of its biodegradability, is now used as a substitute for petrochemicals. Hence, at present, agricultural waste has become a burning issue (Aziz *et al.,* 2023; Gismatulina *et al.,* 2018). Agro-waste has immense potential for extracting high-value cellulose, especially crop residues rich in their cellulose content. Apart from agri-food waste, exploring

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non-food competing crops on marginal lands offers exciting possibilities for maximizing biomass utilization and creating valuable products (Kopania *et al.,* 2012) and contributes to sustainable agriculture and the environment (Qiu *et al*., 2023). Numerous plants are used for producing cellulose, such as cotton, hemp, wheat straw, corn stalks, pineapple leaves, and even nettle. Also, banana leaves, an unexplored area, have shown similar potential (Kopania *et al.,* 2012).

Cellulose is special because each glucose unit has three hydroxyl groups. This makes cellulose a prime candidate for extensive esterification. In theory, all three hydroxyl groups on each glucose unit can be replaced with nitrate groups, creating a highly nitrated cellulose nitrate (cellulose trinitrate). The degree of nitration significantly affects the properties of cellulose nitrate. Highly nitrated forms (over 12.5% of nitrogen content) are highly inflammable and unstable, making them ideal for propellants such as guncotton. Less nitrated forms are more stable and have applications in films, lacquers, and even early (synthetic) plastic (Alinat *et al.,* 2014; Yi *et al*., 2022).

This research aimed to explore the potential of banana stem waste by extracting cellulose and crafting nitrocellulose from it. Furthermore, the effect of composition and reaction time of nitrating acid on nitrocellulose yield along with solubility of banana stems was also targeted. Hence, the research aimed to transform agro waste into valuable resources. Banana stems offer a sustainable and cost-effective alternative to traditional nitrocellulose feedstocks, eventually promoting circular economy and combating resource depletion. Because nitration affects flammability and solubility, this research focused on finding the optimum level of nitration to produce plant-based nitrocellulose for optimum yield with safety measures and a good source of calcium and potassium (Zhang *et al.*, 2023).

Materials and Methods

Fresh samples of banana pseudo stems were collected from Agricultural Research Farm, Malakhandher, Peshawar, Pakistan. The samples were washed with distilled water to remove impurities, followed by oven-drying at 55°C for 10 h. The samples were further homogenized and sieved with 70-mesh sieve.

Sample preparation

Cellulose extraction

Cellulose extraction was carried out using the protocol followed by Lohmousavi *et al.* (2020) and Sundarraj *et al.* (2018). A mixture of 100-mL (80%) CH_3COOH and 10-mL (70%) HNO_3 was added to 5 g of sample. The mixture was kept on an oil bath at 120°C for 20 min, followed by cooling. Oil bath was used to have temperature higher than 99°C, which is the upper limit of water bath in a biochemical laboratory. The mixture was filtered after addition of 60-mL distilled water. The filtrate was rinsed with ethanol till the removal of acidic residues. The filtrate was oven-dried at 60°C. After acidic hydrolysis of samples, the filtrate was subjected to removal of lignins and hemicellulose by soaking in 4% NaOH solution with continuous stirring with magnetic stirrer at 75 rpm, followed by vacuum filtration. After filtrate was subjected to basic treatment, it was washed with distilled water and dried at 80°C for 5 h. The powder was then bleached with 20% H_2O_2 and stored at 85°C. Finally, the bleached cellulose filtrate was washed for several times with de-ionized water to remove all residues. Hence, the resultant pure filtrate was oven-dried at 50°C for 10 h.

Synthesis of cellulose nitrate via different nitrating mix

HNO_3+H_2SO_4 Method (cellulose nitrate A)

The protocol adopted by Cheung (2014) was followed to prepare cellulose nitrate A. Cellulose sample, 175 g, was added to acidic medium comprising 49-mL HNO_3 and 91-mL H_2SO_4. The reaction was sustained for 2 h in thermostat-fixed ice water at 0°C. White precipitates were simply filtered and washed for several times until neutralized.

HNO_3+P_2O_5 Method (cellulose nitrate B)

Mixture of HNO_3–P_2O_5 was prepared in a ratio of 3:5 (HNO_3:P_2O_5) according to a protocol followed by Cheung (2014). The mixture was initially stirred at 0°C in an ice bath. The agglomerates of polyphosphoric acid were eliminated by filtration; 1.75-g of sample was added to a mixture comprising 100-mL P_2O_5. The mixture was again kept in ice bath at 0°C for 3 h. The reaction was stopped after the appearance of white precipitate, which was filtered and washed for several times until neutralized.

Degree of substitution

Concerning the current research, degree of substitution referred to an average number of hydroxyl (OH) groups in a cellulose molecule that were replaced by nitrate (NO_2) groups:

$$\text{Degree of Substitution (DS)} = \frac{3.6 \times \text{Nitrogen Content (\%)}}{31.11 - \text{Nitrogen Content}}$$

Effect of nitration time on cellulose nitrate yield, solubility, and nitrogen content

In order to find out the effect of time on nitrating ratio and solubility, the procedure adopted by Adekunle (2010) was followed. Nitrating acid–cellulose ratios of 20:1, 40:1, 50:1, 60:1, 80:1, and 100:1 were used at an interval of 30, 60, and 90 min to determine the effect of time on acid mixtures. For determining stability, the nitrated material was repeatedly boiled in water/methanol after each filtration to eliminate adsorbed residues. The resulting solid was rinsed with water, filtered after 10 min, followed by centrifugation at 1,400 rpm. Afterwards, it was boiled for 3 h in refluxing water. Finally, it was rinsed then suction- and oven-dried at 50°C. Standard micro-Kjeldahl technique was followed for determining yield, solubility, and nitrogen content; solubility tests were also performed.

Statistical analysis

The effect of nitrating time on nitrocellulose synthesis was analyzed using one-way ANOVA in SPSS, version 24 (IBM Corporation, Armonk, NY).

Results and Discussions

Isolation of cellulose from banana stem

In order to prepare cellulose nitrate, crude cellulose from banana stem was prepared by chemical hydrolysis. The resultant material was pale yellow in color, which indicated the presence of other lignocelluloses. The material post-acid hydrolysis was treated with alkali and bleaching agent to remove hemicellulose and lignin. The study determined 45.2% of pure cellulose, 26% hemicellulose, and 28.8% lignin from banana stem.

The change in color from pale yellow to cream white indicated the removal of hemicellulose and lignin. Abraham *et al.* (2011) explored the potential of banana stems as an agricultural waste for production of cellulose fiber. The authors investigated the use of banana stems combined with other agricultural residues, such as rice straw (reportedly containing 33% cellulose), soybean hulls (with 43.7% cellulose), and sugarcane bagasse (having 40% cellulose). This approach aligned with the existing literature, suggesting that banana stems have comparatively higher cellulose content.

Production of cellulose nitrate by using combination of nitrating acids

Two nitrating mixtures, HNO_3+H_2SO_4 and HNO3+P_2O_5, were explored in the current study. As per the literature, the potential explosiveness of nitrating mixture was assessed by nitrogen contents (Table 1).

Table 1. Percentage of nitrogen of nitrocellulose A and nitrocellulose B because of different nitrating acid mixtures.

Type	Nitrogen content (%)
Nitrocellulose A	8.64
Nitrocellulose B	5.68

The highest nitrogen (8.64%) was found with HNO_3+ H_2SO_4 mixture whereas HNO_3+ P_2O_5, mixture was found to have low (5.68%) nitrogen. Hence, this suggested a higher potential of H_2SO_4 to nitrate for cellulose, compared to P_2O_5.

Nitrocellulose from both mixtures exhibited varying degree of nitration, which was a measure of enhanced reactivity. Along with nitrogen content, degree of substitution was also determined to choose optimal nitrating agent based on the desired level of nitration. Degree of substitution was determined by the above-mentioned standard equation.

Mattar *et al.* (2020) suggested the effectiveness of H_2SO_4 and P_2O_5 as nitrating agents for cellulose hinges on the degree of substitution. Our findings revealed a low degree of substitution (0.80) for P_2O_5, compared to H_2SO_4 (1.38). At a lower degree of substitution, H_2SO_4 readily substituted hydroxyl groups with nitro groups, while increase in degree of substitution exhibited a contrasting behavior.

Stability of nitrocellulose A and nitrocellulose B

The stability of both nitrocellulose A and nitrocellulose B was followed as per Cheung (2014). Nitrocellulose prepared from both methods exhibited lower nitrogen content (13%), being into nonexplosive category. The findings were in a safe range as higher nitrogen content leads to higher flammability. The resultant nitrocellulose was washed extensively for removal of adsorbed acids from cellulose fibers. Nitrocellulose cannot be stored dry

Table 2. Degree of substitution for synthesized nitrocellulose.

S. No.	Type	Nitrogen content (%)	Degree of substitution (esterification)*
1.	Nitrocellulose A	8.64	1.38
2.	Nitrocellulose B	5.68	0.80

*Degree of substitution is calculated using the equation mentioned in the text.

due to potential deflagration hazards causing rapid burning. Additionally, stabilization of resulting nitrocellulose was accomplished in boiled water to remove completely acid residues. During the stability process, sodium bicarbonate ($NaHCO_3$) was added to adjust pH. It was observed in the current study that addition of $NaHCO_3$ decreased mass by 2.59% in nitrocellulose A and by 3.57% in nitrocellulose B. The pH can efficiently stabilize the nitrocellulose.

Effect of nitrating time on nitrocellulose A and nitrocellulose B

The current study also aimed to determine the effect of nitrating time on yield. It was revealed that nitrating time of 90 min for both nitrocellulose A and nitrocellulose B resulted in the highest yield, compared to nitrating period of 30 and 60 min. This suggested that longer exposure optimized extraction of cellulose nitrate. The retained exposure time impacted the conversion of active sites in cellulose to nitrates. Hence, the dependence of effectiveness of nitrating agent on the accessibility of these sites can be measured. Nitrating mixtures are quite exothermic, enabling cellulose conversion to nitrates at lower temperatures, thereby forming "nitronium" ions, which then react with cellulose. The nitrating time was limited to 90 min, as further exposure could be hazardous. All the findings against different periods of nitrating cellulose are depicted in Table 3.

Effect of nitrocellulose ratios

Effect of different ratios of nitrating acid mixtures and cellulose on nitrocellulose

The current study also determined the yield because of different ratios of HNO_3-H_2SO_4–cellulose, that is, 20:1, 40:1, 50:1, 60:1, 80:1, and 100:1. The results are shown in Figure 2. Maximum yield (91.13) was obtained with HNO_3-H_2SO_4–cellulose ratio of 60:1, while minimum yield (45.26) was obtained with HNO_3-H_2SO_4–cellulose ratio of 40:1. It was evident from the current research that yield increased when subjected to the following order of mixture ratios: 60:1 > 100:1 > 80:1 > 20:1 > 50:1 > 40:1. A significant linear relationship of 70% was

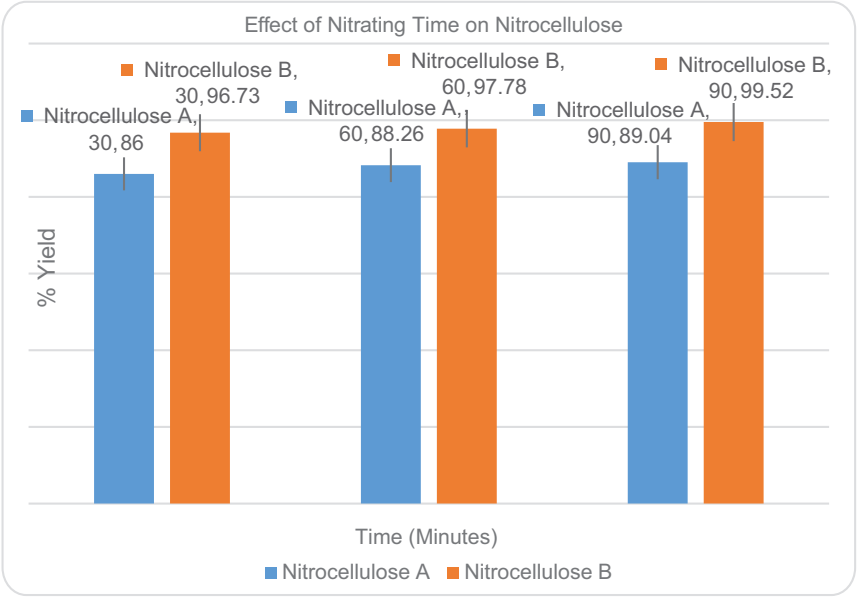

Figure 1. Effect of nitrating time on nitrocellulose A and nitrocellulose B.

Table 3. ANOVA (time × type) for synthesized nitrocellulose.

S. No.	Type	Time (30 min)	Time (60 min)	Time (90 min)	Mean
1.	Type A	86.36^{c}	88.26^{d}	88.71^{d}	87.78^{b}
2.	Type B	96.57^{c}	97.78^{b}	99.40^{a}	97.92^{a}
	Mean	91.47^{c}	93.02^{b}	94.05^{a}	

Superscribed letters (a–e) denote statistically significant differences between groups at $p < 0.05$.

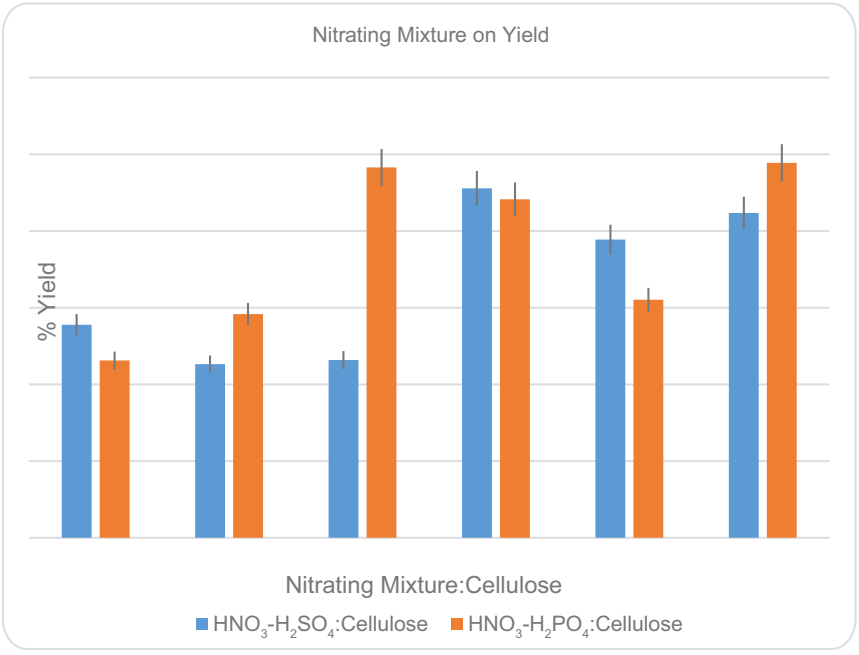

Figure 2. Effect of different ratios of nitrating acid mixture and cellulose on nitrocellulose.

found. Similarly, yield was also determined when exposed to different ratios of nitrating mixture (HNO_3-H_2PO_4–cellulose). The variation ranged from 45.23% to 97.78%. The highest yield (97.78%) was discovered with HNO_3-H_2PO_4–cellulose ratio of 100:1, followed by 96.57% with a nitrating acid mixture and cellulose ratio of 50:1. In contrast, minimum yield (46.23%) was discovered with a nitrating acid mixture and cellulose ratio of 20:1. The following trend with different nitrating acid mixture and cellulose ratios was observed: 100:1 > 50:1 > 60:1 > 80:1 > 40:1 > 20:1. The correlation was found as 60%.

Effect of nitrating acid composition and solubility tests

The results revealed that both synthesized nitrocellulose A and nitrocellulose B were insoluble in solvents such as ethanol and benzene but sparingly soluble in acetone (cold) and 1,4-dioxane (cold). Additionally, these were found soluble in hot ester but sparingly soluble in cold ester. Also, these were found soluble in pyridine.

The current study also determined solubility along with factors affecting the solubility of cellulose nitrate and its potential in industrial application. It was observed that solubility of nitrocellulose directly depended on nitrogen content. Higher the nitrogen content, higher the solubility proportion with selected solvents, such as acetone, esters, pyridine, and 1,4-dioxane. It was also noted that addition of water affected the rate of solubility.

Nitrocellulose was found insoluble in 1,4-dioxane with water but soluble in heated acetone. Similarly, cellulose nitrate was soluble in esters and pyridine but not

Table 4. Solubility test with various solvents.

Composition of nitrating acid (%)			Solubility test of nitrocellulose A and nitrocellulose B in various solvents											
			Acetone		Ethanol		Ester		Benzene		Pyridine		1,4-dioxane	
Nitrocellulose A														
HNO_3 (mL)	H_2SO_4 (mL)	H_2O (mL)	C	H	C	H	C	H	C	H	C	H	C	H
50	40	10	SS	SS	I	I	S	S	I	I	S	S	SS	S
50	50	0	SS	S	I	I	S	S	I	I	S	S	S	S
Nitrocellulose B														
50	40	10	SS	SS	I	I	SS	S	I	I	S	S	SS	S
50	50	0	SS	S	I	I	SS	S	I	I	S	S	I	I

HNO_3 = nitric acid; H_2SO_4 = sulfuric acid; C = cold; H = hot; SS = sparingly soluble; S = soluble; I = insoluble.

in heated acetone with addition of water in nitrating mixture. The findings further confirmed that acetone and esters are suitable storage solvents for cellulose nitrate because of their better solvency, hence could be used in different industries, such as plastics, paints, etc., as reported by Jesuet *et al.* (2019); John *et al.* (2024); Sandewicz (2016); and Tonkinson and Stillman (2002).

Conclusion and Recommendations

The current findings revealed successful extraction and isolation of cellulose from banana stems after removal of impurities, resulting in 45% yield. Additionally, two types of nitrocellulose were prepared with separate nitrating mixtures. Maximum nitrogen content was observed for nitrocellulose A. Maximum yield of nitrocellulose was recorded for nitrocellulose B. Furthermore, nitrocellulose B also exhibited maximum solubility in various solvents along with shorter reaction time.

This research suggests production of nitrocellulose in Pakistan from banana stems, considered as a cheap and abundant source of cellulose. This approach not only offers economic benefits but also manages agricultural waste. The resulting nitrocellulose exhibits promising properties for industrial applications, such as paints, plastics, detergents, and films. Additionally, its potential use in eco-friendly food packaging warrants further exploration. Optimizing the exothermic nitration process and acid regeneration during neutralization through further research could enhance the overall feasibility and sustainability of this method.

Conflict of Interest

The authors declared no conflict of interest.

Author Contributions

Conceptualization, Maria Hassan; methodology, Afia Zia; software, Muhammad Nauman Ahmad; validation, Muhammad Baseer us Salam; formal analysis, Maria Siraj, investigation, Shahida Sabir; resources, Abdulrahman Alshammari.; data curation, Muhammad Arif.; writing—original draft preparation, Tahir Naveed Farooq.; writing—review and editing, Tariq Aziz; visualization, Maria Hassan; Supervision, Afia Zia and Tariq Aziz .; project administration, Abdulrahman Alshammari

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References

Abraham, E., Deepa, B., Pothan, L.A., Jacob, M., Thomas, S., Cvelbar, U., et al. 2011. Extraction of nanocellulose fibrils from lignocellulosic fibres: a novel approach. Carboh Polym. 86(4): 1468–1475. https://doi.org/10.1016/j.carbpol.2011.06.034

Adekunle, I.M. 2010. Production of cellulose nitrate polymer from sawdust. J Chem. 7: 709–716. https://doi.org/10.1155/2010/807980

Alinat, E., Delaunay, N., Costanza, C., Archer, X. and Gareil, P. 2014. Determination of the nitrogen content of nitrocellulose by capillary electrophoresis after alkaline denitration. Talanta. 125: 174–180. https://doi.org/10.1016/j.talanta.2014.02.071

Aziz T, Qadir R, Anwar F, Naz S, Nazir N, Nabi G, et al. 2024. Optimal Enzyme-Assisted Extraction of Phenolics from Leaves of Pongamia pinnata via Response Surface Methodology and Artificial Neural Networking. Appl Biochem Biotechnol. 22, 1–8. https://doi.org/10.1007/s12010-024-04875-w.

Aziz T, Shah Z, Sarwar A, Ullah N, Khan AA, Sameeh MY, et al. 2023. Production of bioethanol from pretreated rice straw, an integrated and mediated upstream fermentation process. Biomass Conv. Bioref. 2023, 1–8. https://doi.org/10.1007/s13399-023-04283-w

Cheung, C. 2014. Studies of the Nitration of Cellulose-Application in New Membrane Materials. Doctoral dissertation, University of British Columbia: Canada. https://doi.org/10.14288/1.0072160

Gismatulina, Y.A., Budaeva, V.V. and Sakovich, G.V. 2018. Nitrocellulose synthesis from miscanthus cellulose. Propellants Explos Pyrotech (PEP). 43(1): 96–100. https://doi.org/10.1002/prep.201700210

Jesuet, M.S.G., Musa, N.M., Idris, N.M., Musa, D.N.S. and Bakansing, S.M. 2019. Properties of nitrocellulose from *Acacia mangium*. J Phy Conf Sr. 1358(1): 012035. IOP Publishing. https://doi.org/10.1088/1742-6596/1358/1/012035

John, J., Archana, K.S., Thomas, A.M., Thomas, R.L., Thomas, J., Thomas, V., et al. 2024. Nitrocellulose unveiled: a brief exploration of recent research progress. Sustain Chem Eng. 5(1): 147–168. https://doi.org/10.37256/sce.5120243950

Kopania, E., Wietecha, J. and Ciechańska, D. 2012. Studies on isolation of cellulose fibres from waste plant biomass. Fibres Text East Eur. 6B(96): 167–172.

Li, K., Fu, S., Zhan, H., Zhan, Y. and Lucia, L. 2010. Analysis of the chemical composition and morphological structure of banana pseudo-stem. BioResources. 5(2): 576–585. https://doi.org/10.15376/BIORES.5.2.576-585

Lohmousavi, S.M., Abad, H.H.S., Noormohammadi, G. and Delkhosh, B. 2020. Synthesis and characterization of a novel controlled release nitrogen-phosphorus fertilizer hybrid nanocomposite based on banana peel cellulose and layered double

hydroxides nanosheets. Arab J Chem. 13(9): 6977–6985. https://doi.org/10.1016/j.arabjc.2020.06.042

Mattar, H., Baz, Z., Saleh, A., Shalaby, A.S., Azzazy, A.E., Salah, H., et al. 2020. Nitrocellulose: structure, synthesis, characterization, and applications. Water Energy Food Environ J. 3: 1–15. https://doi.org/10.18576/wefej/010301

Qiu, S., Yang, H., Zhang, S., Huang, S., Zhao, S., Xu, X., et al. 2023. Carbon storage in an arable soil combining field measurements, aggregate turnover modeling and climate scenarios. Catena. 220: 106708.

Sandewicz, R.W. 2016. Formulation of nail care products. In: Dayan, N. (Ed.) Handbook of Formulating Dermal Applications: A Definitive Practical Guide. Wiley, Hoboken, NJ, pp. 539–588.

Sundarraj, A.A. and Ranganathan, T.V. 2018. A review on cellulose and its utilization from agro-industrial waste. Drug Invent Today. 10(1): 89–94.

Shouket S, Khurshid S, Khan J, Batool R, Sarwar A, Aziz T, et al. 2023. Enhancement of shelf-life of food items via immobilized enzyme nanoparticles on varied supports. A sustainable approach towards food safety and sustainability. Food Res Int. 169:112940. https://doi.org/10.1016/j.foodres.2023.112940.

Tonkinson, J.L. and Stillman, B.A. 2002. Nitrocellulose: a tried and true polymer finds utility as a post-genomic substrate. Front Biosci. 7(3): c1–c12. https://doi.org/10.2741/A755

Yi, J., Li, H., Zhao, Y., Zhang, H. and Liu, M. 2022. Assessing soil water balance to optimize irrigation schedules of flood-irrigated maize fields with different cultivation histories in the arid region. Agric Water Manag. 265: 107543. https://doi.org/10.1016/j.agwat.2022.107543

Zhang, T., Song, B., Han, G., Zhao, H., Hu, Q., Zhao, Y., et al. 2023. Effects of coastal wetland reclamation on soil organic carbon, total nitrogen, and total phosphorus in China: a meta-analysis. Land Degrad Develop. 34(11): 3340–3349. https://doi.org/10.1002/ldr.4687