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Understanding the removal and regeneration potentials of biogenic wastes for toxic metals and organic dyes

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ABSTRACT

This work highlights the removal dynamics of some industrial dyes, such as Congo Red (CR) and Methylene Blue (MB), Cd^{2+} and Pb^{2+} by two low-cost and readily available tree wastes (*Pentaclethra macrophylla* tree bark (PMTB biosorbent) and *Malacantha alnifolia* tree bark (MATB biosorbent). In this research work, experimental variables such as pH, biomass dose, initial solute ion concentration, agitation time and temperature were optimised. The surface textures of PMTB and MATB biosorbents were characterised using pH of Point of Zero Charge (pHPZC), Fourier Transform Infra Red Spectroscopy (FTIR), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) respectively. Proximate Analysis (PA) and Bulk Density (BD) of these biosorbents were also determined. The highest Langmuir saturation monolayer adsorption capacity, $q_{\max_L}$ for the removal of CR by MATB biosorbent was obtained as 800.00 mg/g. The pseudo-second order model provided the best fit for the kinetic data obtained for the removal of CR, MB, Cd^{2+} and Pb^{2+} by PMTB and MATB biosorbents. This implied that chemisorption might be the mechanism of the solute ions–biosorbents interaction in this study. Weber–Morris intraparticle diffusion model showed that intraparticle diffusion was not the only rate limiting step of the adsorption processes. Film/pore diffusion process might have played an important role in the rate limiting step of the adsorption processes. Thermodynamic data indicated that (ΔG°) for the removal of CR, MB, Cd^{2+} and Pb^{2+} onto PMTB and MATB biosorbents were non spontaneous at all temperatures. Also, (ΔH°) and (ΔS°) for the removal of CR, MB, Cd^{2+} and Pb^{2+} onto the biosorbents depicted the adsorption processes being exothermic with decreasing of the chaos.

1. Introduction

The perils of synthetic dyes and toxic metal ions in the ecosystem have risen to an alarming rate. This has stirred a dire consciousness in environmental scientists in the quest for lasting panaceas to these problems [1,2].

Human beings suffer from the adverse effects of synthetic dyes (like Methylene Blue (MB) and Congo Red (CR)) that are contained in polluted water. This leads to the release of teratogens, mutagens and carcinogens in the human system [3–5]. Water bodies suffer from the mass transport of $\leq$ 20% of the dyestuffs, which is approximately $(0.7–2.0) \times 10^5$ tons are released into water bodies yearly [6,7]. Toxic metal ions are also regarded as environmental toxins that find their way into the biota through potable water sources. Toxic metal ion concentrations have been detected at elevated levels in rural areas of the world [8]. Cadmium (Cd) and lead (Pb) are toxic metal ions that pollute natural potable water sources, culminating into dreaded illnesses in human beings such as disruption of protein metabolism, induced sterility, neonatal death, calcium substitute in bones, hypertension, cancerous growth, and accumulation in food chain causes the declination of wildlife and species diversity [9–12]. Heavy metals as pollutants accumulate in the living system or stay in the environment. The fact that toxic metal ions accumulate in living system or stay in the environment has attracted the global attention of researchers to proffer sustainable alternative to reduce their ill-effects [13–15].

The panacea to rescue the environment from these harmful substances led to the utilization of some conventional techniques such as ion exchange, precipitation, reverse osmosis, solvent extraction, solid phase extraction, evaporation, membrane filtration and adsorption [16] (for toxic metals), and sonochemical degradation [17], chemical oxidation, flocculation, photocatalytic decomposition [18] and electro-catalytic degradation [19] (for synthetic dyes).

Biological based materials that comprise the natural biota and reduce the possibilities of environmental interference, which change

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Table 1
Physicochemical properties of PMTB and MATB biosorbents.

	PMTB	CR-loaded PMTB	MB-loaded PMTB	Pb^{2+}-loaded PMTB	Cd^{2+}-loaded PMTB
FTIR (cm^{-1})					
O–H and N–H str.	3383	3411	3417	3412	3409
C–H str.	2925	2925	2930	2925	2925
N–H bend	1618	1622	1622	1622	1622
C=C str.	1450	1450	1449	1451	1450
C–H bend	1349	1319	1334	1370	1338
C–O str.	1233	1236	1237	1233	1234
C–O bend	1033	1035	1033	1033	1032
	MATB	CR-loaded MATB	MB-loaded MATB	Pb^{2+}-loaded MATB	Cd^{2+}-loaded MATB
FTIR (cm^{-1})					
O–H and N–H str.	3427	3428	3434	3429	3453
C–H str.	2927	2926	2925	2926	2930
N–H bend	1626	1627	1627	1627	1627
C=C str.	1422	1457	1462	1424	1458
C–H bend	1318	1318	1318	1318	1318
C–O str.	1250	1245	1254	1263	1265
C–O bend	1035	1036	1035	1035	1036

the balance of the ecosystem have found application in the remediation of the environment from these harmful substances [15]. According to the treatises of various researchers, some agricultural/biological wastes that have been used to adsorb Cd and Pb are castor seed hull [20], walnut tree sawdust [21], rice straw [22], *Nauclea diderrichii* seed biomass [23], *Zea mays* stalk sponge [24], soybean hull [25], palm shell [26], peanut husk [27]. Also, adsorbents of biological origin that have been used to adsorb MB and CR are pine cone [28], peanut husk [29], poplar leaf [30], macauba palm *Acrocomia aculeata*) cake [31], waste red mud [32], waste orange peel [33], palm kernel seed coat [34], gastropod (*Achatina achatina*) shell-derived $Ca(OH)_2$ and $CaCO_3$ [35] among others.

P. macrophylla Benth., the oil bean tree, is the sole member of the genus occurring naturally in the humid lowlands of West Africa. It is a leguminous tree (family *Leguminosae*, sub-family *Mimosoideae*). A related species known as *Pentaclethra macroloba* (Wild) is indigenous to South America. The diverse native *Pentaclethra* species enhances agroforestry development in the humid tropics [36]. This species is relatively fast-growing and seedlings will achieve a height of 1.5 m in the first year on good sites. *P. macrophylla* grows from Senegal to Angola and also to the Islands of Principe and Sao Tome. It is endemic to the humid and some parts of the sub-humid zones of West Africa. It does not occur in the highlands although, growth can be good where rainfall is adequate and temperatures are never $<18\ ^{\circ}C$. After 2 years of growth in the forest, trees become relatively fire resistant and resprout readily when lopped [36]. The natural distribution of *P. macrophylla* suggests that it is endemic to relatively acid soils, though will tolerate water logging in the low altitudinal river regions of South Eastern Nigeria, Togo and Cameroon [36]. Nutritive oil is extracted from *P. macrophylla* pods and thus constitutes a colossal amount of bark wastes. Moreover, the bark of *P. macrophylla* has no medicinal or nutritive importance and it is economically valueless. These reasons informed our choice of exploring this waste as a biosorbent for this research [36].

M. alnifolia is from the family; *sapotaceae*, genus; *malacantha* is a perennial plant commonly found in the tropical rain forest especially Ghana, Togo and Nigeria. The leaves are tomentose becoming more or less glabrescent obviate elliptic, up to 20–25 cm long, 6–12 cm broad with 15–120 pairs of very prominent lateral nerves. The flowers are sessile, clustered with light brown rusty calyx. It is called “Akala” by Yoruba natives of South Western Nigeria [37]. The phytochemical, haematological and toxicological properties of the methanolic stem extract investigated on rats were found to contain some antioxidants such as flavonoids and saponins. The methanolic stem extract is also used to treat diarrhoea and stomach ache in traditional folk medicine. The cotyledons from the seeds are used in the treatment of vaginal and dermatological infections in South Western Nigeria [37]. A large amount of *M. alnifolia* tree bark heaps into obnoxious waste has no nutritive importance and it is economically valueless. On this ground, this biosorbent was chosen for this research. Some of the biomasses used by researchers in literature are not locally available in abundant amounts and easily sourced. But PMTB and MATB biosorbents are locally available, relatively abundant and easily sourced. Hence, this work is aimed at the removal of pollutants from potable water using PMTB and MATB biosorbents.

To the best of the authors’ knowledge, these wastes (*P. macrophylla* tree bark (PMTB biosorbent) and *M. alnifolia* tree bark (MATB biosorbent)) are used as new class of biosorbents, adding to the literature of biomasses for the sequestration of Cd, Pb, MB and CR respectively.

2. Materials and methods

2.1. Preparation of PMTB and MATB biosorbents

The PMTB biosorbent was obtained from the University of Ibadan Botanical Garden, Ibadan (7° 23′ 16" North, 3° 53′ 47" East), Nigeria. It was air dried for 4 weeks and later oven dried for 22 h at 70 °C. The dried bark was cut into small pieces and pulverised. Further drying was carried out for 6 h. The pulverised PMTB biosorbent was sieved to 425 μm and used for various experiments. Also, The MATB biosorbent was obtained from the University of Ibadan Botanical Garden, Ibadan (7° 23′ 16" North, 3° 53′ 47" East), Nigeria. It was air dried for 4 weeks and later oven dried for 72 h at 70 °C. The dried bark was cut into small pieces and pulverised. The pulverised MATB biosorbent was also sieved to 425 μm and used for various experiments.

2.2. Surface textural characterisation of PMTB and MATB biosorbents

2.2.1. pH of Point of Zero Charge (pHPZC), Fourier Transform Infra Red Spectroscopy (FTIR), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM)

The FTIR analyses of the native, and toxic metals/dyes loaded PMTB and MATB biosorbents were carried out by Perkin Elmer FT-IR Spectrophotometer (Spectrum Version 2) at the scanning