LATERITE GRAINS AS A LOW-COST ADSORBENT TO TREAT HEAVY METAL-CONTAMINATED WATER: A REVIEW

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ABSTRACT: Heavy metal contamination of water sources is an alarming issue across the globe. It may cause several health problems in humans in addition to its damage to aquatic organisms and its adverse effects on the environment. Among the wastewater treatment techniques of heavy metals, adsorption is much favored due to its cost-effectiveness and easy availability, especially in developing countries in tropical and semi-tropical climate regions. Moreover, natural geo-adsorbents like laterite and its crushed grains can be adopted as an attractive alternative adsorbent in floatation and filtration water treatment systems. In this review, the application of natural and pre-treated laterite grains as a low-cost adsorbent was examined based on selected journal articles published during 1990–2020. This paper summarizes basic physical and chemical properties including surface charge and element compositions of tested samples, batch adsorption results including initial conditions, isotherm and kinetic models, and adsorption and thermodynamic parameters such as the maximum adsorption capacity, removal percentage, and Gibbs free energy that categorize the natural and pre-treated laterite grains. In addition, the results of some previous studies of column experiments and desorption/regeneration of adsorbed heavy metals are described together with prospects for future studies and the applicability of laterite in wastewater treatment for heavy metal remediation.

Keywords: Laterite, Heavy Metals, Adsorbent, Adsorption, Wastewater Treatment

1. INTRODUCTION

Water is vital for sustainable development, and good quality water is essential for socio-economic development, healthy ecosystems, and human health [1-3]. Among contaminated waters, surface, and groundwater rich in heavy metals and heavily metal-contaminated wastewater from various industries have serious negative impacts on the environment and human health; in particular, water polluted with heavy metals triggers several diseases and disorders in living organisms and degrades biodiversity [4,5]. Many reports have pointed out that many developing countries, including India, Vietnam, Sri Lanka, are severely affected by these toxic elements and face lethal threats [6,7].

Because a large global population faces the consumption of unsafe polluted water, effective treatment technologies are urgently required to treat it. Many physical and chemical remediation technologies, such as membrane filtration, reverse osmosis, precipitation, ion exchange, coagulation flocculation, electrochemical processes, and conventional oxidation, and electroflotation, therefore, have been implemented over the last few decades [8-12]. Among them, adsorption technology attracts the most attention because of its simple, cost-effective, efficient, and ease of operation conditions [13-15]. Moreover, natural, and locally easily available adsorbents to treat heavy metals in wastewater have attracted much

attention compared to other commercially available adsorbents in developing countries due to their low cost and user-friendliness [16]. Among natural and locally easily available adsorbents, many researchers have paid attention to laterite rock and soil in most developing countries.



Fig.1 Laterite block (Thach That district, Hanoi, Vietnam), and crushed sieved grains

Laterite (Fig. 1) is widely distributed in tropical and semi-tropical climates in the world [17-20] and has a wide variety of (pH-dependent) surface charges due to the presence of metal oxides and hydroxides (resulting in a rusty red color) [21,22]. These oxides and hydroxides play a vital role in the adsorption of toxic elements. Especially, active hydroxides (-OH2+) on the surface under acidic conditions have a strong association with anionic ions like As, Cr, and phosphate in water (see Table 2). Laterite is normally formed by an intensive and prolonged weathering of the underlying parent rock. Laterite is a versatile building material with unique characteristics such as good aesthetics, ease of cutting, and hardening with age [20,23,24]. Laterite is abundant in Central Vietnam where it is used as a construction and building material [23]. Thus, laterite waste can be considered a construction material after the demolishing of buildings. Moreover, it has been reported that scrap laterite during excavation reaches 25%-30% in the Konkan region of Maharashtra, India [17].

2. RESEARCH SIGNIFICANCE

Laterite is cheaper and widely available in most of the regions in tropical and subtropical countries. At present, many researchers focused on heavy metal adsorption onto laterite. In this regard, this review summarizes past studies of laterite as an adsorbent and aims to characterize its physiochemical properties of laterite and examine its capacity to absorb and remove heavy metals in water. Based on the review, some prospects for further study and improvement of wastewater treatment using laterite are discussed.

3. METHODOLOGIES

A data review was done using three main keywords: i) laterite, ii) adsorption and iii) wastewater. Several wastewater types, such as greywater, industrial wastewater, and contaminated groundwater, were considered. Accordingly, a total of >30 papers published in the Web of ScienceTM (Clarivate Analytics) during 1990–2020 and other international journals were selected. Summarization and comparison of key findings on basic physicochemical properties of tested laterite, experimental conditions for equilibrium, maximum adsorption capacity, other tested experiments, and pretreatment methods for treated laterite were done after a thorough review.

4. RESULTS AND DISCUSSION

4.1 Physico-Chemical properties

Based on past studies, three types of

pretreatments have been adopted for preparing the laterite adsorbents: i) crushed and sieved grains dried at a temperature of $\leq 110^{\circ}$ C (hereafter, non-treated laterite), ii) crushed, and sieved grains heated at a temperature of $\geq 550^{\circ}$ C (hereafter, thermally treated laterite), and iii) crushed and sieved grains treated with acid solutions or surface syncretization of tetravalent ions (hereafter, chemically treated laterite). According to these categories, Physico-chemical and mineralogical properties are summarized in Table 1.

The grain size tested for treating heavy metals was generally < 2 mm. In many studies, specific surface area (SSA) and pore volume (VT) were measured by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJT) methods [25] to characterize the pores of tested laterite grains. Both SSA and VT varied widely depending on the source region/country. SSA ranged from 11 to 112 m²/g, and VT ranged from 0.025 to 0.55 cm³/g. The measured SSA values of laterite grains were similar to those of kaolinite [26] and other porous grains such as autoclaved aerated concrete grains [27] and crushed waste clay brick [28]. The characteristics of surface charges of grains were assessed mostly by measuring the zero point of charge (ZPC). ZPC values ranged mostly from 6 to 7. On the other hand, some studies showed ZPC values lower than 4 [41,51–53], which are similar to those of Japanese Andisols (rich in variable charges) [56].

As shown in Table 1, either energy dispersive X-ray fluorescence analysis (EDX; fundamental parameter method) [e.g., 57] or energy-dispersive X-ray spectroscopy (EDS) analysis was used to characterize the metal/hydroxides and element composition of tested samples in the previous studies. All tested laterites were rich in Fe, and Al as well as Si, and the % of Fe exceeded 40% [32,36,42,43,50] and the % of Al exceeded 15% [29,35,36,45,50] for some laterite samples.

4.2 Adsorption Characteristics of Heavy Metals in Water onto Laterite Grains

The adsorption properties of laterite grains are normally investigated by using a batch adsorption test [e.g., 58]. The adsorption studies and measured isotherm parameters are summarized in Table 2. The target metals were mostly chemical species that became negatively charged ions in water (i.e., anions) such as As(III), As(V), PO₄(III), and F(I). The initial pH (pH_i) of the heavy metal solution was set to around neutral (~7), but many studies also examined the effect of the pH of the solution on the adsorption capacity because the surface charges of laterite grains are rich in variable pH-dependent charges [18,19,30–33,36,37,40,43,46,47,50,54,55]. As shown in Table 2, S:L [the ratio of adsorbent (g) to the heavy metal solution (mL)] varied greatly among studies, and the values ranged from 1:2000 (small amount of adsorbent) to 1:10 (a large amount of adsorbent). The target concentration of a heavy metal solution (C) can be divided into low and high depending on the target heavy metals in water: i.e., a low concentration with < 5 mg/L for As and PO₄(III), and F(I), and a high concentration with 50-600 mg/L for Cr(VI) and Pb(II), indicating that the former mainly target the treatment of heavy metals in surface and groundwater and the latter targets heavy metals in industrial wastewater.

Agitation conditions of batch adsorption tests varied. Agitation (shaking time) of 24 hours at rpm of 150 or 300 under a temperature between 25–30°C was especially common, but some researchers applied a shorter agitation time of less than 4 h. The measured adsorption isotherms were commonly fitted to Langmuir [59] and Freundlich models [60]. The isotherm model underlined in Table 2 gave the best fit among tested isotherm models, indicating that the Langmuir model (L in the Table) best characterized the adsorption isotherm in many studies. In addition to isotherm studies, kinetics was also investigated in many studies. The best fit kinetic model for the adsorption process was different among of tested studies, but the pseudofirst-order model (FO in the table) was likely to perform better than others.

From batch adsorption tests, the two parameters of removal % (R) and maximum adsorption capacity (Q_m in mg/g) can be calculated based on the Langmuir model. The R values for target heavy metals mostly exceeded 90% for tested samples. For both "natural laterite" and "thermal-treated laterite," the Q_m values of As(III) and As(V) ranged from 0.1 to 0.9 and those of F(I) became 0.48 and 0.85. In particular, very high Q_m values of 7.25 and 8.38 have been reported for Cr(II) and Sr(II) [30]. Experimental conditions such as L/S, initial C of heavy metals, and pH summarized in Table 2 are different; however, it can be understood that anions have a high affinity to laterite grains. Except for [34], the Q_m values of "chemically treated laterite" were much higher than those of "natural laterite" and "thermally treated laterite", showing that the surface alteration functioned well to improve the adsorption capacity.

The adsorption mechanism is of utmost importance. The main adsorption mechanism proposed in the previous studies was surface complexation (SC) and chemical bonding mechanisms including chemisorption (CS) and inner sphere sorption (IS). This suggests that the adsorbed ions strongly bound onto the laterite grain surface. In addition, both the Gibbs free energy (Δ G) and entropy (Δ H) of tested samples became negative (-), assisting the high affinity of target heavy metals, i.e., spontaneous and favorable adsorption occurred in the adsorption process.

4.3 Column Experiments to Characterize the Adsorption of Heavy Metals in Water onto Laterite Grains

Batch adsorption experiments reveal the adsorption behavior under full contact conditions. In practical applications such as fixed-bed filtration, constructed wetland, and embedded permeable reactive barrier systems, however, the target heavy metals cannot access the full surface area of grains (i.e., full sorption site of adsorbents) under flowing water conditions. Thus, the adsorption capacity of target heavy metals would be reduced. Normally, the adsorption capacity can be examined using column and/or tank experiments in the laboratory and field. The assessment of heavy metal adsorption capacity of laterite under flowing water conditions, however, is still limited compared to those revealed tests by the batch adsorption [18,31,42,46,48,51,54,55]. As shown in Tables 1 and 2, the material properties and adsorption capacity under batch conditions vary depending on the sampling sites of tested laterite. Further studies are needed to determine key parameters that control the heavy metal adsorption capacity of laterite such as Q_m and b in the Langmuir model under flowing water conditions, fully considering the site-specific characteristics of tested laterite materials.

4.4 Desorption/Regeneration of Adsorbed Heavy Metals, and Other Experiments

Desorption/regeneration of adsorbed heavy metals is necessary to treat worn-out adsorbents with the end of service in the filtration system. Without treating the materials that adsorbed heavy metals, those adsorbents become hazardous and toxic solid waste [27]. Nguyen et al., for example, tested deionized water, 0.5 M NaOH, 0.5 M HCl, 0.5 M NaCl, and 5% EDTA to investigate the desorption/regeneration of adsorbed As(III) and As(V) onto tested laterite grains [18]. Hue and Tung investigated the desorption/regeneration of adsorbed PO₄(III), and F(I) [55]. Both studies showed that an alkaline solution was effective to remove the strong-bonded heavy metals from the laterite adsorbents. Nguyen et al. show that laterite regeneration is easier and cheaper [29]. Moreover, the adsorption of heavy metals onto laterite grains is affected by many factors such as the presence of competitive ions and other organic and inorganic compounds in water. Nguyen et al., examined the effects of co-existing anions on As(III) and As(V) adsorption and showed that the co-existing anions such as HPO₄(II), SiO₃(I), and CO₃(II) hampered greatly the adsorption of target metals [18]. As well, many factors (L:S, pH_i, temperature, etc.) affect the heavy metal adsorption onto laterite (see Table 2).

Table 1 Physico-chemical properties of laterite samples

	_	~	~		~~ .	* *		700	and a		Metal oxid	les		Element		
	Parameters	Grain size	G_s	WAD	SSA	V_{T}	pН	ZPC	CEC	SiO ₂	Fe ₂ O ₃	Al_2O_3	Si	Fe	Al	Ref.
		mm		%	m²/g	cm ³ /g			meq/kg		%			%		
Natu	ral laterite															
1	Thach That district, Hanoi, Vietnam (Dried at 85°C for 24 h)	0.5 – 1	*	*	155	0.55	*	*	*	14.0	48.7	18.2	*	*	*	[18]
2	Lamdong province, Vietnam (Dried at 105°C for 24 h)	0.45 – 2	*	0.43	11.0	*	*	6.69	*	*	*	*	34.3	7.8	19.9	[29]
3	ChenZhou, Hunam province, China (Dried at 55°C for 48 h)	< 0.106	2.65	*	48.5	*	*	*	250	*	*	*	19.4	7.0	14.5	[30]
4	Abengourou, Côte d'Ivoire (Dried at 70°C for 24 h)	1 - 2	*	*	37.6	*	*	*	*	50.3	24.5	14.0	*	*	*	[31]
5	Kg. Tom province, Cambodia (Dried at 50°C)	0.6 - 1.0	*	*	104	0.083	*	*	*	*	*	*	2.45	37.3	1.25	[32]
6	Misiones province, Argentina (Dried at room temperature)	< 2	*	*	42.5	0.14	5.7	7.2	203	55	16.0	22.4		*	*	[33]
7	Burdwan district, West Bengal, India (dried at 105°C for 24 h)	1 - 1.7	*	*	31.6	0.02	*	*	*	*	*	*	*	*	*	[34]
8	*	0.45 - 2	*	0.43	11.0	0.01	*	7.97	*	*	*	*	34.3	7.8	19.9	[35]
9	Sinematialy, Côte d'Ivoire	< 0.25	*	*	34.1	*	*	*	377	*	*	*	20.2	45.1	17.9	[36]
10	Burdwan district, West Bengal, India (dried at 110°C)	0.6 - 0.85	*	*	23.0	0.011	*	*	*	*	*	*	*	*	*	[37]
11	Skudai, Johor state, Malaysia (Dried at 103°C for 24 h)	1.18 - 2.13	*	*	112	*	*	*	*	6.7	83.6	8.3	*	*	*	[38]
12	Kurumbukari, Madang Province, Papua New Guinea	_	*	*	81.2	*	*	*	*	*	91°)	*	*	*	*	[39]
13	South-Western part, Sri Lanka	< 0.63	*	*	24	*	*	*	*	21.1	40.9	29.2	*	*	*	[40]
14	Mount Lofty Ranges, Australia Kangaroo Island, Australia (Dried at 104°C)	0.053 – 0.212	*	*	*	*	*	3.47 ^{d)} 6.05 ^{d)}	*	36.6 11.3	9.2 2.5	24.3 69.6	*	*	*	[41]
15	Misiones province, Argentina	-	*	*	*	*	4.46	*	183	*	*	*	*	*	*	[19]
16	Midnapore district, West Bengal, India	0.3 - 0.6	*	*	17.5	0.02	6.65	7.49	*	*	*	*	32.4	49	14.4	[42]
17	Sukinda, Odisha province, India	< 0.1	*	*	74.7 68.4			6.95 6.70	*	*	*	*	*	46.3 28.6	*	[43]
18	Munbai, India	< 2	*	*	28.8	0.025	6.5	*	389	37.0	16.3	12.3	*	*	*	[44]

Table 1 Cont.

Parameters		Grain size	Gs		SSA	VT	pН	ZPC	CEC		Metal oxid	des	Element			Ref.
	Parameters	Grain size	U _s	W _{AD}	35A	V T	рп	ZPC	CEU	SiO_2	Fe_2O_3	Al_2O_3	Si	Fe	Al	Kel.
		Mm		%	m^2/g	cm ³ /g					%			%		
19	Toayuan Country, Taiwan	< 0.074	*	*	32.3	*	*	*	143	*	*	*	20.8	14.1	15.4	[45]
20	Midnapore district, West Bengal, India	$0.165 - 0.385^{\ e)}$	*	*	18.6	*	*	7.49	*	28.7	47.3	21.1	*	*	*	[46]
21	Prestea, Ghana	< 0.063	*	*	32	*	8.6 ^{g)}	*	*	12.5	64.7	13.7	*	*	*	[47]
22	Midnapore district, West Bengal, India	0.164 ^{e)}	*	*	15.4	0.013	*	6.96	*	*	*	*	35.0	52.1	8.6	[16,48,49]
23	Midnapore district, West Bengal, India	$0.165 - 0.385^{\ e)}$	2.46	*	18.1	*	6.7	7.49	*	*	*	*	39.3	45.6	14.8	[50]
24	Bankura district, West Bengal, India	$\begin{array}{c} 0.25-0.5 \\ 0.25-1.5 \\ ^{\text{h})} \end{array}$	1.79	1.12	13.0	*	*	3.98	*	72.9	3.7	14.5	*	*	*	[51,52,53]
Ther	mal treated laterite															
25	Surathkal, India (Heated at 700°C for 2 h)	< 0.425	*	4.2	*	*	*	5.42	*	*	37.9	*	48.7	37.9	0.99	[54]
26	Kg. Tom province, Cambodia (Heated at 550°C for 1 h)	0.6 - 1.0	*	*	110	0.089	*	*	*	*	*	*	2.47	49.1	2.16	[32]
Cher	nical treated laterite															
27	Thach That district, Hanoi, Vietnam (M ⁴⁺ - doped)	0.1 - 0.5	*	*	*	*	*	*	*	*	20.5	13.8	*	*	*	[55]
28	Burdwan district, West Bengal, India (Treated with 2 N HCl)	1 - 1.7	*	*	40.6	0.04	*	*	*	*	*	*	*	*	*	[34]
29	Midnapore district, West Bengal, India (Treated with 2 N HCl at ~ 70 °C)	0.3 - 0.6	*	*	181.5	0.35	7.2	7.5	*	*	*	*	30.7	51	12.5	[42]

* Data not available. Gs: Specific gravity; wAD: air-dried water content; SSA: Specific surface area; VT; Pore volume; ZPC: Zero point charge; CEC: Cation exchangeable capacity at natural pH

^{a)} pH measured at $L/S = 2\sim5$ and ZPC measured at $L/S = \sim25-50$ using distilled water; ^{b)} CEC measured at initial pH= $\sim6-9$; ^{c)} 91% of Goethite (FeOOH); ^{d)} Isoelectric point (ISP); ^{e)} Five-grain sizes with mean sizes of 0.385, 0.324, 0.273, 0.215, and 0.165 mm were used; ^{f)} Mean grain size, g)Point of zero net charges (PZNC); ^{h)} Four-grain sizes, 1.0–1.5, 0.75–1.0, 0.5–0.75, 0.25–0.5 mm, were used; ⁱ⁾ BET surface area and VT were measured by BJH adsorption.

Table 2 Summary of adsorption studies and measured isotherm parameters

Adsorbent		Polluta	Initial condition			Agita	tion cond	ition	Ado	opted model	Ad	sorption parameters	Mecha	Thermodyn	
		nt	S:L	C (mg/L)	$p\mathrm{H}_{\mathrm{i}}$	rnm		Temp. (°C)	Isotherm	Kinetic	R Q _{max} (%) (mg/g)		nism	amics	Ref.
Natu	ral laterite														
1	Thach That district, Hanoi, Vietnam (Dried at 85°C for 24 h)	As(III), As(V)	7.5:1000	0.1-25	7	24	160	10,30,5 0	<u>L</u> , F, RP	FO, <u>SO</u> , E	*	As(III): 0.41 (10°C) 0.51 (30°C) 0.60 (50°C) As(V): 0.51 (10°C) 0.58 (30°C) 0.64 (50°C)	SC	(+)ΔH, (+)ΔS, (-)ΔG	[18]
2	ChenZhou, Hunam province, China (Dried at 55°C for 48 h)	Cr(VI) Sr(II)	1:100	50-600	7	1, 1.5	*	25	L, F	FO, SO	*	Cr(VI): 7.25 Sr(II): 8.35	IE, SC	(+)ΔH, (+)ΔS, (-)ΔG	[30]
3	Abengourou, Côte d'Ivoire (Dried at 70°C for 24 h)	PO ₄ (III)	8:1000	5-250	6.5-7	24	300	*	<u>L, F</u>	FO, SO	*	8.3	*	*	[31]
4	Kg. Tom province, Cambodia (Dried at 50°C)	As(III)	5:1000	0.5- 1.25	7	10	150	25	<u>L, F</u>	*	*	0.1	*	*	[32]
5	Misiones province, Argentina (Dried at room temp., 24 h)	F(I)	4:1000	1-50	8	1	300	23	<u>L, F</u> , DA	FO, SO	*	0.48	PS	*	[33]
6	Burdwan district, West Bengal, India (Dried at 105°C for 24 h)	As	1:10	1	6	5	150	30	*	*	*	As: 0.006 F(I): 0.21	*	*	[34]
7	Burdwan district, West Bengal, India	Pb(II) Cr(VI)	1:100 1:100	5-20 5-20	6 6	4	150 150	32 32	<u>L</u> , F <u>L</u> , F	FO, <u>SO, MW, E</u> FO, <u>SO, MW, E</u>	95 74	2.95 *	* IE	*	[37]
8	(Dried at 110°C) South-western part, Sri Lanka	Ni(II)	5:1000	*	7	24	*	25	<u>L,</u> F, RP, H	*	*	*	SC	(-)ΔG	[40]
9	Misiones province, Argentina	As	1:10	0.5, 1, 2	4.5, 5.9, 8.6	0.17	*	*	L, F	*	99	*	*	*	[19]
10	Midnapore district, West Bengal, India	As(III), As(V)	1:2000	0.2-20	7	24	150	32	<u>L</u> , F	*	*	As(III): 0.17 As(V): 0.31	*	*	[42]
11	Sukinda, Odisha province, India	Pb(II)	1:500	50-500	5.23	1	*	42	<u>L</u> , F	<u>FO</u> , SO	*	NL:33,NH:50.25	*	(+)ΔH,(+)ΔS, (-)ΔG	[43]

Table 2 Cont.

Adsorbent		Polluta	Init	Initial condition		Agitation condition			Adopted	l model	Adsor	ption parameters		Thermo-	
		nt	S:L	C (mg/L)	pH_{i}	Time (hour)	rpm	Temp. (°C)	Isotherm	Kinetic	R (%)	Q _{max} (mg/g)	Mechanism	dynamics	Ref.
				(IIIg/L)		(liour)		(0)			(70)	0.569 (C= 5-20)			-
12	Midnapore district, West Bengal, India	As(V)	1:50	0.2-20	5.5	24	150	32, 29, 15	<u>L</u> , F	<u>FO</u> , SO	*	mg/g) 0.238 (C= 0.5-5	CS	(+)ΔH, (+)ΔS, (-)ΔG	[46]
13	Prestea, Ghana	As(III), As(V)	1:200	0.1-2	7	As(III): 2 As (V): 1	*	22	L, <u>F</u>	LF	*	mg/g) As(III): 0.909 As (V): 0.714	As(III): IS As(V): OS	(+)ΔH, (+)ΔS, (-)ΔG	[47]
14	Midnapore district, West Bengal, India	As	1:50	-	7.2	0.5	170	15, 29, 42	<u>L</u> , F, DR	<u>FO</u> , SO	98	0.18	FD	(+)ΔH, (+)ΔS, (-)ΔG	[48]
15	Midnapore district, West Bengal, India	As(III)	1:50	0.3-5	7.2	16	150	15, 29, 42	<u>L</u> , F, DR	LF	94	0.15 (15°C) 0.17 (29°C) 0.21 (42°C)	LE, IE	(+)ΔH, (+)ΔS, (-)ΔG	[50]
16	Bankura district, West Bengal, India	F(I)	1:1000	10-50	6.8	3.25	400	30	<u>L</u> , F	*	*	0.85	*	(+)ΔH, (+)ΔS, (-)ΔG	[51]
							Therma	l treated late	rite						
17	Surathkal, India (Heated at 700°C for 2 h)	PO ₄ (III) F(I)	*	5-30	*	*	220	20, 30	LI, L, F	*	*	0.69	*	*	[54]
18	Kg. Tom province, Cambodia (Heated at 550°C for 1 h)	As(III)	5:1000	0.5- 1.75	6	10	250	30	L, F	FO, SO	*	0.16	CS	(+)ΔH, (+)ΔS, (-)ΔG	[32]
							Chemica	al treated late	erite						
19	Thach That district, Hanoi, Vietnam (M ⁴⁺ -doped)	PO ₄ (III) F(I)	1:100	*	6	3	*	20, 30, 40	<u>L</u> , F	<u>FO</u> , SO	*	PO ₄ (III): 31.25 F(I): 10.99	*	*	[55]
20	Burdwan district, West Bengal, India (treated with 2 N HCl)	As F(I)	1:10	1	6	5	150	30	*	*	*	As: 0.009 F(I): 0.85	*	*	[34]
21	Midnapore district, West Bengal, India (treated with 2 N HCl at ~70°C)	As(III), As(V)	1:2000	0.2-20	7	24	150	32	<u>L</u> , F	FO, SO	*	As (III): 8 ± 1.4 As(V): 24.8 ± 3.9	*	*	[42]

*Data not available. L: Langmuir; F: Freundlich; DR: Dubinin-Radushkevic; LI: Linear model; DA: Dubinin-Ataskhov; RP-Redlich-Peterson; H: Hill; FO: Pseudo first order; SO: Pseudo second-order; E: Elovich; ID: intra-particle diffusion; MW: Morris-Weber model; LF: Lagergren first-order rate model; SC: Surface complexation; IE: Ion exchange; CS: Chemisorption; PS: Physical sorption; IS: Inner sphere sorption; OS: Outer sphere sorption; LE: Ligand exchange; Δ H: enthalpy; Δ S: entropy; Δ G: Gibbs free energy; (+): Positive energy; (-): Negative energy; NH: High Iron content, NL: Low Iron content

5. CONCLUSIONS

Recent studies on the applicability of laterite as an effective adsorbent in the removal of heavy metals from wastewater were reviewed in this paper. According to most of the literature, many developing countries in Asia have paid attention to laterite as a low-cost and easily available adsorbent to remove heavy metals from wastewater. The physicochemical properties of laterite tested in previous studies such as specific surface area, point of zero charges, and percent of metal oxides and hydroxides varied widely depending on the origin of the laterite. Many studies adopted a batch experiment and determined the effect of pH on the adsorption capacity due to the existence of the pHdependent surface charge of laterite. From the viewpoint of reported adsorption capacities, both non-treated (natural) and pre-treated laterite are effective to treat heavy metals existing as anions in wastewater. But still limited studies for investigating the heavy metal adsorption capacity under the water flowing condition. In addition, further studies with a well-conceived experimental plan are needed to assess the characteristics and mechanisms of adsorption of heavy metals onto laterite to develop a proper design and conditions of wastewater treatment systems utilizing laterite.

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7. REFERENCES

- [1] UNDP SGDs Goals 6, https://www.un.org/sustainabledevelopment/wa ter-and-sanitation/
- [2] Tyagi S., Sharma B., Singh P., and Dobhal R., Water quality assessment in terms of water quality index. American Journal of Water Resources, Vol. 1, 2013, pp. 34-38.
- [3] Nikagolla C., Meredith K.T., Dawes L.A., Banati R.B., and Millar G.J., Using water quality and isotope studies to inform research in chronic kidney disease of unknown etiology endemic areas in Sri Lanka. Science of the Total Environment, Vol. 745, 2020.
- [4] Kobya M., Demirbas E., Senturk E., and Ince M., Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. Bioresource Technology, Vol. 96, Issue 13, 2005, pp.1518-1521.
- [5] Abdolali A., Ngo H.H., Guo W., Zhou J.L., Zhang J., Liang S., Chang S.W., Nguyen D.D., and Liu Y., Application of a breakthrough

biosorbent for removing heavy metals from synthetic and real wastewaters in a lab-scale continuous fixed-bed column. Bioresource Technology, Volume 229, 2017, pp. 78-87.

- [6] Chu H.T.T., Vu T.V., Nguyen T.K.B., and Nguyen H.T.H., Accumulation of arsenic and heavy metals in native and cultivated plant species in a lead recycling area in Vietnam. Minerals. Vol. 9, 2019.
- [7] Zaidi J., and Pal A., African Review on heavy metal pollution in major lakes of India: Remediation through plants. Journal of Environmental Science and Technology, Vol. 11, Issue 6, 2017, pp. 255-265.
- [8] Li Z., Wang L., Meng J., Liu X., Xu J., Wang F., and Brookes P., Zeolite-supported nanoscale zero-valent iron: New findings on simultaneous adsorption of Cd(II), Pb(II), and As(III) in aqueous solution and soil. Journal of Hazardous Materials, Vol. 344, 2018, pp 1-11.
- [9] Chan B.K.C., and Dudeney A.W.L., Reverse osmosis removal of arsenic residues from bioleaching of refractory gold concentrates. Minerals Engineering, Vol. 21, 2008, pp 272-278.
- [10] Ouhadi V.R., Yong R.N., Shariatmadari N., Saeidijam S., Goodarzi A.R., and Zanjani M.S., Impact of carbonate on the efficiency of heavy metal removal from kaolinite soil by the electrokinetic soil remediation method. Journal of Hazardous Materials, Vol. 173, Issue (1-3), 2010, pp. 87-94.
- [11] Huisman L.J., Schouten G., and Schultz C., Biologically produced sulphide for purification of process streams, effluent treatment and recovery of metals in the metal and mining industry. Hydrometallurgy, Vol. 83, 2006, pp. 106-113.
- [12] Ku Y., and Jung I.L., Photocatalytic reduction of Cr(VI) in aqueous solutions by UV irradiation with the presence of titanium dioxide, Water Research, Vol. 35, 2001, pp. 135-142.
- [13] Mishra P.C., and Patel R.K., Removal of lead and zinc ions from water by low-cost adsorbents. Journal of Hazardous Materials, Vol. 168, 2009, pp. 319-325.
- [14] Mondal M.K, Removal of Pb(II) ions from aqueous solution using activated tea waste: adsorption on a fixed-bed column. Journal of Environmental Management, Vol. 90, 2009, pp. 3266-3271.
- [15] Aklil A., Mouflihb M., and Sebti S., Removal of heavy metal ions from water by using calcined phosphate as a new adsorbent. Journal of Hazardous Materials, Vol. A112, 2004, pp. 183-190.
- [16] Maji S.K., Pal A., Pal T., and Adak A., Modeling and fixed-bed column adsorption of As(III) on laterite soil. Separation and

Purification Technology, Vol. 56, 2007, pp. 284–290.

- [17] Jain S.K., Patil P.G., and Thakor N.J., Engineering properties of laterite stone scrap blocks, Agric Eng Int: CIGR Journal, Vol. 13, 2011.
- [18] Nguyen T.H., Tran H.N., Vu H.A., Trinh M.V., Nguyen T.V., Loganathan P., Vigneswaran S., Nguyen T.M., Trinh V.T., Vu D.L., and Nguyen T.H.H., Laterite as a low-cost adsorbent in a sustainable decentralized filtration system to remove arsenic from groundwater in Vietnam, Science of the Total Environment, Vol. 699, 2020.
- [19]Bundschuh J., Bhattacharya P., Sracek O., Mellano M.F., Rami rez A.E., Storniolo A.D.R., Marti n R.A., Corte s J., Litter M.I., and Jean J., Arsenic removal from groundwater of the Chaco-Pampean Plain (Argentina) using natural geological materials as adsorbents. Journal of Environmental Science and Health A, 2011, 46, pp. 1297–1310.
- [20] Lemougna P.N., Chinje Melo U.F., Kamseu E., and Tchamba A.B., Laterite based stabilized products for sustainable building applications in tropical countries: Review and prospects for the case of Cameroon. Sustainability, Vol. 3, 2011, pp. 293-305.
- [21] Wood R.B., and McAtamney C.F., Constructed wetlands for wastewater treatment: the use of laterite in the bed medium in phosphorus and heavy metal removal. Hydrobiologia, Vol. 340, 1996, pp. 323-331.
- [22] Dang S.V., Kawasaki J., Abella L.C., Auresenia J., Habaki H., Gaspillo P.D., and Kosuge H., Removal of arsenic from synthetic groundwater by adsorption using the combination of laterite and iron modified activated carbon. Journal of Water and Environment Technology, Vol. 6, 2008, pp. 43-54.
- [23] Linh P., Laterite houses stand proud in central Vietnam villages. https://e.vnexpress.net (assessed on 14 December 2021)
- [24] Carlsson C., Surrounded by laterite in Duong Lam. https://explorationvacation.net (accessed on 14 December 2021)
- [25] TriStar® II 3020, Operator's Manual V3.00 https://www.micromeritics.com/Repository/Fil es/TriStar_II_Operator_Manual_v3.00.pdf (assessed on 14 December 2021)
- [26] Heister K., The measurement of the specific surface area of soils by gas and polar liquid adsorption methods—Limitations and potentials. Geoderma, Vol. 216, 2014, pp. 75-87.
- [27] Kumara G.M.P., Saito T., Hamamoto S., Asamoto S., and Kawamoto K., Evaluation of autoclaved aerated concrete (AAC) fines for removal of Cd(II) and Pb(II) from wastewater.

Journal of Environmental Engineering., ASCE, 2019, 145. DOI: 10.1061/(ASCE)EE.1943-7870.0001597.

- [28] Kumara G.M.P., and Kawamoto K., Applicability of crushed clay brick and municipal solid waste slag as low-cost adsorbents to refine high concentration Cd (II) and Pb (II) contaminated wastewater. International Journal of GEOMATE. Vol. 17, 2019, pp. 133-142.
- [29] Nguyen P.T.T., Yacouba S., Pare S., and Bui H.M., Removal of arsenic from groundwater using Lamdong laterite as a natural adsorbent. Polish Journal of Environmental Studies, Vol. 29, 2020, pp. 1305-1314.
- [30] He Y., Chen Y., Zhang K., Ye W., and Wu D., Removal of chromium and strontium from aqueous solutions by adsorption on laterite. Archives of Environmental Protection, Vol. 45, 2019, pp. 11-20.
- [31]Kpannieu D.E., Mallet M., Coulibaly L., Abdelmoula M., and Ruby C., Phosphate removal from water by naturally occurring shale, sandstone, and laterite: The role of iron oxides and soluble species. Comptes Rendus Geoscience, Vol. 351, 2019, pp. 37-47.
- [32] Saadon, S.A.; Salmiati, Yusoff, A.R.M.; Yusop, Z.; Azman, S.; Uy, D.; Syafiuddin, A. Heated laterite as a low-cost adsorbent for arsenic removal from aqueous solution. Mal. J. Fund. Appl. Sci. 2018, 14, 1-8.
- [33] Iriela A., Bruneelb S.P., Schenonea N., and Cirelli A.F., The removal of fluoride from aqueous solution by lateritic soil adsorption: Kinetic and equilibrium studies. Ecotoxicology and Environmental Safety, Vol. 149, 2018, pp. 166-172.
- [34] Rathore V.K. and Mondal P., Stabilization of arsenic and fluoride bearing spent adsorbent in clay bricks: Preparation, characterization and leaching studies. Journal of Environmental Management, Vol. 200, 2017, pp. 160-169.
- [35] Sanou Y., Pare S., Phuong N.T.T., and Phuoc N.V., Experimental and kinetic modeling of As (V) adsorption on granular ferric hydroxide and laterite. Journal of Environmental Treatment Techniques, Vol. 4, 2016, pp. 62-70.
- [36] Coulibaly L.S., Akpo S.K., Yvon J., and Coulibaly L., Fourier transform infra-red (FTIR) spectroscopy investigation, dose-effect, kinetics and adsorption capacity of phosphate from aqueous solution onto laterite and sandstone. Journal of Environmental Management, Vol. 183, 2016, pp. 1032-1040.
- [37] Mitra S., Thakur L.S., Rathore V.K., and Mondal P., Removal of Pb(II) and Cr(VI) by laterite soil from synthetic wastewater: single and bi-component adsorption approach. Desalination and Water Treatment, Vol. 57,

2015, pp. 1-11.

- [38] Fulazzaky M.A., Khamidun M.H., Din M.F.M., and Yusoff A.R.M., Adsorption of phosphate from domestic wastewater treatment plant effluent onto the laterites in a hydrodynamic column. Chemical Engineering Journal, Vol. 258, 2014, pp. 10-17.
- [39] Aredes S., Klein B., and Pawlik M., The removal of arsenic from water using natural iron oxide minerals. Journal of Cleaner Production, Vol. 60, 2013, pp. 71-76.
- [40] Rajapaksha A.U., Vithanage M., Weerasooriya R., and Dissanayake C.B., Surface complexation of nickel on iron and aluminum oxides: A comparative study with single and dual-site clays. Colloids and Surfaces A: Physicochemical and Engineering Aspects, Vol. 405, 2012, pp. 79-87.
- [41] Jahan N., Guan H., and Bestland E.A., Arsenic remediation by Australian laterites. Environmental Earth Sciences, Vol. 64, 2011, pp. 247-253.
- [42] Maiti A., Basu J.K., and De S., Development of treated laterite for arsenic adsorption: Effects of treatment parameters. Industrial and Engineering Chemistry Research, Vol. 49, 2010, pp. 4873-4886.
- [43] Mohapatra M., Khatun S., and Anand S., Kinetics and thermodynamics of lead (II) adsorption on lateritic nickel ores of Indian origin. Chemical Engineering Journal, Vol. 155, 2009, pp. 184-190.
- [44] Kadam A.M., Nemade P.D., Oza G.H., and Shankar H.S., Treatment of municipal wastewater using laterite-based constructed soil filter. Ecological Engineering, Vol. 35, 2009, pp. 1051-1061.
- [45] Wanga T.H., Li M.H., Yeh W.C., Wei Y.Y., and Teng S.P., Removal of cesium ions from aqueous solution by adsorption onto local Taiwan laterite. Journal of Hazardous Materials, Vol. 160, 2008, pp. 638-642.
- [46] Maiti A., DasGupta S., Basu J.K., and De S., Batch and column study: Adsorption of arsenate using untreated laterite as adsorbent. Industrial and Engineering Chemistry Research, Vol. 47, 2008, pp. 1620-1629.
- [47] Partey F., Norman D., Ndur S., and Nartey R., Arsenic sorption onto laterite iron concretions: Temperature effect. Journal of Colloid and Interface Science, Vol. 321, 2008, pp. 493-500.
- [48] Maji S.K., Pal A., and Pal T., Arsenic removal from real-life groundwater by adsorption on laterite soil. Journal of Hazardous Materials, Vol. 151, 2008, pp. 811-820.
- [49] Maji S.K., Pal A., Pal T., and Adak A.,

Modeling and fixed-bed column adsorption of As(V) on laterite soil. Journal of Environmental Science and Health A, Vol. 42, 2007, pp. 1-9.

- [50] Maiti A., DasGupta S., Basu J.K., and De S., Adsorption of arsenite using natural laterite as adsorbent. Separation and Purification Technology, Vol. 55, 2007, pp. 350-359.
- [51] Sarkar M., Banerjee A., Pramanick P.P., and Sarkar A.R., Design and operation of fixed bed laterite column for the removal of fluoride from water. Chemical Engineering Journal, Vol. 131, 2007, pp. 329-335.
- [52] Sarkar M., Banerjee A., Pramanick P.P., and Sarkar A.R., Use of laterite for the removal of fluoride from contaminated drinking water. Journal of Colloid and Interface Science, Vol. 302, 2006, pp. 432-441.
- [53] Sarkar M., Banerjee A., and Pramanick P.P., Kinetics and mechanism of fluoride removal using laterite. Industrial and Engineering Chemistry Research, Vol. 45, 2006, pp. 5920-5927.
- [54] Sreekumar U., Thalla A.K., and Nair V.V., Comparative evaluation of phosphate abatement using laterite soil and activated carbon. International Journal of Environmental Science and Technology, Vol. 16, 2019, pp. 4493-4502.
- [55] Hue N.T., and Tung N.H., Study on simultaneous adsorption of phosphate and fluoride from water environment by modified laterite ore from Northern Vietnam. Green Processing and Synthesis, Vol. 7, 2018, pp. 89-99.
- [56] Hirai H., Katsutoshi Sakurai K., and Kyuma K., Characteristics of brown forest soils developed under beech forests in the Kinki and the Tohoku districts with special reference to their pedogenetic processes. Soil Science and Plant Nutrition, Vol. 37, 1991, pp. 497-507.
- [57] TriStar® II 3020, Operator's Manual V3.00 Available online: https://www.ssi.shimadzu.com/sites/ssi.shimad zu.com/files/Products/literature/xray/C142-E044C.pdf (accessed on 14 December 2021).
- [58] Organization for Economic Co-operation and Development Publications (OECD). Guidelines for the Testing of Chemicals. 2000. Available online: https://www.oecd.org/chemicalsafety/testing/oe cdguidelinesforthetestingofchemicals.htm
- (accessed on 11 December 2021).
 [59] Langmuir I., The adsorption of gases on plane surfaces of glass, mica, and platinum. Journal of American Chemical Society, Vol. 40, 1918, pp. 1361-1403.
- [60] Freundlich H.M.F., Over the adsorption in solution. Journal of Physical Chemistry, Vol. 57, 1906, pp. 385-471.

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