

Review on Adsorption and Desorption of Heavy Metals on Natural Low-Cost Adsorbents

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Abstract: Adsorption and desorption studies on different types of adsorbents, including natural materials Agricultural Waste, Nigerian bentonite (UAB) coffee wastes, waste from coconut milk, Delonix regia biomass & pods for removal of Ni(II), Mn(II), Cu(II), Cd(II), Pb(II), Zn(II) metal ions are summarized. The kinetics, thermodynamics, sorption/desorption mechanism of different metal ions on different adsorbents under different experimental conditions are discussed. It is found that different eluants are useful for desorbing the metal ions. All the metal ions are desorbed using eluants like distilled water, KI, HCl, H₂SO₄, EDTA and NaCl in most of the cases.

Keywords: Adsorption, desorption, heavy metals, eluant.

I. INTRODUCTION

Clean drinking water is a necessity in today's world, but water pollution remains a significant issue to tackle. Environmentalists and government agencies are actively working to address this challenge. Heavy metal poisoning in organisms poses serious health risks, mentioning need of the water treatment processes. Among these, adsorption emerges as a highly effective method. Nowadays, low-cost adsorbents derived from animal, plant, and industrial waste are being utilized as greener alternatives in water treatment. To fully utilize this process, both adsorption and desorption aspects need thorough study to make them commercially viable. This review paper aims to summarize the different types of natural low cost adsorbents, their use as adsorbent to remove divalent metal ions, their reuse, regeneration, and eluants used for recovery in heavy metals reported by researchers. Adsorption being surface phenomenon where ions from a fluid adhere to the surface of a solid adsorbent material, due to attractive forces between the adsorbate ions adsorbent surface whereas in Desorption adsorbed ions are released from the adsorbent surface In water treatment, adsorption is employed to remove contaminants like heavy metals, organic pollutants, and dyes from water by trapping them onto the surface of the adsorbent. In water treatment systems, desorption may involve techniques such as flushing the adsorbent material with a solvent or changing the pH of the solution to release the adsorbed contaminants. These fundamental processes of adsorption and desorption help in designing efficient and effective water purification system.

1.1 Adsorption Desorption Experiments with low cost adsorbents

Many researchers used many adsorbents like Desiccated Coconut Waste (Abdul Rahman Abdul Rahima, 2019), synthesized zeolite from coal fly ash (Amalia Ekaputri Hidayat, 2021), Delonix regia pods and leaves (Bolanle M. Babalola, 2020), natural pumice for iron (Indah, Helard, & Binuwara, 2017), on groundnut husk (Jonas Bayuo, 2020), Agricultural Waste (M. Bansal, 2009), Magnetic hydroxyapatite nanoparticles (MNHAP) (Yuan Fenga, 2010) for removal of divalent heavy metal ions. Batch experimental studies are carried out and best efficiency of adsorbent is determined by optimizing factors like pH, contact time, adsorbent dose, etc. At optimized conditions different researchers reported maximum efficiency of the low cost adsorbents are as follows-

1. Abdul Rahman Abdul Rahima et al, studied adsorption of Pb (II) ions from aqueous solution using Desiccated coconut waste as low-cost adsorbent and reported maximum Pb (II) adsorption capacity of 50.33 mg/g at pH 6 solution.
2. Amalia Ekaputri Hidayat et al, studied adsorption of Zinc and Copper ions from acid mine drainage by zeolites synthesized from coal fly ash. And revealed that synthetic zeolite are most effective adsorbent due to its high purity and high removal efficiency.

3. Bolanle M. Babalola et al studied the adsorption of Ni(II) and Cu(II) ions from aqueous solutions by powdered *Delonix regia* pods and leaves in batch analysis and reported monolayer adsorption capacity of 5.88 mg g⁻¹ for the *Delonix regia* pods and 5.77 mg g⁻¹ leaves was and for Ni(II) ions respectively and 9.12 and 9.01 mg g⁻¹ for Cu(II) ions respectively. The efficiency of the powdered pods and leaves of *Delonix regia* with respect to the removal of Ni(II) and Cu(II) ions was greater than 80 %, except for the sorption of Ni(II) ions onto the leaves.

4. G.Z. Kyzas et al, studied Copper ions removal from aqueous solution with adsorbent coffee wastes as low-cost materials at solution pH 2.

5. Manjeet Bansal et al, studied adsorption of Ni(II) ions by use of agricultural waste from its aqueous solutions with its kinetics studies and different parameters factors affecting it.

6. Yuan Feng et al, studied adsorption of Cd (II) and Zn (II) from aqueous solutions using magnetic hydroxyapatite nanoparticles as adsorbents and reported the adsorption capacities of 1.964 mmol g⁻¹ and 2.151 mmol g⁻¹ for Cd (II) and Zn (II) respectively.

Following table no 1 gives the summary of adsorbents and their adsorption capacities –

Sr no	Adsorbent	Metal ions adsorbed	q _{max}	Reference
1	Agricultural Waste	Ni(II)	7.63 mg/g	(M. Bansal, 2009)
2	Nigerian bentonite (UAB)	Nickel	200 mg g ⁻¹	(Kovo G. Akpomie, 2015)
3	Nigerian bentonite (UAB)	Manganese	166.7 mg g ⁻¹	(Kovo G. Akpomie, 2015)
4	Coffee wastes	Copper	70 mg g ⁻¹	(G. Z. Kyzas, 2013)
5	Magnetic hydroxyapatite nanoparticles	Cd (II) and Zn (II)	1.964 mmol g ⁻¹ 2.151 mmol g ⁻¹	(Yuan Fenga, 2010)
6	Waste from coconut milk	Pb (II)	55.865 mg/g	(Abdul Rahman Abdul Rahima, 2019)
7	<i>Delonix regia</i> biomass	Ni(II) Cu(II)	5.88 mg g ⁻¹ 5.77 mg g ⁻¹	(Bolanle M. Babalola, 2020)
8	<i>Delonix regia</i> pods	Ni(II) Cu(II)	9.12 mg g ⁻¹ 9.01 mg g ⁻¹	(Bolanle M. Babalola, 2020)

1.2 Methodology

Adsorption experiments are carried out by natural & some nanoparticle adsorbents in batches and effect of different parameters like contact time, pH, adsorbent dose, concentration is studied. After adsorption, used adsorbents are sundried and used for desorption experiments. In desorption experiments, the used adsorbent is taken in eluant solutions like acid, base or EDTA solutions and shaken in horizontal shaker. And concentration of residual solution is determined spectrophotometrically. Adsorption Isotherm & Kinetic Models are applied to adsorption process different isotherm models like Freundlich isotherm, Langmuir isotherm models are employed. Similarly, to study kinetics & to explain the adsorption rate different kinetic models are applied.

Adsorption of the different metals on adsorbents, their isotherm and kinetics is given below

Table 2-

Sr no	Adsorbent	Metal ions adsorbed	ISOTHERM	KINETICS	Ref
1	Agricultural Waste	NI(II)	Langmuir isotherm with R ² value = 0.969 pseudo	First & second order (PSO)	(M. Bansal, 2009)
2	Nigerian bentonite (UAB)	Nickel		pseudo-first & second order	Kovo
3	Nigerian bentonite (UAB)	Manganese			(Kovo G. Akpomie, 2015)
4	coffee wastes	Copper	Langmuir, Freundlich and	Pseudo-	G. Z. Kyzas,

			Langmuir-Freundlich model (L-F)	first,second and -third order	2013)
5	magnetic hydroxyapatite nanoparticles	Cd (II) and Zn (II)	Langmuir isotherm	Pseudo second order	(Yuan Fenga, 2010)
6	magnetic hydroxyapatite nanoparticles	Zn (II)	Langmuir isotherm	Pseudo second order	(Yuan Fenga, 2010)
7	Waste from coconut milk	Pb (II)	Langmuir isotherm	-Pseudo second Order	(Abdul Rahman Abdul Rahima, 2019)
8	Natural pumice	Fe(II)	Langmuir freundliuchisotherm	-Pseudo second Order	(Indah, Helard, & Binuwara, 2017)
9	<i>Delonix regia</i> biomass	Ni(II) Cu(II)	Langmuirfreundliuchisotherm	Pseudo second order	(Bolanle M. Babalola, 2020)
10	<i>Delonix regia</i> pods	Ni(II) Cu(II)	Langmuir isotherm	Pseudosecond order	(Bolanle M. Babalola, 2020)

Table 2 Summary of the Isotherm & Kinetics of adsorption of metal on adsorbents

Such Kinetic and isotherm modeling helps us to calculate different parameters such as 2 sorption capacity, sorption intensity by plotting graphs and with linear regression and help to understand the mechanism involved in adsorption

1.3. Details of Desorption of metal ions are given below-

Sr No	Adsorbent	Desorbed metal ions	Desorbing agent	Removal %	Ref
1	Agricultural Waste	NI(II)	0.0125 -0.150 M KI & HCL	60.19% by KI 78.93% by HCl(0.15M)	(M. Bansal, 2009)
2	Groundnut husk	[Cr(VI	0.1 M HCl & H ₂ SO ₄	76.1%	(Jonas Bayuo, 2020)
3	Groundnut husk	[Pb(II)]	0.1 M HCl & H ₂ SO ₄	82.1%,	(Jonas Bayuo, 2020)
4	Synthesized zeolite from coal fly ash	Zinc in acid mine drainage	2% H ₂ SO ₄ 10% HNO ₃ 3M NaCl 34M NaCl	150,39% 151.82% 4,17% 1,90%	(Amalia Ekaputri Hidayat, 2021)
5	Synthesized zeolite from coal fly ash	Copper in acid mine drainage	2% H ₂ SO ₄ 10% HNO ₃ 3M NaCl 34M NaCl	118,82% 120,87% 3,46% 1,09%	(Amalia Ekaputri Hidayat, 2021)
6	Nigerian bentonite (UAB)	Nickel	DW 0.1 M HCl for 20 min	30.1% 90%	(Kovo G. Akpomie, 2015)
7	Nigerian bentonite (UAB)	Manganese	DW 0.1 M HCL for 20 min	32.6% 90%	(Kovo G. Akpomie, 2015)
8	Coffee wastes	Copper	Acid Base	94% 21%	(G. Z. Kyzas, 2013)
9	Magnetic	Cd (II) and	EDTA	66.2%	(Yuan Fenga,

	hydroxyapatite nanoparticles	Zn (II)			2010)
10	magnetic hydroxyapatite nanoparticles	Zn (II)	EDTA	67%	(Yuan Fenga, 2010)
11	Waste from coconut milk	Pb (II)	HNO ₃ solution for 1 day	23%	(Abdul Rahman Abdul Rahima, 2019)
12	Natural pumice	Fe(II)	0.1M HCl for 60 min	37.89%	(Indah, Helard, & Binuwara, 2017)
13	<i>Delonix regia</i> biomass	Ni(II) Cu(II)	1M HNO ₃	14.3% 33.3%	(Bolanle M. Babalola, 2020)
14	<i>Delonix regia</i> pods	Ni(II) Cu(II)	1M HNO ₃	74.4 % 78.9%	(Bolanle M. Babalola, 2020)

Table 3-Summary of the different eluants used for different metal ions adsorbed on adsorbents and their percentages .
Regeneration processes –

Manjeet Bansal et al ,studied Ni(II) ions removal from it's solution with agricultural waste adsorbents and got maximum 51.8% removal at 20g/L adsorbent rice husk dosage at pH 6 . Regeneration of the used rice husk is reported 78.93% Ni(II) ions removal with HCl eluant in desorption experiment.

Jonas Bayuo et al studied use of ground nuts as adsorbents for Cr(VI) & Pb(II) ions removal , and adsorbed ions are desorbed with 0.1M HCl & H₂SO₄ as eluting agents.The exhausted groundnut husk was regenerated up to five cycles, and and reported removal efficiency of Cr(VI) and Pb(II) ions on the recycled groundnut husk at 53.5% and 54.6%, respectively, in third cycleand by 20.0% and 26.7% after fifth cycle.

Amalia Ekaputri Hidayat et al reported Adsorption and desorption of zinc and copper in acid mine drainage with synthesized zeolite from coal fly ash with adsorption selectivity order for adsorption of Fe²⁺> Cu²⁺> Zn²⁺> Mn²⁺ . For desorption ,NaCl, H₂SO₄, and HNO₃ as eluant were used as desorption agent. After three cycles the synthetic zeolite showed decrease in for Zn²⁺ and Cu²⁺ adsorption efficiency of about 10%. Furthermore, the desorption study shows the but further more are reported as ineffective in use.

Abdul Rahman Abdul Rahima et al, studied removal of Lead (II) Ions from Aqueous Solution Using Desiccated Coconut Waste as Low-Cost Adsorbent with adsorption capacity 50.33% at pH6. In the regeneration study, DCW adsorbent has remained stable up to two adsorption cycles. Thus, these satisfactory results revealed that the use of DCW as an alternative low-cost adsorbent for the removal Pb (II) from aqueous solution is feasible.

G.Z.Kyzas et al, studied Copper removal from aqueous systems with coffee wastes adsorbent showed 70mg/g adsorption capacity..Also, the effTen cycles of adsorption-desorption were carried out revealing the strong reuse potential of these low-cost adsorbents; the latter was confirmed from a brief economic approach.The adsorption properties are also reproducible. After saturation, the adsorption capacity value remains unchanged. Practically and numerically, there are coffee residues with no further use in nutrition cycle (coffee) which can be used and re-used up to 10 times adsorbing approximately 70 mg of Cu(II) per gram. This is directly comparative with other examples of coffee residues, where the cost of preparation was higher. According to Baek et al (2010), the comparison between the cost of the use of activated carbon and low-cost materials is up to 15 times larger.

S. Indah et al, studied on desorption and regeneration of natural pumice from Sungai Pasak, West Sumatra, Indonesia for iron removal from aqueous solution in adsorption-desorption cycles with eluting agents HCl, NaOH and aquadest and 0.1M HCl showed the 37.89% highest desorption efficiency with 60 minutes . The removal efficiency of iron ions in reused natural pumice could be maintained up to 90% in the third cycle of adsorption.

III. CONCLUSION

Adsorption and desorption studies showed the capacities of adsorbents of a material in designing large-scale applications. So in future so effective low cost adsorbent can be used the water treatment. But in industry proper designs for industrial use are needed. Gap between experimental and industrial use must be shortened. More efforts

are required. There is vast scope for research in this field for successful implementation of adsorbents. Modifications should be done in adsorbent and its environmental impact also should be checked. Future research should be carried out on the extension of batch tests.

Although much research has been done on the sorption/desorption field, there are still some gaps to be filled. Laboratory-scale experiments should be applied in the field. In the adsorption study, multicomponent system should be given more priority because the aqueous system contains various metal ions as the contaminants and interaction between different metal ions play an important role in sorption efficiency of different metal ions. The choice of low cost, effective and recyclable adsorbents is important. The adsorbents should have high sorption capacity, with easy separation from aqueous solution, low cost and recycling use. Similarly, in the desorption study, choice of suitable eluant is important. The eluant should be metal-selective, economically feasible and desorption rate should be high. Successful adsorption studies will transpire through collaboration and technology transfer with/from experts in the respective fields.

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