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REVIEW ARTICLE **OPEN ACCESS**

Cd Removal from Aqueous Medium using Various Modified / Non-Modified Adsorbent Materials: A Review

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ABSTRACT

Rapid industrialization, constantly posed some secondary unavoidable issues such as heavy metallic contamination, wastewater which want answer as quickly as possible. Industrial wastewater is the fundamental motive of infection of water. Toxic heavy metals like lead, copper, cadmium, nickel, chromium, zinc, arsenic and mercury which are hazardous and bio-accumulate in nature. These are rather soluble in the aquatic mediums. Therefore, there is a dire want for the elimination and/or restoration of these toxic, non-biodegradable and lengthy lasting heavy metals from the industrial wastewater. From closing few years, giant lookup has been carried out for simple, easy, environment friendly and low value adsorbents for the elimination of heavy metals. This evaluate article tries to talk about the workable use of a variety of adsorbents for the elimination of cadmium. Several elements influencing adsorption technique such as pH, interaction time, preliminary concentration, adsorbent dose, temperature as properly as the pronounced most adsorption efficiency is summarized. This overview additionally covers distinct adsorption kinetics and isotherms models followed.

Keywords: *Adsorbent, Zeolites, Multiwalled, Efficiency, Cd(II) adsorption*

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INTRODUCTION

Now-a-days pollution of water bodies through heavy poisonous metals is one of the most serious environmental troubles due to the fact they have tendency to bio-accumulate and cause serious fitness troubles to human beings and animals. Among these heavy metals, Cadmium (Cd^{2+}) is very poisonous and carcinogenic. Cadmium contaminants consist of alkaline batteries, photographic development, ceramic, electroplating and metallic plating. Other such sources are industrial wastewater, mining operation, incineration, industrial fertilizer, and combustion of oils along with coals. Recently Cd infection has been broadly growing due to the expansion in its use for the manufacturing of our every day wanted materials. The United States Environmental Protection Agency (USA EPA) has satisfied a most of 0.005 mg/L infection degree for cadmium in potable water and the World Health Organization (WHO) has set a most awareness of 0.003 mg/L. This distinction infers the wished need of elimination of Cd from industrial waste water to make it protected for us **[1]**.

Recently, membrane separation, adsorption, ion-exchange, reverse osmosis, electro-dialysis and chemical precipitation have already been used to deal with heavy metallic ions in water bodies. Among all these, adsorption is most beneficial and tremendous technique due to the fact of its excessive efficiency, low cost, easy running approach and not in addition inflicting any kind of pollution. It used to be counselled that all different adsorbent substances like graphene, ferrites, meso-porous silica, clays, composites, oxides, zeolite, carbon nan-otubes can adsorb heavy metallic ions from polluted water. However, they are high-priced and complicated in nature due to which their use is restrained somehow **[2]**.As stated above, there is want to enhance new eco-friendly adsorbent materials, such as sludge, activated carbon, fly ash waste, bio-sorbents and agricultural waste such as rice husks, rice barn and pea-nut shells however some of these substances have lower adsorption capacity, consequently lookup is now cantered on getting higher alternatives as adsorbent materials **[3]**.

FACTORS AFFECTING ON Cd ADSORPTION BY VARIOUS MATERIALS

Effect of Initial conc.

The effect of initial conc. of metal ion has great impact on adsorption capacity. Generally with lower initial conc. adsorption capacity is higher. As conc. increases there is competition between metal ions for the active adsorbent site. Maximum Cd removal occurred for low initial conc. of Cd that verified gradual depletion when initial conc. of Cd was stepped up further from 200 mg/L. It also could be because of fixed conc. of adsorbent dosage. Maximum adsorption of178.57 mg/g was obtained at 50 mg/L concentration of Cd for TiO_2-PAN-(FMWCNT/GO)-g-PCA nano-fibers**[11]**and minimum adsorption capacity of 18.49 mg/g was reported at 200 mg/L initial concentration of cadmium with industrial palm oil sludge **[12]**. Table No. 1 shows various adsorbents capacities at different initial concentrations of cadmium.

Table No. 1 Effect of initial concentration

Adsorbent	Initial conc. mg/L	Adsorption capacity mg/g	Reference
Magnetized activated carbons (MAC-300)	60	73.3	**[4]**
cow dung (DB)biochar	20	40	**[5]**
rGO-Fe0/Fe3O4-PEI nanocomposite	2	54.47	**[6]**
modified coal fly ash (NMFA)	100	90.27	**[7]**
β-Cyclodextrin conjugated graphene oxide	50	117.07	**[8]**
double network porous hydrogel PS(H)-PAA	100	109.89	**[9]**
bimetallic Ag-Fe MOF	100	265	**[10]**
TiO_2-PAN-(FMWCNT/GO)-g-PCA nanofibers	50	178.57	**[11]**
industrial palm oil sludge	200	18.49	**[12]**
zeolite hollow fibers	100 ppm	2.0 mmol/g	**[13]**
modified drinking water treatment plant sludge	25	40.3	**[14]**

Effect of pH

The designated find out about for the pH impact published that Cd confirmed greater adsorption at pH vary 5 to 9. Above and beneath this range adsorption ability goes on decreasing. This may additionally be due to opposition created by means of H^+ and OH^- ions for adsorption sites in greater acidic and greater basic conditions. Max. adsorption of 404.858 mg/g confirmed at pH eight for the multi-walled carbon nano-tubes (MWCNTs) **[17]** and graphene oxide (GO) acquired max. adsorption of 23.9 mg/g at pH 6 to 7**[20]**.Table No.2 shows different adsorbents and the respective pH for max. adsorption.

Table No. 2 Effect of pH

Adsorbent	pH	Adsorption capacity mg/g	Reference
$ZnCl_2$-activated carbon(ZnAC)	7	94.2	**[15]**
Chitosan/Phosphorylated Nanocellulosebiosorbent	5.5	232.55	**[16]**
multiwall carbon nanotubes (MWCNTs)	8	404.858	**[17]**
Nano-composite materials	5.5	148.32	**[18]**
magnetic ferrite	9	44.13	**[19]**
graphene oxide (GO)	6.0–7.0	23.9	**[20]**
magnesium hydroxide gel beads CXB@MH	7	234	**[21]**
SiO2@Fe3O4-SB nano-hybrids silica coated iron-oxide nano-hybrids	7	98	**[22]**
silica-calcium phosphate hybrid nanoparticles	5	153	**[23]**
viticultural industry wastes	5.5 and 6	0.67 mmol/g	**[24]**
Acrylamide grafted chitosan based ion imprinted Polymer	6	167	**[25]**
Terpolymers	7.0.	77.56	**[26]**

Effect of Interaction Time

From the interaction time studies, the style can be assignment to the truth that as the interaction time will increase extra is the adsorbate-adsorbent interaction and as a consequence leads to greater adsorption

and consequently percent elimination of metal ions additionally receives raised with respect to enlarge in contact time. But every now and then over interaction time might also lead to desorption of adsorbed metallic ions. Hence right time for interaction is to be decided specifically. We discovered minimal time of 5 min for meso-porous oil palm shell-based activated carbon with adsorption ability 227.27 mg/g **[27]** and magnetic layered double hydroxide / guargum bio-nano-composites GLF8% with most adsorption potential 258 mg/g **[31]** Maximum of two hours for the most adsorption for rice husk biochar**[29]**, activated carbon/zirconium oxide DSAC/ZrO_2 composite**[32]** and Fly ash **[33]** was once reported. Table No. 3 shows interaction time for the adsorbent and metal ions for the maximum adsorption efficiency.

Table No. 3 Effect of Interaction Time

Adsorbent	Time Min	Adsorption capacity mg/g	Reference
mesoporous oil palm shell-based activated carbon	5	227.27	**[27]**
rice bran	10	5.79	**[28]**
rice husk biochar	120	17.8	**[29]**
oxidized multiwalled carbon nanotubes (oxMWCNT6h)	20	13.5	**[30]**
magnetic layered double hydroxide/guargumbionanocomposites GLF8%	5	258	**[31]**
activated carbon/zirconium oxide composite DSAC/ZrO2	120	166.7	**[32]**
Fly ash	120	9.18–48.5	**[33]**
3D sulfonated reduced graphene oxide (3D–SRGO)	20	234.8	**[34]**
nano-zirconium silicate (ZrSiO4-NPs)	30–40	2.100 mmol/ g	**[35]**
γ – Alumina- polymer	11	220	**[36]**

Effect of temperature

Generally, all adsorption experiments are done at room temperature as it is convenient. But some adsorbents show greater adsorption capacity at elevated temperature. This is because adsorption process for those adsorbents is endothermic.Table No. 4 showed temperature effect on adsorbent capacity of various adsorbent used.

Table No. 4 Effect of Temperature

Adsorbent	Temp	Adsorption capacity	Reference
	°C	mg/g	
Activated carbon	25	3.13	**[37]**
Modified Palm shell powder (MPSP)	30	153.9	**[38]**
silty clay	45	5.48	**[39]**
COOH-KCC-1/polyamide 6 composite	25	109.2	**[40]**
Chitosan/Poly (Acryl amide -Acrylic Acid) Hydrogels	25	17.12	**[41]**
sulfonated hyper-crosslinked polystyrene (SHCP)	25	0.7 mmol/g	**[42]**

Effect of adsorbent dose

For adsorbent dosage, usually it used to be considered that percent elimination of Cd will increase with enlarge in adsorbent dosage. This vogue can be attributed due to the fact of extra surface vicinity uncovered to metal ion solutions, so that extra metallic ions could be adsorbed into the porous areas of the adsorbent therefore extra is percent removal. 736.38 mg/g adsorption capacity was obtained for the synthesized zeolites from power plant rice husk ash with adsorbent dose of 0.3 g/L **[50]** and MWCNTs showed 181.8 mg/g adsorption capacity at 1g/L adsorbent used **[45]**.Table No. 5 Showed details of adsorbent dose taken and its effect of adsorption capacity obtained.

Table No. 5 Effect of adsorbent dose

Adsorbent	Adsorbent dose	Adsorption capacity mg/g	Reference
dried orange peel powder [DOPP]modified with nanosilica [SiO2@DOPP]	0.03 g	142	**[43]**
bio-sorbent from Capparis decidua (CDB)	0.1 g/100mL	248.62	**[44]**
MWCNTs	1 g/L	181.8	**[45]**
ZnO@activated carbon nanocomposites	1 mg/ml	96.2	**[46]**
zeoliticimidazolate framework –L / graphene oxide composite	0.2 g/L	188.68	**[47]**
Zeoliticimidazolate framework - L incorporated graphene oxide hybrid ZIF- L / GO 20 and ZIF- L / GO 50	0.2 g/L	172.42 and 188.68	**[48]**
Copper oxide nanoblades	0.5 mg/ml	192.3	**[49]**
synthesized zeolites from power plant rice husk ash	0.3 g/L	736.38	**[50]**

ADSORPTION ISOTHERM AND KINETICS:

Adsorption isotherm

Table No. 6 gives detailed analysis of isotherm models followed by various adsorbent proposed. Analysis showed most of the adsorbents followed Freundlich and Langmuir models and some also showed Temkin for Poly (2 -hydroxyethyl methacrylate) grafted graphene oxide (GPHM) model **[56]** and Redlich - Peterson model for PAN / chitosan / UiO-66-NH_2nanofibrous**[58]** with max. adsorption capacity of 10.667 mg/g and 415.6 mg/g respectively.

Table No. 6 Adsorption Isotherm

Adsorbent	Isotherm	Adsorption capacity mg/g	Reference
Activated carbon	Freundlich	260	**[51]**
magnetic bioadsorbent Fe3O4-CMC	Langmuir	48	**[52]**
Al_2O_3/MWCNTs alumina-decorated multi-walled carbon nanotubes	Langmuir	27.21	**[53]**
humic acid / Mg-Al-layered double hydroxide composite (HA / Mg-Al-LDH)	Langmuir	155.28	**[54]**
chitosan-based hybrid (chitosan(CS)/SF)/BF)	Freundlich	419	**[55]**
Poly (2- hydroxyethyl methacrylate) grafted graphene oxide (GPHM)	Temkin	10.667	**[56]**
Amino-decorated magnetic metal-organic framework	Langmuir	693	**[57]**
PAN/chitosan/UiO-66-NH_2nanofibrous	Redlich-Peterson	415.6	**[58]**
poly urea-formaldehyde	Freundlich	76.3	**[59]**
modified chitosan TiO_2 and SiO_2 hydrogel nanocomposites	Freundlich	303	**[60]**
amorphous calcium phosphate/Fe_3O_4 composites ACP/Fe3O4 composite	Langmuir	454.5	**[61]**

Adsorption Kinetics

Table No. 7 show's reaction order followed by adsorption process for different adsorbent materials used for cadmium removal.

For most of the cases pseudo-first-order and pseudo-second-order kinetics was followed by adsorbents used.

Table No. 7 Kinetics of adsorption

Adsorbent	Order of reaction	Adsorption capacity mg/g	Reference
granular AC supported mg-hydroxide (Mg-GAC)	pseudo-second-order	8.08	**[62]**
KOH modified N-enriched biochar (KNB)	pseudo-second-order	135.7	**[63]**
natural clay (NC)	pseudo-second-order	5.65	**[64]**
aluminium-manganese binary oxide composite	pseudo-second-order	45.58	**[65]**
cattle horn core / iron nanoparticles composite	pseudo-first-order	392.3	**[66]**
CaFu MOF	pseudo-first-order	781.2	**[67]**
novel core-shell mesoporous ion-imprinted polymer	pseudo-second-order	201.9 mmol/g	**[68]**
granular sludge-clay (GSC)	pseudo-second-order	1.53	**[69]**
palm oil mill sludge biochar (POSB)	pseudo-second-order	46.2	**[70]**
magnetic zeolite	pseudo-second-order	204.2	**[71]**
hydrogel nanocomposites	pseudo-second-order	78.13	**[72]**

CONCLUSION

From the past few decades, the need for improving quality of industrial effluent is increasing rapidly. Various methods like adsorption, bio-sorption, coagulation / flocculation, chemical precipitation, ion-flotation, electro-dialysis, membrane filtration, ion-exchange have been used to recover heavy metals in industrial effluents. Among all those methods adsorption by cheap adsorbents and bio-sorption is found to be efficient and cost effective and can be applied for lesser conc. of heavy metals. Also, new methods are emerging for the handling of industrial effluent.

Among various heavy metals, recently Cd received more attention, for the greater need of its removal and recovery. To increase the adsorption capacity, variety of adsorbents has been studied for the adsorption of Cd through aqueous medium. Some of those widely used adsorbents are bio-sorbents, mofs, hybrids, composites, clays, nano-materials, zeolites, oxides, graphene oxides, polymers and sludge derived adsorbents and AC. Adsorption process for these adsorbent materials was decided by several operating parameters viz. pH, interaction time, dosage, temperature along with time. In the majority of the cases Langmuir isotherm and pseudo second order model were found to well fit for experimental data. Also, the thermodynamic studies convinced the process of Cd adsorption is endothermic in nature predominantly.

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