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Research paper

Various Impregnation Methods Used for the Surface Modification of the Adsorbent: A Review

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Abstract

The water contamination is an important crisis which is to be addressed in the recent time. The pollutants present in wastewater are treated by adsorption using activated carbon, which is considered as one of the effective method. The adsorbent has to be modified to improve the adsorption capacity and the surface properties. Various methods such as physical, chemical treatment, impregnation and functionalization techniques are available. Impregnation is one of the effective method carried out for surface modification and to increase the adsorption capacity. Therefore, current study investigates the different impregnation methods used for the surface modification of the adsorbent. It also reviews the various precursors used for adsorbent preparation, the impregnating agent, the operating conditions and the adsorption capacity of the adsorbent.

Keywords: *impregnation, porous material, modification, adsorbent, surface property*

1. Introduction

In the recent time, water pollution is becoming an issue of concern all over the world. Because of the overgrowing population there is a requirement to produce more resources to meet the daily needs of the society. Therefore these activities results in producing and releasing the pollutants into the environment [1]. The chemical industries namely pulp and paper, electroplating, petroleum refineries, fertilizer industries and various manufacturing industries releases wastewater containing different pollutants [2]. Therefore it is required to treat these pollutants before it is released into the environment. Various treatment methods such as chemical precipitation, membrane separation, ultrafiltration, pervaporation, adsorption using activated carbon and advanced oxidation methods can be used to treat the wastewater containing contaminants [3]. Adsorption using porous adsorbent is an efficient process which removes the toxic pollutants from wastewater [4]. It also requires low cost and less energy in comparison with other treatment methods and also the used adsorbent can be regenerated [5]. The activated carbon which is having high affinity to most of the contaminants and possessing large surface area makes it favorable for the process [6].

2. Different Types of Surface Modification Methods

Various treatment methods are used for modifying the surface of the adsorbent so that the affinity of the solute towards the adsorbent can be improved and the adsorption capacity can be increased. The prominent methods used are chemical treatment and physical treatment methods. Various chemicals such as acids, bases, surfactants, oxidizing agents, metal salts are used for the above processes [7, 8, 9]. The modification of the surface can be done by metal impregnation, chemical grafting and functionalization techniques [10, 11, 12]. In chemical grafting method, the chemical species are fixed onto the solid surface by covalent bonds formed between the surface and the species. This method has advantages that adsorption kinetics is faster, exhibit stable properties during regenerating of the adsorbent. On the other hand they have lower adsorption capacity because of the lower surface area. In the impregnation method the chemical species are blended inside the pores physically to modify the surface. The preparation technique is simple and it shows high adsorption capacity. The pore volume and pore diameter was enhanced by regulating the solid structure [12].The impregnation methods can be dry impregnation [13] or wet impregnation method [14, 15] depending on the way by which the solvent is added onto the surface of the adsorbent. In dry impregnation method the fixed quantity of solvent is added in such a way that the pores of the adsorbent are just filled, whereas in wet impregnation solvent more than the volume of the pores are added and after filling the pores, the excess chemical is dried and the loading of the chemical species can be controlled [16].

The impregnation on the solid surface was performed by using anionic surfactants which will increase the active sites [8]. It was reported that by impregnating the surface with metal salts results in the formation of oxide film on the surface. This modified surface has the capability to decrease the regeneration temperature and increase the life time of the adsorbent [17]. The impregnated adsorbent has the advantage that it is stable and has promising regeneration capacity in comparison with normal adsorbents [10]. The mesoporous materials have large surface area, better porous arrangement, thus these porous materials are produced by incipient- wetness impregnation technique [18]. The impregnation method is generally carried out in two steps. In the first step a layer of material is applied in order to change the surface and texture of the adsorbent. The second step comprises of depositing the material which is used for thermal activation [19]. The second step also facilitates in retaining the chemical species inside the inter particle space [20].

3. The Importance of Porous Materials

Porous materials have disadvantages that they are non-selective and inefficient to some of the pollutants. The preparation of adsorbent from expensive materials is also considered to be a problem of concern. Thus the adsorbents can be produced from low cost materials. The idea of preparing adsorbent from waste material also solves the problem of waste disposal [21, 22]. The adsorbent prepared from carbonaceous materials have disadvantages that it is hygroscopic in nature, pores inside may be blocked and may lead to combustion at higher temperature [23]. Because of dissimilar chemical characteristics between the metal species and solid surface, the attractive forces for the adsorption will be inhibited [8]. Thus the activated carbon without any modification have less adsorption capacity, therefore surface modification is required to improve the properties [17, 24, 25].

The modified adsorbent can have higher capacity because of chemisorption of pollutants onto the adsorbent surface [26]. The surface chemistry of the materials changes because of the impregnation [27, 28, 29]. The modification of the adsorbent reduces the amount of the adsorbent required for the process [30]. Through the process of impregnation the carbonaceous materials which are unstable may be provided support [23]. The impregnated materials have the advantages that regeneration is not necessary during oxidation [31]. The stability of the impregnated materials increases and provides higher surface area necessary for removing the pollutants [32].

It was discussed that by treating the carbon with amine improves the affinity of the adsorbent towards polar molecules where stronger forces than the van der Waals forces are produced [33]. The modification was done by using surfactants where the surfactant molecule layer gets arranged on the solid surface by a mechanism called self-associated clusters [34]. It was reported that some of the fine materials like iron and iron oxide when used as adsorbents becomes difficult to handle in the process. Therefore impregnation of these materials are required for preventing the loss of material and for implementing to scale- up of the process [35]. The porous materials were used to pre-concentrate the hazardous pollutants in the wastewater treatment and can be used for most of the separation processes [36]. It was studied that porous materials have pore sizes which can be adjusted and stable chemical structure which is a necessary requirement for the adsorption [37]. These porous materials are applied in the field of catalysis, purification techniques and separation processes [23]. Therefore an effort has been made to review the various modifications done on the surface of the adsorbent material to improve the properties and adsorption capacity.

The summarization of all the parameters such as various precursors, impregnating agent used for adsorbent preparation, the pollutant removed, the operating conditions and the adsorption capacity are listed in Table 1. The interesting findings from the recent literature like the advantages of different methods, the impregnating agent, and the possible reasons for the adsorption process are discussed below.

Table 1: The summarization of the parameters such as precursors used, impregnating agent, experimental conditions for surface modification and the adsorption capacity

Sl. No.	Precursor for adsorbent	Chemical used for impregnation	Pollutant	Experimental conditions	Adsorption capacity	Ref.
1	Saw dust	Aluminium chloride, manganese chloride, potassium permanganate	Arsenic	0.1 and 0.4 mM, 1g/L, 24 h, 25°C, pH 6	17.76	[38]
2	Sugarcane bagasse	Ferric chloride	chromium	25-130 mg/L,0.1-0.6g/50 mL, 20 – 40°C,pH 1-10, 200 rpm, 72 h	13.72	[39]
3	Granular activated carbon	Ferric chloride	copper	1×10^{-5}, 1×10^{-4} M, 0.2 g/100 mL, 25°C, pH 2-9, 24 h	99% removal	[40]
4	Collagen fiber	zirconium	Vanadium	2-6 mmol/L, 0.1 g/100 mL, pH 5, 303-323 K, 24 h	3.18 mmol/g	
			chromium	0.4-2 mmol/L, 0.1 g/100 mL, pH 7, 303-323 K, 24 h	0.691 mmol/g	[41]
5	chitosan	cerium	arsenic	0-60 mg/L, 20 mg/100 mL solution, pH 2-11, 150 rpm	57.5	[42]
6	Sugar beet pulp	Iron	arsenic	100, 500, 1000 µg/L, 0.05g/100mL	2.936	
		Hydrogen peroxide, iron			3.246	
		Manganese dioxide, iron			16.844	[43]
7	Amberlite XAD-8	Di-(2-ethylhexyl) Phosphoric Acid	chromium	10 mg/L, 0.1g/25 mL, pH 1-5.5, 298 K, 150 rpm, 2 h	5.64	[44]
8	Bamboo	Nickel	lead	50 mg/L, 1g/L, 288-308K, pH 1-7, 24 h	142.7	[45]
9	Activated carbon	Humic acid	copper	6.1 mg/L, 20 mg/40mL of solution, pH 2-6, 120 rpm, 20°C, 2 h	5.95	[46]
10	SBA 15 mesoporous materials	Al_2O_3 and Fe_2O_3	arsenic	1-50 mg/L, 0.5g/L, pH 6.5, 25°C, 200 rpm, 24 h	43.5	[47]
11	Peganum harmala seeds	ZnO	chromium	10-100mg/L, 1-10 g/L solution, 10-50°C, 0-300 rpm, pH 2-8, 10-80 min	68.49	[48]
12	Silica beads	2-hydroxy-5-nonylacetophenoneoxime, γ-aminopropyltriethoxysilane	copper	5 mmol/dm^3, 0.1-5 g/25cm^3 solution, pH 4, 48 h	0.0806mmol/g	[49]
13	Polyaniline	Cerium oxide	chromium	1-49 mg/L, 0.1-1 g/100 mL solution, pH 2-10, 20-100 min, 30-90°C	357	[50]
14	Rice husk ash	$AlCl_3$,$FeCl_3$, sodium carbonate	Lead	1-10 min, pH 6-9, 1-100 mg/L solution, 27°C, 10 mg/L conc	416	
			Iron	1-10 min, pH 6-9, 1-70 mg/L solution, 27°C, 4 mg/L conc	222	
			Manganese	1-10 min, pH 6-9, 1-70 mg/L solution, 27°C, 3 mg/L	158	
			arsenic	1-10 min, pH 6-9, 1-28 mg/L solution, 27°C, 1.5 mg/L	146	[51]
15	Volcanic raw	magnesium oxide	cadmium	5-40 mg/L, 2-10 g/L solution, pH 3-	31.25	[52]

	tuff soil			11, 0-360 min, 20^{o}C		
16	Polysulfone membranes	Zeolite particles	Lead	500 mg/L, 25^{o}C, pH 6, 1 bar	91% recovery	
			nickel		42% recovery	[53]
17	Saw dust	Iron doped amino group	Arsenic (III)	1-50 mg/L, 0.1 g/100 mL solution, pH 3-9, 24 h, 150 rpm	10.1	
			Arsenic (V)		43.7	[54]
18	chitosan	Fe_3O_4 nanoparticles	Arsenic(III)	0.2-50 mg/L, 0.05g/50mL solution, pH 6.8, 140 rpm	35.3	
			Arsenic(V)		35.7	[55]
19	coal	K_2S powder	mercury	24 mmol/L, 1g/100 mL solution, 25-45^{o}C, 120 oscillations/min, 72 h	1.24 mmol/g	[56]
20	Tea waste	Fe_3O_4	nickel	50-100 mg/L, 0.4-0.6 g/in 50mL solution, 303-323K, 100 rpm, pH 4	38.3	[57]
21	Activated carbon	iron hydroxide	arsenic	300 g/L, pH 7, 25^{o}C, 15 mg/20 mL solution,	0.847	[58]
22	Fly ash	Aluminium sluphate	phenol	200mg/L, 5-25g/L solution, 3-15 h, pH 2-10, 25-45^{o}C	12.67	[59]
23	Pine sawdust	H_3PO_4	Copper	1-10 mg/L, 2mg/8mL solution, pH 4.5, 120 h		
			cadmium			[60]
24	Chestnut shell	$FeCl_3$,$FeCl_2$	arsenic	0.2-50mg/L, 20mg/ 50mL solution, 298K, pH 2-11, 24 h	45.80	[61]
25	Rice straw char	$FeCl_3$	Arsenate	25-200 mg/L, 10g/L solution, 48 h, 150 rpm, 25^{o}C	9.70	
			cadmium		9.75	[62]
26	Corn straw	$FeCl_3$	arsenic	0.25-100 mg/L, 0.1g/20mL solution, 80^{o}C, 48 h	6.80	[63]
27	Powdered activated carbon	Fe_3O_4	Lead	50-300 mg/L, 0.5-2g/L solution, pH 2-10, 300 min, 20-50^{o}C	99.80	
			aniline		206.6	[64]
28	silica and lime	Potassium dihydrogen phosphate	cadmium	10-60 mg/L, 0.3 g/L solution, 130 r/min, pH 5, 10 h, 25^{o}C	236.41	[65]
29	Graphene oxide	Trioctylamine	chromium	100 mg/L, 0.2g/50 mL solution, pH 2.5	232.55	[66]
30	alginate	Iron oxide	Arsenic(III)	7-500mg/L, 0.040g/40 mL solution, 168 h, 100 rpm	47.8	
			Arsenic(V)		55.1	[67]
31	alginate	zirconium oxide	chromium	10-500 mg/L, 0.05g/20mL solution, 25^{o}C, 150 rpm	12.584	[68]
32	Peanut shell	manganese oxide nanoparticles	Lead	3-53 mg/L,0.2 g/L solution, pH 6, 298 K	67.9	
			cadmium	3-33 mg/L, 0.2 g/L solution, pH 6, 298 K	22.3	[69]
33	Wheat straw	Bismuth oxide	Arsenic	5-200 mg/L, 0.01-1 g/50 mL solution, 25^{o}C, 150 rpm, 24 h	0.273	
			Phosphorus	60-1800 mg/L	1.48	
			chromium	5-200 mg/L	12.23	[70]

The adsorption of arsenic from aqueous solution using sawdust impregnated with aluminium oxide was studied by Wu et al. 2017. It was investigated that the functional group of oxygen present in aluminium oxides were mainly responsible for adsorption of the pollutant and it was because of surface complexation [38].

Yang et al. explored the feasibility of the activated carbon impregnated with iron used for removing copper from wastewater. The adsorbent exhibits a stronger acid proof property which is beneficial in treating wastewater [40].

The adsorption of vanadium and chromium on collagen fiber impregnated with zirconium was studied to be through ion exchange. The single charged vanadium species and the double charged chromium species were found to adsorb on the surface of the zirconium and thus it favours adsorption process [41].

Zhang et al. addressed the removal of arsenic from water with the help of cerium impregnated chitosan adsorbent. It was investigated that monodentate and bidentate complexes formed between arsenite and hydroxyl groups and also the partial oxidation of As(III) to As(V) were mainly responsible for the adsorption process [42].

Activated carbon loaded with iron were employed as adsorbent for removing arsenic from wastewater by Lodeiro et al. The results showed that the adsorption was because of the surface iron content and the strong acidic groups on the adsorbent surface [43].

Bamboo charcoal impregnated with nickel was used as a potential adsorbent for the removal of lead. The authors justified that because of modification, the nickel modified adsorbent had better porosity and surface area compared to the untreated adsorbent. This was beneficial for the adsorption of the pollutant [45].

The capability of humic acid loaded activated carbon was tested for the removal of copper by Liu et al. It was understood that some functional groups are formed on the adsorbent surface that provides excess active sites required for the adsorption of pollutant. The adsorption performance of the adsorbent was almost the same in the wastewater and in the pure water showing the ability of the adsorbent [46].

In the adsorption of chromium using cerium oxide modified adsorbent it was observed that formation of electrostatic attractive forces and the complexation between the negatively charges chromium species and the positive charge (NH+) on the adsorbent surface were responsible for the adsorption [50].

The potential of rice husk ash treated with iron and aluminium was used as adsorbent for the removal of lead, iron, manganese and arsenic from wastewater. Using rice husk ash addresses the issue of depending on the low cost by product materials which are treated as waste materials [51].

The removal of lead and nickel from aqueous solution using polysulfone membranes loaded zeolite particles was explored by Yurekli. Various possible mechanisms were explained for the removal of metal ions. They are convective flow of the metal ions from the bulk solution to the membrane interface, diffusional flow of the ions from the membrane to the inside of the pores and the ion exchange inside the membrane framework [53].

The arsenic adsorption from wastewater chitosan beads impregnated with magnetic particles were studied by Wang et al. The magnetic adsorbent has the feature that it can be separated from the wastewater by applying external magnetic field. It was also found that the hydroxyl groups present on the solid surface were enhancing the adsorption [55].

In the work reported by Panneerselvam et al. on the adsorption of nickel onto tea waste, impregnation was carried out by using magnetic nanoparticles. The adsorption happening was mainly due to the ion exchange process. The authors inferred that hydrogen ion groups of the adsorbent gets attached to metal ions through electrostatic attraction [57].

The impregnated adsorbent was observed to be having more oxygen containing functional groups and having larger surface area. Also because of increase in the OH and COOH groups in the modified adsorbent there was a strong affinity between the adsorbent and the pollutant and thus the adsorption capacity increased [60].

The adsorption of arsenic using magnetic gelatin modified biochar was investigated by Zhou et al. It was discussed by the authors that the sorption on the adsorbent surface was because of speciation of the metal ions and the surface charge of the adsorbent [61].

In the work reported by He et al. iron impregnated biochar was used for the adsorption of arsenic from wastewater. The modified adsorbent exhibited improved properties like greater surface area, better porous structure, and larger oxygen containing groups which are beneficial for adsorption process [63].

Zhu et al. explored the capability of fluorhydroxyapatite composites for removing cadmium from wastewater. The adsorption was found to be because of ion-exchange process between the adsorbent and the adsorbate [65].

In the adsorption of chromium from wastewater trioctylamine treated graphene oxide was used as efficient adsorbent. The interaction between the protonated amine and the chromate anion was contributing towards the adsorption [66].

4. Conclusion

The current work explored the feasibility of the impregnation process for improving the property and the adsorption capacity of the adsorbent. The study reviewed the advantages and disadvantages of porous materials as adsorbent for wastewater treatment. The adsorbent surface can be modified by subjecting to various treatment methods. It also investigates the features and significance of different treatment methods. It discusses the various precursor materials used for adsorbent preparation, the impregnating agent, the pollutant removed, the experimental operating conditions and the adsorption capacity. Thus it can be inferred that through the process of impregnation, the type of impregnating agent used the adsorption capacity increases. Therefore selecting the precursor material and the impregnating agent is important in making the adsorbent more efficient and the wastewater treatment process economical.

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