



Enhancing adsorption capacity of nano-adsorbents via surface modification: A review

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ABSTRACT

In this review, the role of surface modification of nanoparticles to enhance their performance as adsorbents was explored. Performance was assessed by comparisons on adsorption capacities of differently modified nanoparticles (silica, iron, and alumina based nanoparticles) on different heavy metal ions (Cu, Cd, Co, Ni, Pb, As, Cr, Zn, Mn, and Hg). A comparison of pure and modified materials revealed that the modified materials gave superior adsorption capacities. A close relationship was observed between the various modification methods and the adsorption capacities of particles synthesized by hydrothermal methods giving the highest adsorption capacities. Surface modification also had a direct effect on the specific surface area which decreased with the degree of functionalization. The adsorption capacity was however generally observed to increase with the degree of functionalization.

1. Introduction

The continued increase in surface and ground water pollution in recent years has become a major challenge and a great cause of concern to both governments and industrialists all over the world. A number of factors have been linked to these escalating pollution levels and they include growth in global population, rapid industrialization and industrial growth, excessive exploitation of natural resources as well as persistent droughts (Que et al., 2018; Gehrke et al., 2015; Hao et al., 2012; Singh et al., 2013; Xu et al., 2013).

The growth of the industry as noted by Singh et al. (2013) and Xu et al. (2013) and Ge et al. (2012a,b) has directly or otherwise led to an unprecedented increase in the use of heavy metals in various chemical and process industries and these have subsequently found their way into water bodies through industrial effluents. Examples of such industries include, metal plating, textiles, paints and dyes, fertilizer, pharmaceuticals, tanneries, petroleum refining, ceramic and glass, battery manufacturing and mineral processing industries, just to name a few (Hao et al., 2012; Rostamian et al., 2011; Aguado et al., 2009; Badruddoza et al., 2013; Tan et al., 2012; Jin et al., 2011; Heidari et al.,

2009). It should be noted that all these industries are increasingly posing a potential threat to both humanity and the environment. Owing to their high toxicity levels, bio-accumulation and non-biodegradability tendency (Ge et al., 2012; Tan et al., 2012), heavy metals have been labeled dangerous to both human and aquatic life resulting in several diseases and health disorders. Several researchers have reported chronic poisoning with metals such as Arsenic and Chromium. The metals have been noted to be cancer causing (Badruddoza et al., 2013; Li et al., 2012). Long term exposure to Arsenic, for instance, through drinking contaminated water has been linked to cancers of the skin, lungs, bladder, the kidneys apart from other skin problems like pigmentation changes and thickening (Singh et al., 2013). Badruddoza et al. (2013) also further noted that Chromium is not only a carcinogen but also a mutagen as well as teratogen. Lead is another heavy metal that has been labeled highly toxic. For example according to Sing et al. (2013), the metal has been associated with damage of various internal body systems such as the nervous and reproductive systems as well as the kidneys. It has also been linked to high blood pressure problems and anemia. Lead has also been reported to cause brain damage apart from mental disturbances and retardation as well as serious reduction in

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hemoglobin production. (Hao et al., 2012; Heideri et al., 2009; Tan et al., 2012; Rahmani et al., 2010).

All these problems associated with heavy metals have led to stricter and more stringent environmental regulations on the release of heavy metals into surface water streams. According to Rostamian et al. (2011) this implies the necessity to come up with effective and highly efficient mitigation methods. The methods should be such that they are cheap both in terms of operation and installation. They should be environmentally friendly, with minimal or zero secondary pollution and lastly they should be able to handle large volumes of effluent and even very low pollutant concentrations.

Today, various traditional methods are being used as pollution mitigates for the removal of heavy metals from industrial waste waters. Examples include: membrane separation, ion exchange, ultra-filtration, filtration, sedimentation, electro dialysis, chemical reduction, electro-chemical treatments, biological treatment, reverse osmosis, flocculation/coagulation as well as adsorption among others (Rostamian et al., 2011; Hao et al., 2012; Xu et al., 2013; Li et al., 2012; Singh et al., 2011; Rahmani et al., 2010; Huang et al., 2009). Most of these conventional methods however have been noted to have technical and/or economical limitations (Zekić et al., 2018; Adeleye et al., 2016). They have been cited to have high capital and operational costs, unacceptable sensitivities to operational conditions, high energy consumption as well as high sludge generation (Adeleye et al., 2016; Tan et al., 2012).

However, a lot of literature reveals adsorption is a better alternative method with immense potential in heavy metal removal from water. The same is evident from Zhu et al. (2009) work and they reported that adsorption has an upper hand over other technologies economically. Li et al. (2011) also cited adsorption as the most promising and most widely used technology mainly due to its superior efficiency and that it is easily applied. Adsorption has generally been shown to be simple, efficient and sludge free. The operation has been noted to be cheap, easy to handle, with potential for regeneration (Aguado et al., 2009; Li et al., 2013; Badruddoza et al., 2013; Tan et al., 2012). Therefore, adsorption has been considered as a better alternative compared to the other technologies.

Several materials have been used as adsorbents (both organic and inorganic), for instance clay minerals, trivalent and tetravalent metal phosphates, bio sorbents, synthetic resins, kaolin, zeolites, fly ash, peat, agricultural residues as well as activated carbon (Najafi et al., 2012; Xinliang Jin et al., 2011; Shin et al., 2011). Among all these materials, activated carbon has emerged the most popular and most widely used adsorbent (Jin et al., 2011; Aguado et al., 2009; Huang et al., 2007). This has also been confirmed by Shin et al. (2011) who noted that carbon based materials attracted a lot of interest due to a number of factors. They are known to be inert to their environment, mechanically stable and possess a highly porous structure that is accompanied by specific surface chemical properties.

In spite of all these pros, activated carbon has had one major drawback that is cost. The high cost of the adsorbent has limited its use, especially in highly contaminated waste waters (Afkhami et al., 2010; Jin et al., 2011). As highlighted by Najafi et al. (2012), activated carbon and the rest of the commercially available sorbents have other disadvantages apart from their prohibitive costs. They have low loading capacities, relatively small metal ion binding constants and small selectivity. In view of these setbacks, extensive research is underway to come up with a low cost adsorbent with efficiency well above that of activated carbon and other commercially available adsorbents. Research is underway to try and utilize agricultural as well as industrial waste as low cost adsorbents (Huang et al., 2007; Tan et al., 2012; Xinliang Jin et al., 2011; Rahmani et al., 2010). Tan et al. (2012) however have pointed out that in most cases the low cost adsorbents are characterized by low adsorption efficiencies. This therefore implies that material properties like for example adsorption capacity should also be considered along with the cost aspect (Jin et al., 2011). An adsorbent should essentially not only satisfy the cost aspect, but should also

provide a competitive adsorption capacity and this is basically dictated by the material's surface area and available active sites. In other cases the material's porosity is also a property worth considering for the enhanced capacity of an adsorbent. Therefore, an ideal adsorbent is expected to exhibit among other desired characteristics, strong affinity for the desired sorbate and possess a large surface area, hence active or binding sites. The adsorbent should also be hydrothermally and chemically stable to be capable of resisting adverse environmental conditions. An ideal adsorbent should be easily regenerated and/or separated from the treated water for reuse (Li et al., 2011).

In recent years, considerable research effort has been directed towards harnessing nano particles as adsorbents. The nano materials have responded very well to the need for high surface area, high adsorption capacity and indeed cheap materials that are capable of efficiently handling metal ion pollutants even in very low concentrations.

Whilst many nano adsorbents have reported quite acceptable adsorption capacities and have exhibited remarkable properties, it is interesting to note that a number still fall short in terms of robustness, efficiency and the prospect of being industrial aspirants. This is due to various reasons including, the tendency to agglomerate, possible oxidation in the case of iron based materials, and regeneration issues. Thus, ways to make the best use of nanoparticles and maximize their applications have to be devised. It is in the context of this paper to review on the role of surface modification on nanomaterials as a means to enhance their adsorption efficiency and explore its undisputed significance and importance in heavy metal adsorption with special emphasis on the adsorption capacity of nanoparticles. Particular reference shall be made to three materials, iron, alumina and silica where comparisons will be made between their pure and functionalized forms.

2. Why surface modification?

It has been outlined earlier that adsorbent materials generally have inherent limitations and that the majority of them have low adsorption capacities. This implies that nanoparticles are not good enough when applied in their pure or naked forms. To surmount the limitations, Najafi et al. (2012) reported that organically functionalized adsorbents like organo-clays, polymer nanocomposites and functionalized silica gel have been developed. Thus, functionalization or surface modification is here put forward a way to eliminate the highlighted constraints associated with nanoparticles so that their advantages over conventional adsorbents are fully realized. According to Huang and Chen, 2009, nanomaterials have had their surfaces modified to alter their bulk properties as well as customize their surface properties like charge density, reactivity, functionality, biocompatibility, stability and dispensability. Surface modification has also been performed to develop hollow nanostructured materials and/or multifunctional nanocomposites. According to Afkhami et al. (2010), nanomaterials have been modified simply to enhance their adsorption capacity. From the work by Singh et al. (2011), it was observed that adsorption efficiency of heavy metal ions onto nanomaterials is directly linked to surface functionality (modification) among other factors such as competitive affinity of metal ions for the adsorbent, amount of surface charge and lastly the availability of active surface sites. Further, with particular reference to magnetic or iron-based nanoparticles, surface modification serves to prevent oxidation of the material together with enhancing its stability and adsorption capacity (Badruddoza et al., 2013). A detailed outline was given by Wang et al. (2010) who noted that magnetic adsorbents are basically iron oxides and as such are vulnerable in acidic environments. Also, the functional groups that are physically attached to the magnetic particles are affected by the mentioned acidic conditions. As a result, Wang et al. (2010) suggested the use of silica as a coating for magnetic particles owing to the stability of the particles in acidic environments as well as its inertness to redox reactions. Moreover, the silica coating shell has an abundant presence of hydroxyl groups so that the magnetic particles are equally functionalized in the

process. In the same context, surface modification of magnetic nanoparticles has also been reported to prevent aggregation, a perennial problem associated with nanoparticles (Hua et al., 2012). The same points were echoed by Ge et al. (2012a,b) who pointed out that the polymer core-shell on magnetic nanoparticles not only helps prevent particle-particle aggregation but also improves the core-shell structure's dispensability in a suspension medium. Also a study on nanoscale zero-valent iron (nZVI) revealed that the problem of aggregation is mainly due to the lack of colloidal stability. Surface coating was suggested as a means to ensure colloidal stability, hence curbing the problem of aggregation (Crane and Scott, 2012).

Therefore, surface modification of nanoparticles has been shown as a tool to significantly improve their applicability in terms of adsorption capacity, adsorption efficiency, dispensability, and stability and/or inertness in harsh environments. Surface modification has also been shown to prevent the problem of particle aggregation. A study on γ -Alumina by Afkhami et al. (2010) has revealed that while the material has exhibited great potential as an adsorbent owing to its large specific surface area, high adsorption capacity, impressive mechanical strength, and low temperature modification, the material, unfortunately, has also been reported a poor adsorbent with other heavy metals. This problem can only be solved by chemical or physical modification of the material surface. Indeed, surface modification has been linked to high adsorption rates or kinetics, a direct result of a high density of reactive sites (Singh et al., 2011). Thus, surface modification, in addition to the already listed advantages, also renders nanomaterials versatile so that they are basically applicable with a wide variety of heavy metal pollutants. Surface modification also guarantees high and/or rapid adsorption rates.

3. Synthesis methods and adsorption capacity

Molecular chemistry or in other words chemical processes have generally been noted to dictate the structure of nanoparticles and hence their inherent properties. As a result, the ability to control the processes becomes a key consideration to the synthesis of nanoparticles (Kulkarni, 2009). Ability to control the synthesis process is largely governed by parameters such as, the system pH, stirring speed, titration rate, reaction time and temperature (Li et al., 2011). These five parameters directly or otherwise dictate the adsorption capacity, a property which is central as far as the applicability of nanoparticles as adsorbents is concerned. Thus, surface modification comes into picture as an integral part of the synthesis process in this regard since it is known to impart certain properties to the nanoparticles. With particular reference to iron oxide nanoparticles, Xu et al. (2013) noted that their application is directly related to their intrinsic properties which are also directly linked to the preparation method as well as the involved modification media. As a result, several methods are available for the preparation of surface modified nanoparticles ranging from single step to multi-step processes. The available methods of synthesis include, grafting, hydrothermal and/or hydrothermal reduction, covalent binding, co-precipitation, co-condensation, surface coating, ligand exchange method, modified Stober method and the sol-gel method. A variety of modified nanoparticles can be synthesized with applications in the adsorption of a whole range of heavy metal pollutants from industrial waste waters.

Extensive research work has been carried out to explore the implications of several modification methods and their resultant nanomaterials in heavy metal adsorption. Afkhami et al. (2010) for example worked on nano size alumina modified with 2,4-dinitrophenylhydrazine. The nanomaterial was prepared via chemical immobilization. The modified nanomaterial was successfully tested for the removal of Pb^{2+} , Cr^{3+} and Cd^{2+} from which, it was revealed that the nanomaterial displayed excellent adsorption efficiencies for the three metal ions. Removal efficiencies for the three ion metals were quoted as 97%, 97.4% and 80.4% respectively, while corresponding adsorption capacities were 100 mg/g, 100 mg/g and 83.33 mg/g.

Li et al. (2011) looked at the effective removal of heavy metals from

waste water using thiol-functionalized magnetic mesoporous silica. In this case, the modified stober method was employed as the synthesis route. The resultant nanomaterial was earmarked for Pb^{2+} and Hg^{2+} removal in which case it reported significant adsorption capacities of 91.5 mg/g and 260 mg/g respectively. The material was also found to be stable in different aqueous environments which included highly acidic and highly alkaline conditions. The stability of the material was further evidenced by its ability to be used repeatedly without an appreciable loss to its adsorption properties. Removal efficiencies remained above 90% after 6 cycles of repeated use and regeneration of the adsorbent. Another work on modified silica was investigated by Najafi et al. (2012). In this work, the synthesis, characterization and adsorption studies for the material were explored in detail. Two materials, silica nano hollow spheres and silica gel were both amino-functionalized using the grafting method. In this review however, silica gel was deliberately left out. The work reported by Najafi et al. (2012) entailed comparing three materials but only two were here considered, that is, the non-functionalized or naked silica nano hollow spheres (SNHS) as well as the functionalized derivative (NH_2 -SNHS). The two materials were tested with Cd^{2+} , Ni^{2+} , and Pb^{2+} ion metals. The results showed the adsorption capacity decreasing in the order $Pb^{2+} > Cd^{2+} > Ni^{2+}$ for both sorbents. A lower adsorption capacity however was witnessed with the pure material as expected. For the three metals, adsorption capacities for the pure adsorbent, SNHS were 26.86 mg/g, 20.82 mg/g and 8.38 mg/g for Pb^{2+} , Cd^{2+} , and Ni^{2+} respectively compared to 96.79 mg/g, 40.73 mg/g and 31.29 mg/g for the same metals using the functionalized NH_2 -SNHS. More research work on modified silica was reported by Rostamian et al. (2011), where silica nano hollow spheres were prepared and were thiol-functionalized to give SH-SNHS. Thiol-functionalized silica nano spheres gave a higher specific surface area (823 m^2/g) compared to the amino-functionalized one (370 m^2/g) from the work by Najafi et al. (2012). However, a comparison between the two materials on the removal of Cd^{2+} and Pb^{2+} shows higher adsorption capacities in favor of NH_2 -SNHS, which recorded 40.73 mg/g and 96.79 mg/g respectively compared to 18.48 mg/g and 13.87 mg/g for the same ion metals.

Feng et al. (2010) studied the adsorption of heavy metal ions Cd^{2+} and Zn^{2+} from waste water. In this particular case, magnetic hydroxyapatite (Fe_3O_4 -HA) nanoparticles were used as an adsorbent. A two-stage co-precipitation synthesis route was followed and the resultant nano material's adsorption capacity was in the order $Zn^{2+} > Cd^{2+}$. Still on iron-based modified materials, Mei et al. (2010) investigated the removal of Cu^{2+} ions from waste water via adsorption using amino-functionalized magnetic nanoparticles (NH_2 - Fe_3O_4). The particles were synthesized by means of the covalent binding method in which 1,6-hexadamine was employed. A high adsorption capacity of 25.77 mg/g was reported. It was also reported that the nanoparticles were exceptionally stable with desorption studies showing exceptionally high efficiencies, constant for 15 cycles. The removal efficiency on Cu^{2+} remained at 100% after 15 cycles of continued use and regeneration for the adsorbent. Examples of methods popularly employed in the modification of different nanoparticles are shown in Table 1.

Among the ten heavy metal ions (Cu, Cd, Co, Ni, Pb, As, Cr, Zn, Mn, and Hg) considered for this review (Table 1), it is interesting to note that copper had the most research coverage with more than 60% of the differently modified nano particles, while arsenic and manganese had the least. A possible relationship between the modification methods and adsorption capacity was explored and the data was presented in Table 1.

3.1. Silica based modified nanoparticles

A variety of nanomaterials with different functionalities were derived from silica nanoparticles via surface modification. It is interesting to note that grafting was the most popularly employed method in the modification of silica nanoparticles. The effect of modification in

Table 1
Adsorption Capacities of differently modified nanoparticles for different heavy metal ions.

Material	Functional Group	Modification Method	Adsorption Capacity (mg/g)										Reference
			Cu	Cd	Co	Ni	Pb	As	Cr	Zn	Mn	Hg	
NH ₂ -SiO ₂	Amino-	Hydrothermal method	138.5	–	–	–	982.1	–	–	–	–	–	(Hao et al., 2012)
NH ₂ -SNHS	Amino-	Covalent attachment	–	4.73	–	31.29	96.79	–	–	–	–	–	(Najafi et al., 2012)
NH ₂ -MCM-41	Amino-	Grafting	–	18.25	–	12.36	57.74	–	–	–	–	–	(Heidari et al., 2009)
G-SBA-15-N-E	Amino-	Grafting	22.24	–	–	–	–	–	–	–	–	–	(Aguado et al., 2009)
G-SBA-15-N-C	Amino-	Grafting	15.25	–	–	–	–	–	–	–	–	–	(Aguado et al., 2009)
G-SBA-15-N-C-H	Amino-	Grafting	24.78	–	–	–	–	–	–	–	–	–	(Aguado et al., 2009)
G-SBA-15-NN-E	Amino-	Grafting	52.74	–	–	–	–	–	–	–	–	–	(Aguado et al., 2009)
NS	Amino-	Post grafting	6.35	0.00	0.00	0.059	–	–	5.20	–	–	–	(Bois et al., 2003)
NNS	Amino-	Post grafting	31.77	1.12	3.54	8.80	–	–	10.40	–	–	–	(Bois et al., 2003)
NNS	Amino-	Post grafting	31.77	0.00	5.89	8.80	–	–	12.99	–	–	–	(Bois et al., 2003)
[NSI-OH-OMIM + Tf2N-]	[OMIM + Tf2N-]-	Acid Activation of Silica	–	–	–	–	269.4	–	–	–	–	–	(Mahmoud et al., 2011)
[NSI-NH2-OMIM + Tf2N-]	[OMIM + Tf2N-]-	Physical adsorption of IL	–	–	–	–	–	–	–	–	–	–	(Mahmoud et al., 2011)
[NSI-NH2-OMIM + Tf2N-]	[OMIM + Tf2N-]-	Chemical immobilization	–	–	–	–	186.5	–	–	–	–	–	(Mahmoud et al., 2011)
SH-SiO ₂	Thiol-	Direct reaction	–	13.87	–	–	18.48	–	–	–	–	208.6	(Rostamian et al., 2011)
Fe ₃ O ₄ -NH ₂	Amino-	Covalent binding	25.77	–	–	–	–	–	–	–	–	–	(Mei et al., 2010)
Fe ₃ O ₄ @PAA-NH ₂	PAA and Amino-	Functionalization via carbodiimide activation	12.43	–	–	–	–	–	11.24	–	–	–	(Ge et al., 2012; Huang et al., 2009)
Fe ₃ O ₄ -NH ₂	Amino-	Hydrothermal reduction	–	–	–	–	40.10	–	–	–	–	–	(Tan et al., 2012)
Fe ₃ O ₄ -NH ₂	Amino-	Hydrothermal method	523.6	446.4	–	–	369.0	–	–	–	–	–	(Xin et al., 2012)
Fe ₃ O ₄ @SiO ₂ -NH ₂	SiO ₂ and Amino-	Sol-gel method	–	–	–	–	243.9	–	–	–	–	–	(Zhang et al., 2013)
Fe ₃ O ₄ @SiO ₂	SiO ₂ -	Surface coating	–	–	–	–	–	–	–	–	–	–	(Wang et al., 2010)
Fe ₃ O ₄ @SiO ₂	Amino-	Surface functionalization	29.87	22.48	–	–	76.66	–	–	–	–	–	(Wang et al., 2010)
Fe ₃ O ₄ @SiO ₂	SiO ₂ -	Surface coating	12.71	–	–	–	82.88	–	–	–	–	–	(Zhang et al., 2013)
Fe ₃ O ₄ @SiO ₂ -TETA	TETA-	Covalent binding	30.50	–	–	–	62.16	–	–	–	–	–	(Zhang et al., 2013)
SH-mSiO ₂ @Fe ₃ O ₄	SiO ₂ and Thiol-	Modified Stober method	–	–	–	–	–	–	–	–	–	–	(Shen et al., 2012)
Fe ₃ O ₄ -EDA	EDA-	–	87.72	–	–	–	–	–	137.0	–	–	–	(Shen et al., 2012)
Fe ₃ O ₄ -DETA	DETA-	–	94.30	–	–	–	–	–	149.3	–	–	–	(Shen et al., 2012)
Fe ₃ O ₄ -TETA	TETA-	–	92.60	–	–	–	–	–	204.1	–	–	–	(Shen et al., 2012)
Fe ₃ O ₄ -TEPA	TEPA-	–	116.8	–	–	–	–	–	370.4	–	–	–	(Shen et al., 2012)
Fe ₃ O ₄ @APS@AA-co-CA	Amino-,APS and AA	Chemical immobilization	126.9	29.60	–	–	166.1	–	–	43.4	–	–	(Ge et al., 2012)
PGHyFeO-COOH	COOH-	Grafting method	–	147.2	–	–	211.4	–	–	–	–	155.0	(Manju et al., 2002)
PPhSi-Fe ₃ O ₄	PPhSi-	Covalent Grafting	–	–	–	–	–	50.50	35.21	–	–	–	(Badrudoza et al., 2013)
Fe ₃ O ₄ -SDS	SDS-	2-stage co-precipitation	24.30	–	–	41.20	–	–	–	59.20	–	–	(Adeli et al., 2017)
Fe ₃ O ₄ -HAP	Hdroxyapatite-	Co-precipitation	–	220.8	–	–	–	–	–	140.6	–	–	(Feng et al., 2010)
Fe ₃ O ₄ -CGT	Cellulose and Amino-	Co-precipitation	95.32	–	–	–	–	–	–	–	–	401.2	(Pan et al., 2012)
Fe ₃ O ₄ -PR	Polyrhodamine	Grafting	–	–	–	–	–	–	–	–	–	179.0	(Song et al., 2011)
CM-β-CD-Fe ₃ O ₄	CM-β-CD-	Chemical immobilization	47.2	–	–	–	–	–	–	–	–	–	(Badrudoza et al., 2011)
DNPH-γ-Al ₂ O ₃	DNPH-	Grafting via Carbodiimide method	–	83.33	41.66	18.8	100.0	–	100.0	–	6.289	–	(Alkhami et al., 2010)
FeAA	Fe3O4	Chemical immobilization	–	–	–	–	28.08	–	–	–	–	–	(Huang et al., 2007)
		FBR-Fenton Reaction	–	–	–	–	–	–	–	–	–	–	

general and the modification method in particular is observed in all the materials that were tested with the various heavy metal ions. A test on copper for example, using four different types of amino-functionalized silica, SBA-15 (Aguado et al., 2009) showed a general increase of the adsorption capacity with degree of functionalization and treatment. A significant jump in adsorption capacity is observed in the case of copper grafted with two amino groups and that with one amino group. Between these two modified silica materials, it is noted that one with two grafted amino-groups (G-SBA-15-NN-E) showed a higher adsorption capacity (0.83 mmol/g) compared to those with a single amino-functional groups (G-SBA-15-N-C, G-SBA-15-N-E and G-SBA-15-N-C-H), which gave 0.24 mmol/g, 0.35 mmol/g and 0.39 mmol/g respectively. A comparison between the four materials shows that the material SBA-15-N-C-H, where (C) and (H) represent calcination at 550 °C for 5 h and further hydration of the material with boiling water for 4 h respectively, had a higher adsorption capacity compared to the material SBA-15-N-C, which only went through calcination at 550 °C for 5 h. Adsorption capacities for the two were 0.39 mmol/g and 0.24 mmol/g respectively. The reason for the higher capacity is explained by an increase in silanol groups – a direct result of the hydration process, (Aguado et al., 2009). Also, the material SBA-15-NN-E exhibited a higher capacity compared to SBA-15-N-E. The difference between the two was in the number of amino-groups. The superior number of the functional groups translated to a superior adsorption capacity. The (E) in this case represent extraction by ethanol refluxing for 24 h. The three processes, calcination, hydration and extraction were template removal processes and it is interesting to note that they also had a bearing on the capacities of the four materials.

A similar scenario is also observed from the work by Bois et al. (2003). In this case silica nanoparticles were functionalized using amino propyl- (-N), amino-ethylaminopropyl- (-NN), 2-aminoethylaminopropyl- (-NNN) as well as mercaptopropyl- (-S) functional groups. It should be noted that the mercaptopropyl-functionalized material was not considered in this review. Thus three modified materials, NS, NNS, and NNNS were considered. The grafting method was again used for the modification process. A comparison of the three modified materials shows a general increase in the adsorption capacity with the increase in the number of amino-groups. Highest capacities were recorded with Cu^{2+} in which a significant increase was noted between NS and NNS. The adsorption capacity however remained constant between NNS and NNNS (Table 2). The same behavior was also observed on Ni^{2+} . This can possibly be explained by the effect of functional group loading. The work reported by Li et al. (2011) revealed that a high loading of

functional groups (Thiol in this case) does not directly translate to a high adsorption capacity and this, they noted, is particularly so with porous materials like silica. On the same note, Hao et al. (2012) also observed that the post grafting method, achieved via covalent linking of organo-silane species with surface free silanol groups exhibited some drawbacks. Firstly, the pore size of the modified nanomaterial is reduced owing to the attachment of layers of functional groups during modification. Secondly, the method is said to result in an inhomogeneous surface, a direct consequence of organic moieties accumulating near pore entrances as well as exterior surfaces. In overview, orthogonal experiments coupled with the hydrothermal method to give a simple amino-functionalized silica ($\text{NH}_2\text{-SiO}_2$) seems the best modification method as witnessed by the highest adsorption capacities on Cu^{2+} and Pb^{2+} metal ions, data shown in Table 1.

3.2. Iron based modified materials

Unlike in the silica case where modification was predominantly by the grafting method, quite an assortment of methods were employed in iron based modified materials synthesis, ranging from grafting, modified Stober method, hydrothermal to the sol-gel method.

From a study by Shen et al. (2012), nano magnetic polymers (NMPs) were functionalized using four different multi-amino-groups: ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA) and tetraethylenepentamine (TEPA). The modified materials were tested on Cu^{2+} and Cr^{6+} metal ions and the results revealed a general increase in the adsorption capacity as the number of amino-functional groups increased in both ions. However, the increase was more pronounced on Cr^{6+} as shown in Fig. 1. An overall analysis of the data from Table 1 again gives the hydrothermal method, from which simple amino-functionalized magnetic nanoparticles ($\text{Fe}_3\text{O}_4\text{-NH}_2$) were prepared, as the optimal method since significantly high adsorption capacities were recorded in the removal of Cu^{2+} , Co^{2+} and Pb^{2+} . A comparative study by Mahmoud et al. (2013) on two materials, $\text{Fe}_3\text{O}_4\text{@SiO}_2$ and $\text{Fe}_3\text{O}_4\text{@SiO}_2\text{-TETA}$ showed higher adsorption capacities on Cu^{2+} for the core-shell material in which further functionalization was done using triethylenetetramine (TETA) to give 3 amino – functional groups. The trend however did not follow on Pb^{2+} metal ions where the adsorption capacity actually decreased with further functionalization.

3.3. Alumina based modified materials

Extensive research has been carried on the modification of magnetic

Table 2

A comparison of adsorption capacities of selected naked and modified nanoparticles.

Nanomaterial	Adsorption Capacity (mg/g)										Reference
	Cu	Cd	Co	Ni	Pb	As	Cr	Zn	Mn	Hg	
SiO_2	6.35	0.00	0.00	0.880	5.20	–	–	–	–	–	(Bois et al., 2003)
NS	6.35	0.00	0.00	0.059	5.20	–	–	–	–	–	(Bois et al., 2003)
NNS	31.77	1.12	3.54	8.80	10.40	–	–	–	–	–	(Bois et al., 2003)
NNNS	31.77	0.00	5.89	8.80	12.99	–	–	–	–	–	(Bois et al., 2003)
SNHS	–	20.82	–	8.38	26.86	–	–	–	–	–	(Najafi et al., 2012)
$\text{NH}_2\text{-SNHS}$	–	40.73	–	31.29	96.79	–	–	–	–	–	(Najafi et al., 2012)
Fe_3O_4	–	–	–	–	–	–	–	–	–	51.5	(Pan et al., 2012)
SH- $\text{Fe}_3\text{O}_4\text{-NMP}$ (0 g Fe_3O_4)	–	–	–	–	–	–	–	–	–	129.9	(Pan et al., 2012)
SH- $\text{Fe}_3\text{O}_4\text{-NMP}$ (1.0 g Fe_3O_4)	–	–	–	–	–	–	–	–	–	254.4	(Pan et al., 2012)
Fe_3O_4	–	–	–	–	–	25.13	14.93	–	–	–	(Badrudodoza et al., 2013)
PPhSi- Fe_3O_4	–	–	–	–	–	50.50	35.21	–	–	–	(Badrudodoza et al., 2013)
Fe_3O_4	25.42	–	–	–	140.9	–	–	–	–	–	(Mahmoud et al., 2013)
$\text{Fe}_3\text{O}_4\text{@SiO}_2$	12.71	–	–	–	82.88	–	–	–	–	–	(Mahmoud et al., 2013)
$\text{Fe}_3\text{O}_4\text{@SiO}_2\text{-TETA}$	30.50	–	–	–	62.16	–	–	–	–	–	(Mahmoud et al., 2013)
Ca-alginate -P.	–	–	–	–	–	–	–	–	–	63.7	(Xu et al., 2013)
Chrysosporium	–	–	–	–	–	–	–	–	–	–	
MNP-Ca-alginate -P.	–	–	–	–	–	–	–	–	–	185.25	(Xu et al., 2013)
Chrysosporium	–	–	–	–	–	–	–	–	–	–	

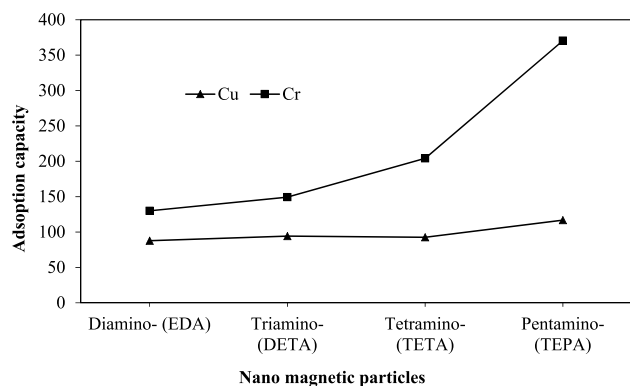


Fig. 1. Effect of multi-functional groups on nano magnetic polymers.

and silica nanoparticles in recent years but no appreciable work has been reported on alumina particles in this regard. From Tables 1 and 2, 4-dinitrophenylhydrazine modified alumina (DNPH- γ - Al_2O_3) gave quite comparable adsorption capacities for the heavy metal ions Cd^{2+} , Co^{2+} , Ni^{2+} , Pb^{2+} , Cr^{3+} and Mn^{2+} . The particles were modified using chemical immobilization. Activated alumina-supported iron oxide is another modified material that was prepared from the FBR-Fenton reaction (Huang et al., 2007). The material was tested on Pb^{2+} removal only. The result however could not compare to DNPH- γ - Al_2O_3 on the same metal ion.

3.4. A comparison of pure and modified nanoparticles

The data in Table 2 compares adsorption capacities of modified nanoparticles with their corresponding naked or pure nanoparticles. The data presents a general increase in the adsorption capacity with the level of functionalization or modification. The only exception according to the data presented in Table 2 is, the modified $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ and its triethylenetetramine (TETA) modified derivative, $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -TETA which showed a reverse trend with Pb^{2+} metal ion. The low adsorption of Pb^{2+} by the former is explained by the change in the surface groups as well as the surface pH, while that of the latter is assumed to be a result of the inclusion of strong selectivity characters into the material that are in favor of Cu^{2+} (Mahmoud and Al-Bishri, 2011). The general upward trend of the adsorption capacity with functionalization is clearly shown in Figs. 2 and 3. From Fig. 2 however, the adsorption of Co^{2+} and Pb^{2+} showed a continuous increase as the number of functional groups increased, between NS and NNNS while with the other two, the capacities were constant between NNS and NNNS and the reason for this behavior has been discussed. Also from the same Fig. 3, it can be observed that there was virtually no change in the adsorption

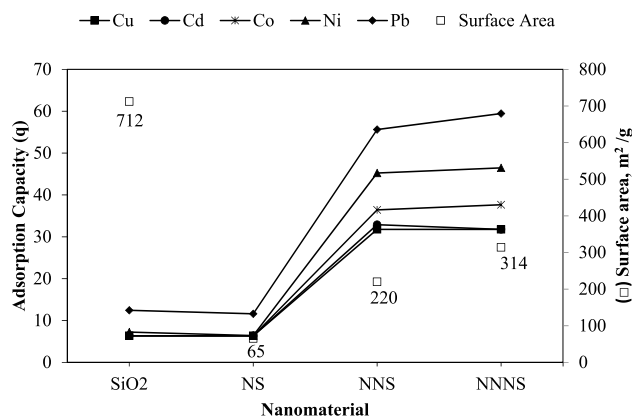


Fig. 2. Comparison of adsorption capacities of naked and modified silica nanoparticles.

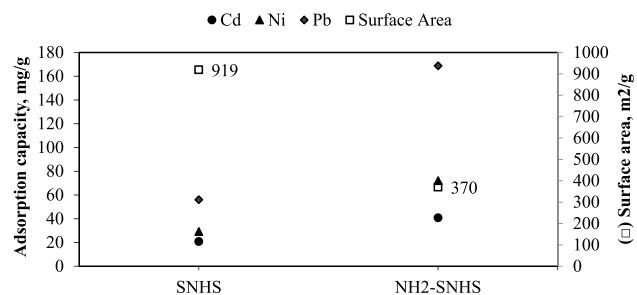


Fig. 3. Behavior of the specific surface area and adsorption capacity with surface modification for silica nano hollow spheres.

behavior of the amino-functionalized silica (NS) and that of the pure silica (SiO_2) as evidenced by the same values of the adsorption capacity. This is possibly because of the sharp drop in the specific surface area shown in Fig. 2 resulting from a possible high accumulation of the amino-functional groups – a general weakness of the post grafting method as outlined by Li et al. (2011) and Hao et al. (2012).

Fig. 3 shows a general increase in adsorption capacity as the specific area is increased with introduction of multi-functional group materials. The increase however does not go beyond 3 amino-group loading possibly due to reasons already explained. However, it has to be appreciated that this trend is not global since it is possibly dictated by the modification method employed.

Furthermore, as presented in Table 2, the modification of magnetic nanoparticles using cationic ligand, phosphonium silane, denoted PPhSi- almost doubled the adsorption capacity of the resultant nanoadsorbents ($\text{PPhSi-Fe}_3\text{O}_4$) on Cr^{6+} and As^{5+} metal ions. For the two metal ions, the pure magnetic nanoparticles, (Fe_3O_4) gave adsorption capacities of 14.93 mg/g and 25.13 mg/g against 35.21 mg/g and 50.50 mg/g of the functionalized particles, ($\text{PPhSi-Fe}_3\text{O}_4$). Another nanomaterial, *Phanerochaete Chrysosporium*, a white rot fungus was immobilized with both Ca-alginate and magnetic nanoparticles to give a modified derivative, MNPs-Ca-alginate immobilized *P. Chrysosporium* (Xu et al., 2013). The material was tested on Pb^{2+} metal ions and from Table 2, it can be seen that the adsorption capacity almost tripled that of Ca-alginate - *P. Chrysosporium*. Thus, the role of surface modification as tool for improving the adsorption efficiency of the various nanomaterials is clearly portrayed in Figs. 2 and 3.

4. Specific surface area and adsorption capacity

Whilst a high specific surface area might not automatically translate to a higher adsorption capacity, it is important to note that the adsorption capacity is to a large extent a function of the particles' specific surface area. Tuutijarvi et al. (2009) reported three maghemite nanomaterials synthesis from three different sources, commercial source (CM), sol-gel synthesis route (SM) as well as the mechanochemical route (MM). Using these materials as adsorbents on Arsenic, the adsorption capacities were in the order $\text{MM} > \text{SM} > \text{CM}$. According to the authors, the trend was explained by their differences in specific surface areas which decreased in the order $\text{MM} (203.2 \text{ m}^2/\text{g}) > \text{SM} (90.4 \text{ m}^2/\text{g}) > \text{CM} (51.0 \text{ m}^2/\text{g})$ respectively.

It should be highlighted that very few comparisons in this work are documented to show how the specific surface area of the synthesized nanoparticles (both modified and unmodified) relates to the adsorption capacity on the various heavy metal ions. However, available information as presented in Table 3 gives quite useful information in this regard. In terms of the specific surface area, it is interesting to note that silica based nanoparticles have higher specific surface areas compared to both the iron based and alumina based nanoparticles. Silica nano hollow spheres, for instance have specific surface areas as high as $919 \text{ m}^2/\text{g}$ while SiO_2 in general was found to be around $712 \text{ m}^2/\text{g}$ (Najafi et al., 2012; Rostamian et al., 2011; Bois et al., 2003). Lim et al.

Table 3

The relationship between the specific surface area and adsorption capacity.

Nanomaterial	SSA (m ² /g)	Adsorption Capacity (mg/g)										Reference
		Cu	Cd	Co	Ni	Pb	As	Cr	Zn	Mn	Hg	
SiO ₂	712	6.35	0.00	0.00	0.88	5.20	–	–	–	–	–	(Bois et al., 2003)
NS	65	6.35	0.00	0.00	0.06	5.20	–	–	–	–	–	(Bois et al., 2003)
NNS	220	31.77	1.12	3.54	8.80	10.4	–	–	–	–	–	(Bois et al., 2003)
NNNS	314	31.77	0.00	5.89	8.80	12.99	–	–	–	–	–	(Bois et al., 2003)
NH ₂ -SiO ₂	553	138.53	–	–	–	982.13	–	–	–	–	–	(Hao et al., 2012)
SNHS	919	–	20.82	–	8.38	26.86	–	–	–	–	–	(Najafi et al., 2012)
NH ₂ -SNHS	370	–	40.73	–	31.29	96.79	–	–	–	–	–	(Najafi et al., 2012)
G-SBA-15-N-E	565	22.24	–	–	–	–	–	–	–	–	–	(Aguado et al., 2009)
G-SBA-15-N-C	345	15.25	–	–	–	–	–	–	–	–	–	(Aguado et al., 2009)
4G-SBA-15-N-C-H	178	24.78	–	–	–	–	–	–	–	–	–	(Aguado et al., 2009)
G-SBA-15-NN-E	246	52.74	–	–	–	–	–	–	–	–	–	(Aguado et al., 2009)
G-SBA-15-NNN-E	48	–	–	–	–	–	–	–	–	–	–	(Aguado et al., 2009)
PPy	85	–	–	–	–	–	–	–	–	–	–	(Lim et al., 2012)
PPy@SiO ₂	306	1.27	1.12	–	1.76	109.82	–	0.52	–	–	194.57	(Lim et al., 2012)
PR-Fe ₃ O ₄	94.65	–	–	–	–	–	–	–	–	–	179	(Song et al., 2011)
CM-β-CD-Fe ₃ O ₄	110.9	47.2	–	–	–	–	–	–	–	–	–	(Badrudodoza et al., 2011)
Fe ₃ O ₄ -HAP	142.5	–	220.78	–	–	–	–	–	140.63	–	–	(Feng et al., 2010)
Fe ₃ O ₄ -CGT	137.7	95.32	–	–	–	–	–	–	–	–	401.18	(Pan et al., 2012)
Fe ₃ O ₄	77	–	–	–	–	–	–	–	–	–	–	(Zhang et al., 2013)
Fe ₃ O ₄ @SiO ₂ -NH ₂	138	–	–	–	–	243.9	–	–	–	–	–	(Zhang et al., 2013)
SNHS	919	–	–	–	–	–	–	–	–	–	–	(Rostamian et al., 2011)
SH-SNHS	823	–	13.87	–	–	18.48	–	–	–	–	209.58	(Rostamian et al., 2011)
PPhSi-Fe ₃ O ₄	105.7	–	–	–	–	–	50.5	35.21	–	–	–	(Badrudodoza et al., 2013)
Fe ₃ O ₄	114.0	–	–	–	–	–	–	–	–	–	–	(Wang et al., 2010)
Fe ₃ O ₄ @SiO ₂ -NH ₂	216.2	29.87	22.48	–	–	76.66	–	–	–	–	–	(Wang et al., 2010)
SH-mSiO ₂ @Fe ₃ O ₄	321	–	–	–	–	91.17	–	–	–	–	260.77	(Li et al., 2011)
NH ₂ -Fe ₃ O ₄	25.94	523.6	446.4	–	–	369.0	–	–	–	–	–	(Xin et al., 2012)
DNPH-γ-Al ₂ O ₃	42.62	–	83.33	41.66	18.18	100.0	100.0	–	–	6.289	–	(Afkhani et al., 2010)
Al ₂ O ₃	127	–	–	–	–	–	–	–	–	–	–	(Huang et al., 2007)
FeAA	170	–	–	–	–	28.083	–	–	–	–	–	(Huang et al., 2007)

(2012) reported the surface area of mesoporous silica which is greater than 1000 m²/g. Magnetic nanoparticles on the other hand have documented areas around 77 m²/g and 114 m²/g (Zhang et al., 2013; Wang et al., 2010). Given these figures, one would expect higher adsorption performances with silica based materials. On the contrary, it should be highlighted that even with these high surface area, silica based materials have generally exhibited lower adsorption capacities compared to iron based particles. High specific surface areas for silica based materials are mainly attributed to their porous nature and this also explains the sharp drop in surface area at the onset of functionalization, as the particles go through surface modification (Fig. 3).

From the data in Table 3, a general decline in the specific surface area with surface modification is observed with mostly silica based materials. Incorporation of functional groups is known to clog particle pores so that the surface area is reduced in the process. However, the surface area seems to increase with introduction of multi-functional group materials. Further work on porous materials was reported by Chomchoey et al. (2013) in which the effect of surface modification was assessed by varying the ratio of activated carbon (AC) to magnetic nanoparticles (MNPs). From Table 4, the decline in surface area is observed based on activated carbon. Again the same effect is explained, where the activated carbon pores are covered by layers of accumulating magnetic nanoparticles thereby reducing the surface area.

Table 4

The BET specific surface area as a function of the degree of modification (Chomchoey et al., 2013).

Material	BET SSA (m ² /g)	V _{microporous} (m ³ /g)
Pure MNPs	80.38	0.3915
AC-MNPs (1:1)	551.51	0.4873
AC-MNPs (2:1)	720.72	0.5083
AC-MNPs (3:1)	750.31	0.4610
Pure AC	1043.64	0.4719

With iron and alumina based materials, no comparative information was available on the effect of functionalization or surface modification to the particle surface area. The same trend however, is expected where the specific surface area decreases with modification even though these materials are generally not porous in nature. In their study on silica coated magnetite particles, Girginova et al. (2010) observed that the particle surface area decreased from 13 m²/g to 11 m²/g when the pure Fe₃O₄ particles were coated with silica. This is so because coating generally increases the particle size, thereby decreasing the surface area (Girginova et al., 2010). This, however, was not the case with activated alumina supported iron oxide. Here, the surface area of the modified material was higher than that of the pure material and the explanation to this effect could not be ascertained.

5. Conclusions

From the present review work, the vital role of surface modification in improving the performance of nano-adsorbents was clearly observed. A comparison between pure and modified particles in terms of adsorption capacities showed that the latter had superior capacities. The modification methods employed on different nano-materials were also found to impact on the performance of the nano-materials in the removal of heavy metal ions from aqueous systems. From the above analysis, it can be concluded that the hydrothermal method is the best modification method for both silica and iron based nanoparticles. The relationship between surface modification, specific surface area and the adsorption capacity was also established. The specific surface area was observed to decrease with the degree of modification and/or functionalization, while at the same time the adsorption capacity was generally observed to increase. With the post grafting method, the adsorption capacity was observed to be dependent on the level of functional group loading. Lastly, surface modification was found to enhance the stability of nano-materials, especially magnetic materials.

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