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A review on reactive adsorption for potential environmental applications

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Abstract The aim of this paper is to present a critical review on reactive adsorption processes. The impact of surface modification on adsorption behavior of various adsorbents in context of reactive adsorption has been reviewed. Various characterization and detection methods involved to access and verify the surface morphology of adsorbent, presence of surface functionalities on adsorbent, and concentration of adsorbate have been concisely presented. The paper also delves into the inadequately researched grey areas of reactive adsorption which require further attention such as modeling and adsorbent regeneration so as to make the process more economic. The applicability of reactive adsorption to ensure a cleaner environment has also been briefly discussed. This article also underlines the areas, in which reactive adsorption can be implemented on a pilot scale.

Keywords Reactive adsorption · Adsorbent modification · Modeling · Adsorbent regeneration · Process intensification

Abbreviations

c_i	fluid phase concentration in interparticle voids, mol/m^3
$c_{p,i}$	fluid phase concentration in pores, mol/m^3
$c_{s,i}$	fluid concentration in pores at the close vicinity of pore surface, mol/m^3
d_p	particle diameter, m
D_e	effective diffusion coefficient in pores, m^2/s
k	reaction rate constant, 1/s
k_a	adsorption rate constant, m/s
k_c	mass transfer coefficient, m/s
K	adsorption linear equilibrium constant
$N_{W,i}$	mass flux, mol/(m^2 s)
q_i	concentration in the solid phase, mol/m^3
r	radial coordinate, m
r	rate of homogeneous reaction, mol/(m^3 s)
r_S	rate of heterogeneous reaction, mol/(m^3 s)
$S_{P,i}$	rate of adsorption (adsorption + reaction), mol/(m^3 s)
t	time, s
u	interstitial fluid velocity, m/s
x	axial coordinate, m
ε	bed porosity
ε_p	particle porosity
ν	stoichiometric coefficient
Ψ	kinetic function

1 Introduction

Various *ex-situ* and *in-situ* environmental remediation technologies such as absorption, chemical oxidation, adsorption, distillation etc., have been proposed to comply with the strict norms of pollution abatement. Among these, adsorption has been cited as the most prevalent separation tool in almost every sector, be it for the purpose of drying air, water treatment, air purification, removal of odor, or for the separation of components from their mixture (Ritter and St 2008). Perhaps, the technology had suffered certain setbacks such as the overall process cannot be optimized though the individual units might operate at optimal conditions. Such drawbacks can be overcome by introducing a unique class of separation process, referred to as Reactive Separation processes.

Reactive separation processes may be defined as the coupling of chemical reaction and physical separation in a single unit operation (Kulprathipanja 2002). Although the technology is not new, the academic and industrial communities

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have recently shown interest in the development and commercialization of such processes in response to the so called ‘Process Intensification’. Among various reactive separation processes, reactive adsorption has received attention over the past few decades (Stankiewicz 2003). This interest is reflected in an increase in number of publications issued over the past few years. Out of a total of around 1800 papers published so far, about 1600 papers have been published since 1993. A reactive adsorption is a combination of chemical reaction and adsorption in single equipment. A single reactor-adsorber unit may reduce the design complexity and capital investment and may yield products of high purity with reduced or even eliminated downstream processing. The technology has proved itself superior to conventional adsorption as it offers an overall optimum point with heat integration benefits, cost effectiveness, and high separation. Furthermore, reaction equilibrium is shifted in a favorable manner. In recent years, the technology has gained attention in response to Process Intensification which would eventually lead to an overall optimized process. The recent advancement is supplemented by the development of better engineered adsorbents.

We have not come across any review paper on reactive adsorption technology till date. This review is an attempt to summarize the significant contributions made so far in the area of reactive adsorption. It further critically analyzes the pitfalls of studies made so far and delves into the grey areas of reactive adsorption which need to be studied in order to make reactive adsorption commercially more attractive. The various types of adsorbents involved and their applications in different areas of pollution abatement have been discussed with the major emphasis on universally accepted activated carbon. The major objective of this review is to study the key aspects associated with adsorbent modification for reactive adsorption process. Modeling and simulation is one of the areas which have been widely researched in simple adsorption processes. Mathematical modeling helps in understanding the process behavior prior to its commercial implementation. Thus, modeling studies are important for designing of complex processes such as reactive adsorption. The areas suitable for potential applications of reactive adsorption have also been emphasized. The review will aid a researcher to select an appropriate adsorbent, modify conditions in order to operate efficiently and direct ones research accordingly.

2 Adsorbent modification for removal of wastewater pollutants by reactive adsorption

The re-use of wastewater after appropriate treatment may contribute to water sustainability. Disposal of wastewater from industrial sources is in itself a challenging task. Most of the large scale industries are well equipped with the on-site wastewater treatment facility, while the others simply discard it into nearby water bodies posing a serious threat to the environment.

Among the different wastewater treatment technologies, adsorption is the most economically viable option. Activated carbon (AC), well known for its wide applications, has a high surface area and porosity to contain components, and ease their separation. However, surface area and porosity alone, can support physical adsorption while the situation is much different and complex for reactive adsorption. Therefore, incorporation of materials such as bases, acids, complexing agents, oxidizing/reducing agents, and metals via various techniques is often required to drive a reaction (Lodewyckx 2006). The most commonly employed technique is impregnation (Shukla et al. 2010; Bagreev and Bandosz 2002; Przepiorski et al. 1997; Matatov-Meytal and Sheintuch 1997; Hu et al. 2011). Other techniques include the introduction of the catalytic phase as a separate component and then blending the materials (Graham and Yuan 2005), reaction in the presence of an active binder (Nguyen-Thanh and Bandosz 2005) etc. Dispersion of the catalytic phase has to be ensured for an effective process.

Reactive adsorption is one step ahead in the world of adsorption. The technology has been successfully tested on a laboratory scale but not yet applied commercially for wastewater treatment. The adsorbent in reactive adsorption can be modified by one of the several ways. The modification procedure depends upon the nature of the adsorbate to be separated from the main stream, and on process conditions. Different laboratory studies to examine the effect of adsorbent modification have been conducted in various application areas. However, very few studies have been commercialized, the others being still investigated for potential applications. Some of the important sectors in which research on the applicability of reactive adsorption has been conducted, are discussed in the proceeding subsections.

2.1 Pharmaceuticals

Pharmaceuticals owing to their high consumption and less absorption by organisms are continuously introduced into the environment. Though, the fate of such pollutants is not yet exactly known, it has been predicted that their presence in environment may be threatening to both aquatic and terrestrial life. It was revealed that the conventional wastewater treatment methods such as adsorption are not always effective to eliminate/degrade the pharmaceutical compounds (Al-Ahmad et al. 1999; Gómez et al. 2007; Hernando et al. 2006; Li et al. 2008). Therefore, some advanced methodology such as reactive adsorption is required for the decontamination of water.

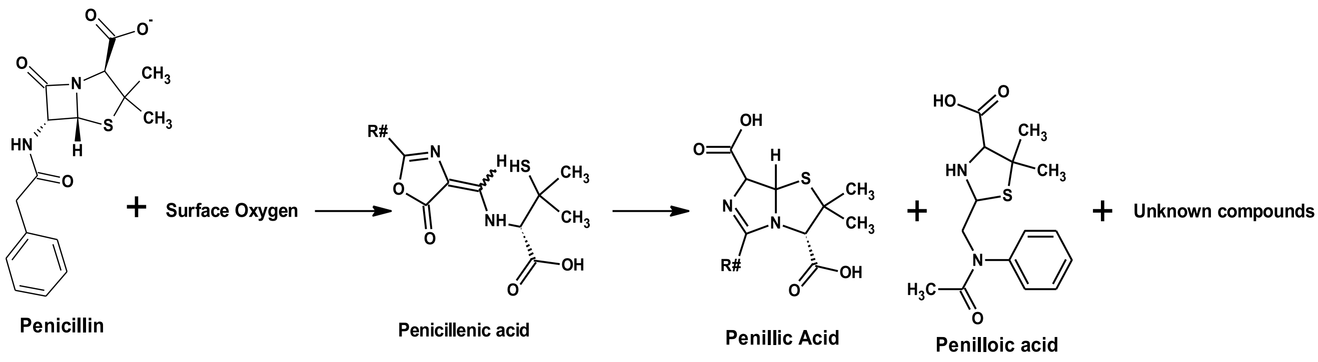


Fig. 1 Degradation of penicillin molecule by the oxygen functionalities introduced on the surface of adsorbent

Ania et al. (2010) showed the dependency of reactive adsorption of commonly used antibiotic, penicillin, on the surface characteristics of the adsorbent (Table 1). The incompatibility of the drug with acids, alkalis, oxidizing agents, naphthalene oils, vitamin B and heavy metal ions may be advantageous in the designing of a suitable reactive adsorbent for its simultaneous adsorption and degradation into some non-toxic product. Oxidation of carbon with nitric acid enhances the simultaneous hydrolysis of penicillin in acidic conditions to non-therapeutic products. In this case, oxygen functionalities created during the acid treatment may be significant for reactive adsorption/separation. The surface oxygen tends to degrade the penicillin molecule into non-toxic compounds. The formation of degradation intermediates was confirmed by HPLC analysis. The major intermediates were Penillic acid and Penilloic acid (Fig. 1).

The quantity of the intermediates formed during degradation was found to depend upon the polarity of the carbons (Fig. 2(a)). The hydrophilic nature of adsorbent (low $\mathrm{pH_{PZC}}$) favors the degradation of penicillin with large amounts of intermediates detected in solution. Moreover, the acidity/basicity of carbons played an important role in the adsorption and degradation of penicillin. The acidic nature of carbon was associated with the low adsorption capacity of penicillin and high reactivity (large amount of intermediates) inside the pores. In contrast, the basic nature enhances the adsorption capacity of penicillin but with less degradation inside the pores (Fig. 2(b)).

The reactive adsorption of penicillin inside the porous carbons was further confirmed by the thermal analysis. DTG profiles of adsorbents after penicillin uptake along with that of fresh adsorbents have been shown in Fig. 3. A peak between 200–400 °C corresponds to the desorption of penicillin and its degradation intermediates retained inside the pores. By virtue of similar chemical formulae of penicillin and its intermediates, both may get adsorbed on the same sites of the carbon and thus desorb in a similar temperature range.

2.2 Dyes

Wastewater from textile industries contains a significant amount of hazardous dyes (Wong and Yu 1999). So far, adsorption has been widely accepted process for the removal of dyestuffs from the effluent streams. The most commonly used adsorbents are clays (Alkan et al. 2005), activated carbon (McKay et al. 1998; Walker and Weatherley 2001), Chitosan and Chitin (Juang et al. 1997; Longhinotti et al. 1998), and cellulosic materials (Bousher et al. 1997). Due to the high operating cost of activated carbon, and the associated regeneration problems, the cost effective alternatives such as reactive adsorption have been looked upon. An ESI-MS study was conducted to study the behavior of a clay mineral, montmorillonite for the adsorption and hydroxylation of methylene blue in presence of hydrogen peroxide (Nogueira et al. 2009). The highly reactive surface of the clay promotes the heterogeneous catalytic oxidation of dye. However, the structure of calcined as well as pillared montmorillonite was completely altered resulting in the loss of reactive surfaces. The ESI-MS analysis suggested the simultaneous adsorption and chemical reactions on the clay surface (Fig. 4(a)). As the time proceeds, the intensity of the dye signal gradually decreased with the subsequent appearance of peaks with different intensities. These peaks may be of the intermediates formed by successive hydroxylation of the dye suggesting the reactive adsorption. Unlike montmorillonite, no intermediates were observed in case of pillared or heated montmorillonite (Fig. 4(b)). However, the peak intensity for the dye decreased with time pointing towards a simple adsorption. The study, therefore, suggests that montmorillonite, as such, can be used as a reactive adsorbent for the removal of methylene blue in presence of hydrogen peroxide.

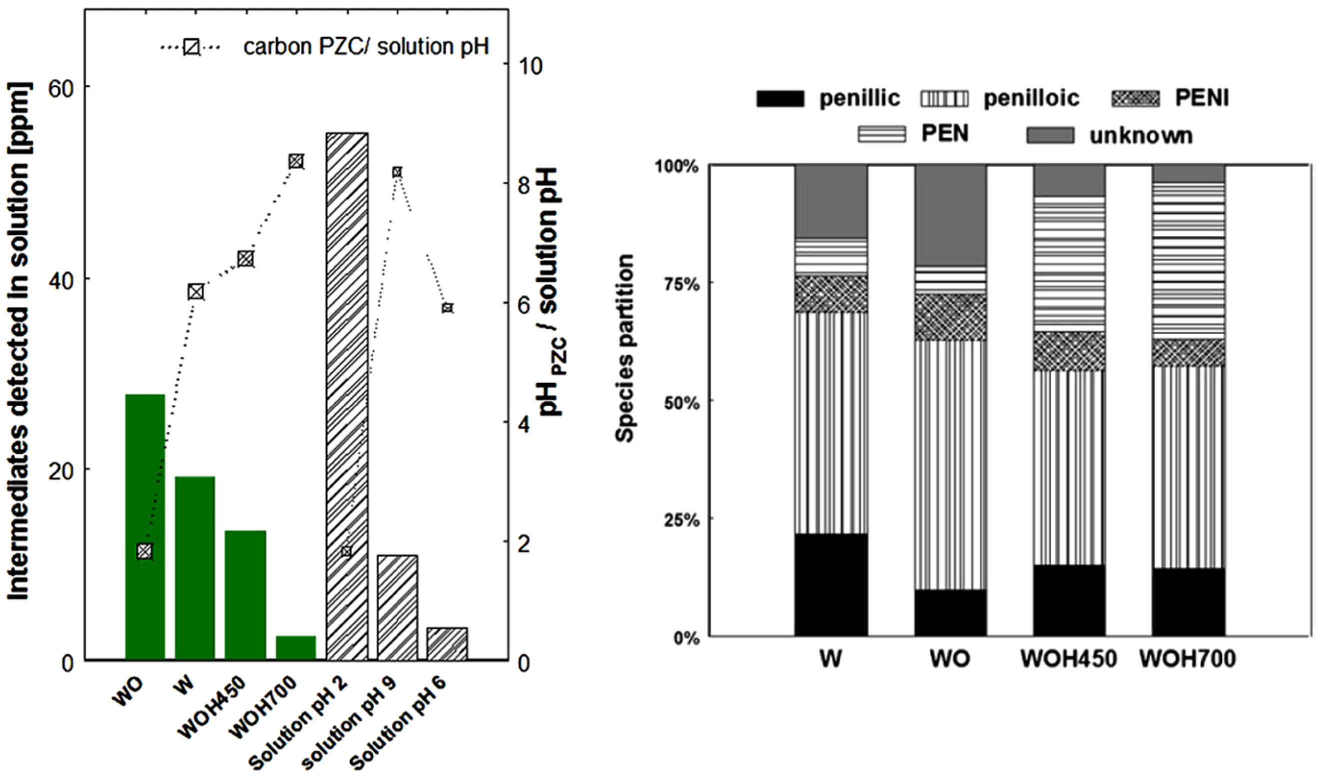
Besides, carbonaceous adsorbents obtained by the processing of sewage sludge have also been examined (Martin et al. 2003; Rio et al. 2005). Such adsorbents, in addition to carbon, contain inorganic oxides/hydroxides (Bagreev et al. 2001; Lu et al. 1995) to enhance the reactive adsorption.

Table 1 Summary of adsorbent modification for reactive adsorption in wastewater treatment

Adsorbate	Adsorbent	Modification procedure(s)	Adsorbent characterization method(s)	Adsorbate detection method(s)	Remark(s)	Reference(s)
Pollutants from wastewater	Activated carbon modified with H_2SO_4 at 150–270 °C	Chemical modification	Nitrogen adsorption, Base titration, FTIR	Sulfur analysis by microcoulometry	Chemical modification increases the mesoporous volume and thus favors the adsorption of large molecules	Jiang et al. (2003)
Penicillin G	Activated carbon modified with nitric acid (20 %)	Wet Oxidation and Thermal Treatment	Nitrogen adsorption, modified mass titration method, Thermal analysis, TPD-MS	UV-Visible spectrophotometer, Reverse-phase HPLC equipped with a photodiode array detector	The surface characteristics of modified carbon promote the reactive adsorption of Penicillin. Acid activated carbon posses low adsorption capacity and high rate of degradation. While it is vice-versa for basic carbon	Ania et al. (2010)
Phenol and its halogen derivatives	GAC modified with metal oxide catalyst	Wet impregnation technique	Nitrogen adsorption	UV-Vis spectrophotometer	Even after 10 cycles of regeneration, the adsorptive capacity remained unaffected	Matatov-Meytal and Sheintuch (1997)
Methylene Blue	Montmorillonite, Pillared clay and heat treated clay	Pillaring with poly (hidroxo aluminium) ions and heat treatment at 900 °C	Atomic absorption, Powdered X-ray diffractometry, Nitrogen adsorption, SEM coupled with energy dispersive spectroscopy, IR spectroscopy, and surface area analysis	UV-Vis spectrophotometer	The reactive surface on Montmorillonite supplements the hydroxylation and oxidation process. Unmodified clay is highly reactive as compared to modified clays	Nogueira et al. (2009)
Phenol and Salicylic Acid	Activated carbons modified with $(NH_4)_2S_2O_8$ and nitric acid respectively	Oxidation with $(NH_4)_2S_2O_8$ and nitric acid at different concentrations, Thermal treatment under N_2 flow at different temperatures	Nitrogen adsorption, elemental and proximate analyses, mass titration method	–	Physical morphology of an adsorbent is affected by the strength of oxidizing agent, temperature of heat treatment and operating conditions	Ania et al. (2002)

Table 1 (*Continued*)

Adsorbate	Adsorbent	Modification procedure(s)	Adsorbent characterization method(s)	Adsorbate detection method(s)	Remark(s)	Reference(s)
Phenol	Cobalt loaded activated carbon	Wet impregnation technique followed by calcination	XRD, EDS, SEM, and TGA	HPLC with UV detector, TOC analyzer	100 % decomposition and 80 % TOC removal was obtained in 60 minutes	Shukla et al. (2010)
	Cobalt/SBA-15	Incipient wetness impregnation followed by calcination	XRD, N_2 adsorption, high resolution transmission electron microscopy (HRTEM), and SEM	4-Aminoantipyrine spectrophotometric method, TOC analyzer, and nitroso-R-salt spectrophotometric method for Cobalt ion detection	Phenol removal >98 %, TOC removal ≈98 %	Hu et al. (2011)
Cadmium	Coconut shell derived activated carbon	Oxidation with nitric acid followed by heat treatment	FTIR, TPD, and Selective neutralization, XANES	Inductively coupled plasma (ICP) atomic emission spectrometer	Oxidation has profound effect on the adsorption of cadmium ions. Heat treatment drastically reduced the adsorption capacity	Jia and Thomas (2000)
Arsenate [As(V)]	Synthetic nanoscale zero-valent iron (NZVI)	Dropwise addition of $NaBH_4$ to Ne gas purged $FeCl_3{\cdot}6H_2O$	FE-SEM, HR-TEM, XRD, XPS, Mossbauer spectroscopy	Spectrometer with a triangular waveform	The adsorbent is effective in the adsorption of As (V) and can be applied to both *in-situ* and *ex-situ* groundwater treatment	Kanel et al. (2006)
Silver	Microparticles of Sulfodiphenylamine and Diaminonaphthalene Copolymers	Chemically oxidative polymerization in neutral acetonitrile/water solution	FTIR, NMR, Thermogravimetric analysis, Elemental analysis, XRD, Particle size measurements	UV-Vis spectrophotometer	The particle morphology is very effective in the elimination and recovery of noble metallic ions in wastewater	Li et al. (2005b)



(a) (b)

Fig. 2 (**a**) Quantification of Penicillin degradation intermediates after contact with carbons, (**b**) Distribution of penicillin and degradation intermediates inside the porous carbons "Reprinted from Adsorption, 17, 2011, 421–429, Reactive adsorption of penicillin on activated carbons, Ania, C.O., Pelayo, J.G., Bandosz, T.J., Figs. 5 and 6, Copyright (2011)"

Industrial sludges after pyrolysis were also tested for the cationic and anionic dyes (Seredych and Bandosz 2007b). Percent dye removal by sludge was found higher than those obtained by the commercial carbon. The reason can be attributed to the presence of minerals with ability of ion exchange and also to the high porosity of the adsorbents.

2.3 Phenol

Phenol and its derivatives are widely used in petroleum and petrochemical industries. By virtue of their toxic nature, it is mandatory to remove phenol from effluent streams. Adsorption is one of the techniques that have been practiced for the isolation of phenol and phenolic compounds. Degradation of phenolic compounds has also been studied by many researchers (Harmankaya and Gündüz 1995; Idris and Saed 2002; Marrot et al. 2008; Siedlecka and Stepnowski 2005). Furthermore, a combination of both adsorption and degradation of organic pollutants such as phenol was extensively studied by Shukla et al. (2010). Highly active sulfate radical with a high potential to oxidize the organic pollutant was used for the study rather than the hydroxyl ions used in other oxidation processes. A cobalt precursor was used as a catalyst for the activation of peroxymonosulfate (PMS). A year later, a recyclable Co/SBA-15 catalyst was employed for the simultaneous adsorption and degradation of phenol (Hu et al. 2011). The catalyst synthesized by wet impregnation technique posses a high activity even after prolonged usage. Cobalt as Co_3O_4 was found to activate the PMS which in turn causes the degradation of phenol present as a contaminant in wastewater. The best results were obtained when 10 wt% Co/SBA-15 was calcined at 400 °C for 5 h with almost complete mineralization of phenol. By virtue of heat treatment, the Co–O–Si species is formed which prevents the cobalt leaching.

2.4 Heavy metals

Increase in the presence of metals such as Silver, Arsenic, Mercury etc., in surroundings over the past few years has posed a serious threat to the environment. The principle sources of metal emissions are: petrochemicals, extractive, mechanical, metallurgical and other chemical industries. Heavy metals such as lead and mercury may alter the metabolism of organisms and in certain cases may even lead to fatal diseases such as cancer. Mercury in oil causes marketing, processing, and environmental hazards. It may attack process equipment made of copper and aluminum. Arsenic

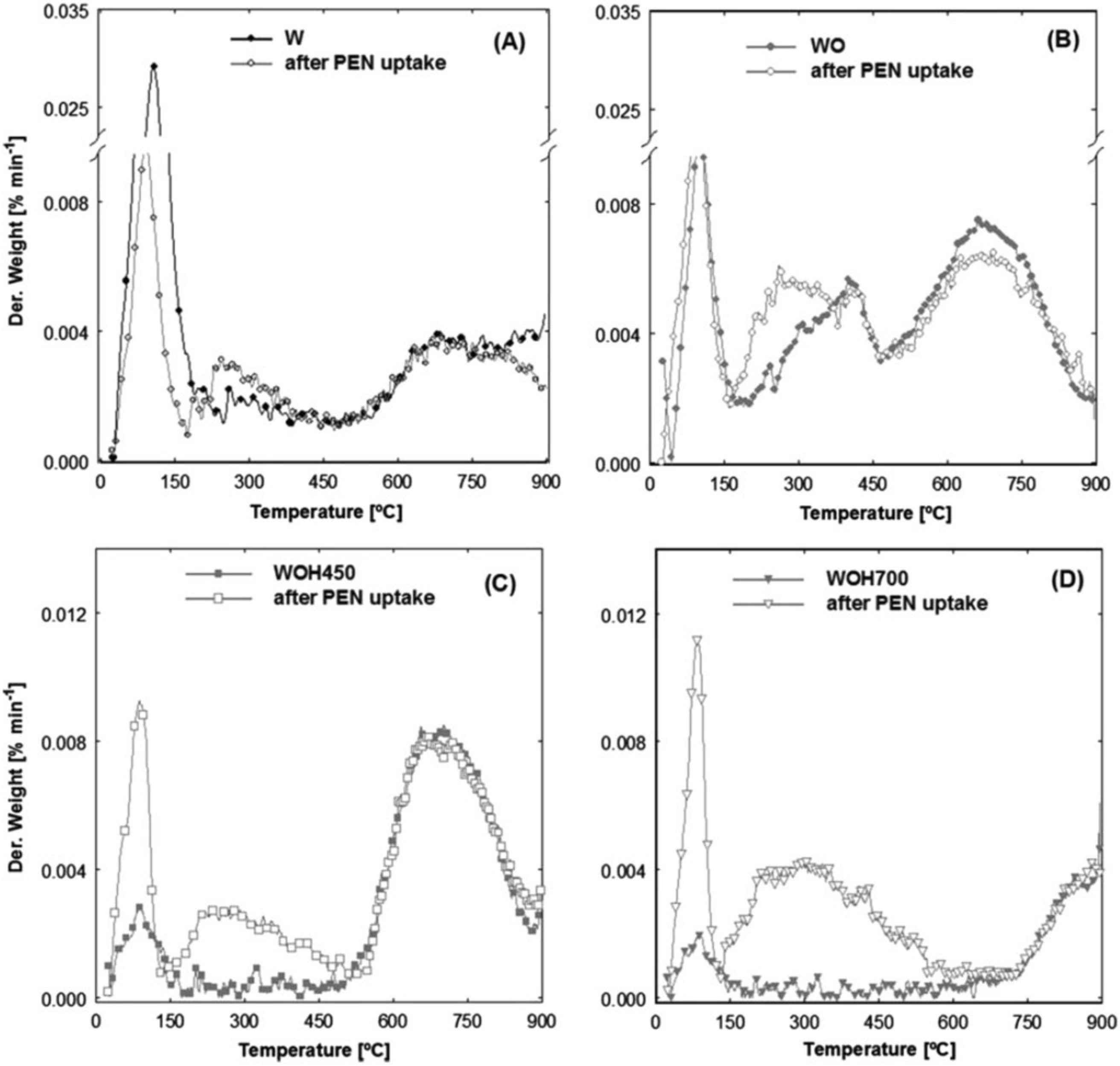


Fig. 3 DTG profiles before and after the uptake of penicillin “Reprinted from Adsorption, 17, 2011, 421–429, Reactive adsorption of penicillin on activated carbons, Ania, C.O., Pelayo, J.G., Bandosz, T.J., Fig. 7, Copyright (2011)”

is one of the most highly toxic elements present in groundwater of countries like Bangladesh, India (West Bengal) and Nepal. According to WHO guidelines, the permissible levels of Arsenic in groundwater should not be more than 10 μg/L (Smith et al. 2000). Therefore, there is an immediate need to remove these contaminants. Various technologies including reactive adsorption have been examined in this regard.

Adsorbents, such as metal oxides (Crawford et al. 1997), activated carbons, (Yue et al. 1999) and biomaterials (Sag et al. 2000) have been traditionally employed to remove heavy metals from solution. Various other methods to achieve high removal of mercury were also analyzed (Yan 1996). Poly (1, 8-diaminonaphthalene) (PDAN) has attracted more attention, due to its high reactivity towards the metal ions including Ag^+, Cu^{2+}, Hg^{2+}, Pb^{2+}, VO^{2+}, and Cr^{3+} (Li et al. 2005a). However, electrosynthesized PDAN film with small specific area and low preparation yield limits its application for the recovery of heavy metals. Chemically oxidative polymerization was a successful attempt to synthesize aniline and pyrrole copolymers (Li et al. 2003, 2005a). Meanwhile, it was found that the small size adsorbent particles because of their high specific area generally

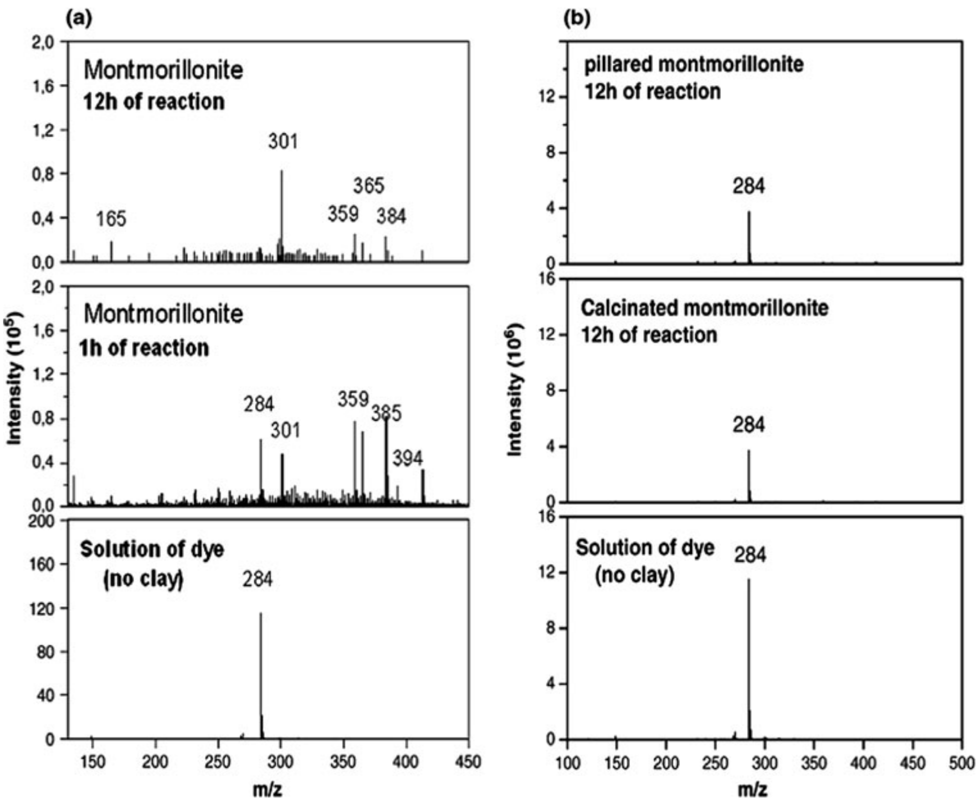


Fig. 4 ESI mass spectra in positive ion mode for monitoring the oxidation of methylene blue in water by montmorillonite and H_2O_2 at different reaction times "Reprinted from Applied Clay Science, 43, Francisco G.E. Nogueira, João H. Lopes, Adilson C. Silva, Maraisa Gonçalves, Alexandre S. Anastácio, Karim Sapag, Luiz C.A. Oliveira, Reactive adsorption of methylene blue on montmorillonite via an ESI-MS study, 190–195, Copyright (2008), with permission from Elsevier"

exhibit high adsorption capacity for heavy metal ions (Li et al. 2004).

An optimal combination of Ag ion complexed with amino or imino groups, redox reaction between Ag and free NH_2 group, and replacement of Na/H of sulfonic groups by Ag was responsible for an effective diffusion of Ag into the microparticles of sulfodiphenylamine and diaminonaphthalene copolymers (Li et al. 2005b). Almost 100 % sorption of total Arsenic was achieved at pH 3–7 when Nano scale zero-valent iron (NZVI) was used as a reactive barrier (Kanel et al. 2006). Up to 80–90 % removal of mercury from oil was accomplished by washing with a dilute aqueous solution of sodium polysulfide (Yan 1990). However, the degree of removal could not be improved further due to the presence of certain unreactive mercuric compounds. Later, an effective process based on high-temperature chemisorption of mercury from oil by CuS/C adsorbent was developed (Yan 1996). The process so developed was successful is achieving around 99 % removal of mercury.

The significant contributions in wastewater treatment by reactive adsorption have been summarized in Table 1. As evident from the table, surface oxygen functionalities on the surface and acidic/basic treatment strongly influence the selectivity and capacity of the adsorbent (Ania et al. 2002; Jia and Thomas 2000; Jiang et al. 2003; Ania et al. 2007a). The acidic treatment increases the mesoporous volume and hence the surface area of adsorbent, which in turn, enhances the adsorption of larger molecules. However, the acidic treatment of an adsorbent is not a good option for the adsorption of small molecules such as iodine. Among the dry and wet oxidation methods, the latter is a preferred choice for introducing surface oxygen complexes since the process can be carried out under relatively mild conditions. In addition, it was suggested that the PZC value can be an excellent reference index for determining the changes in surface chemistry of carbons. Not only the porosity but the amount of catalyst along with its dispersion on the surface should be taken into account (Ania and Bandosz 2006b). The selectivity of AC can, therefore, be enhanced by adopting a suitable modification procedure based upon the nature of the adsorbate under consideration.

The reactions involved in the reactive adsorption of wastewater contaminants are mainly heterogeneous catalytic oxidation, hydrolysis, ion-exchange, oxidation, and redox reactions. The type of reaction involved depends upon the nature of adsorbate, adsorbent and also upon the type of adsorbate-adsorbent interaction. Moreover, the nature of surroundings also has a significant impact on the type of reaction.

3 Adsorbent modification for desulfurization by reactive adsorption

Organosulfur compounds mainly thiophene, benzothiophene, dibenzothiophene (DBT) and their alkyl deriva-

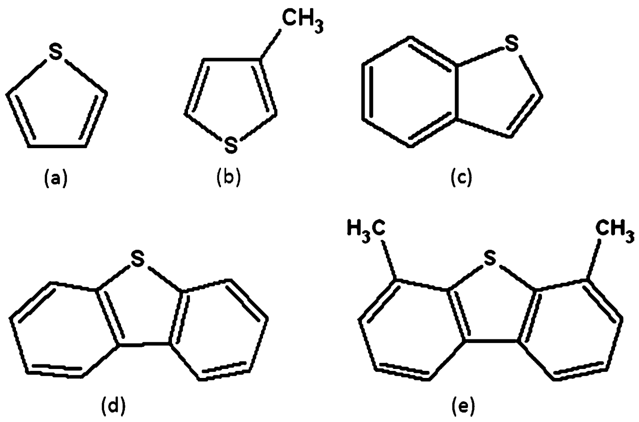


Fig. 5 Thiophenic compounds in fuel oil: (**a**) Thiophene, (**b**) 3-methylthiophene, (**c**) Benzothiophene, (**d**) Dibenzothiophene (DBT), (**e**) 4,6-dimethyldibenzothiophene (DMDBT)

tives are abundantly found in petroleum and petrochemicals (Fig. 5). The presence of sulfur impurities besides imparting a negative effect on environment also interferes with the functioning of process equipment. Consequently, the reduction of sulfur content in major products such as gasoline and diesel to a minimum level is imperative. Conventional hydrodesulfurization (HDS) technology, producing a low sulfur diesel of less than 10 ppm by weight, is the major desulfurization process (Eijsbouts et al. 2007; Kiriyama et al. 2005; Song 2003). However, the removal of polyaromatic sulfur containing compounds using HDS needs process equipment with high capital investment.

Besides the conventional HDS, other low cost technologies including adsorption (Hernandez-Maldonado et al. 2005; Pawelec et al. 2010; Samokhvalov and Tatarchuk 2010; Sentorun-Shalaby et al. 2011; Yang et al. 2003), oxidation (Chica et al. 2006; Rodriguez-Gattorno et al. 2009), extraction (Bösmann et al. 2001; Kulkarni and Afonso 2010), reactive adsorption (Jiang et al. 2003; Ania and Bandosz 2006a; Huang et al. 2010a; Zhang et al. 2010; Fan et al. 2010) and biodesulfurization (Davoodi-Dehaghani et al. 2010; Monticello 2000) have been developed for ultra-deep desulfurization. Among these, adsorptive desulfurization and reactive adsorption, operating at ambient temperature and pressure, are found to be the most promising ones (Samokhvalov and Tatarchuk 2010) and are viewed as a better option to conventional HDS (Yang et al. 2003). Adsorption is preferred over conventional HDS since it can even remove refractory sulfur which would be impossible by HDS. The adsorption can also be easily applied to internal reforming fuel cell systems (Haji and Erkey 2003). In such an approach, metal ion exchanged zeolites (Bhandari et al. 2006) and alumina (Srivastav and Srivastava 2009) have been proved to be good adsorbents, however, their selectivity and capacity is affected by the fuel composition.

The specificity of adsorption is less because of the resemblance of thiophene to most arenes and alkenes in basicity and electron density. HDS causes the unnecessary hydrogenation of aromatic compounds in fuel leading to the undesirable change in octane number (Ania and Bandosz 2006b). Hence, modification of adsorbent is preferable over commercially available adsorbents. Meanwhile, reactive adsorption of sulfur compounds was reported (Kim et al. 2006a; Ma et al. 2005; Velu et al. 2005). The reactive adsorption for sulfur removal is supplemented by the advantage that it remains unaffected by fuel composition. Besides this, it has advantages of both catalytic HDS and adsorptive desulfurization and therefore, it is considered an efficient technology for deep desulfurization (Tawara et al. 2000, 2001).

Transition metals supported on base oxides are generally preferred as adsorbents for reactive adsorption. Ni supported on ZnO is the most recommended adsorbent for this purpose. ZnO is known to act as an acceptor of sulfur released by sulfided Ni species during regeneration, and also as a co-catalyst for hydrogenation of sulfur-containing compounds over the surface Ni particles (Babich and Moulijn 2003; Bezverkhyy et al. 2008; Fan et al. 2010; Huang et al. 2010a, 2010b; Khare 2001; Ryzhikov et al. 2008; Tawara et al. 2000, 2001).

The performance of oxidized NiO/ZnO without any prereduction and the role of hydrogen pretreatment of Ni/ZnO adsorbent for reactive adsorption of thiophene were investigated by Ryzhikov et al. (2008). The sulfidation rate for the reduced adsorbent, by virtue of the formation of Ni–Zn alloy was lesser than that for the unreduced sample. The formation of Ni–Zn alloy can be ascertained from the XRD patterns obtained for both reduced as well as unreduced adsorbents (Fig. 6(a)). After reaction with thiophene, XRD peaks corresponding to compounds other than the parent compounds were observed (Fig. 6(b)). A complete sulfidation of ZnO was observed while the reaction with Ni was partially achieved.

In addition to these results, TEM analysis suggested that sulfidation modifies the textural properties to some extent (Fig. 7). The smaller particles initially present completely disappeared and particles of larger size were observed with a reduction in BET surface area. The shape of the particles was also changed.

Contrary to this, Fan et al. (2010) have stated that reduction improves the pore structure of the adsorbent with no alloy formation (Fig. 8). The round morphology implies that reduction and sulfidation do not affect the surface characteristics and particle size. However, the pore structure improved upon reduction, thereby enhancing the diffusion of sulfide molecules inside the pores and ultimately resulted into desulfurization. During sulfidation, pore volume and pore size consistently decreased as a result of gradual carbon deposition and adsorbent sulfidation.

Moreover, the effect of factors such as high temperature, high pressure, high molar ratios of hydrogen-to-oil, and low

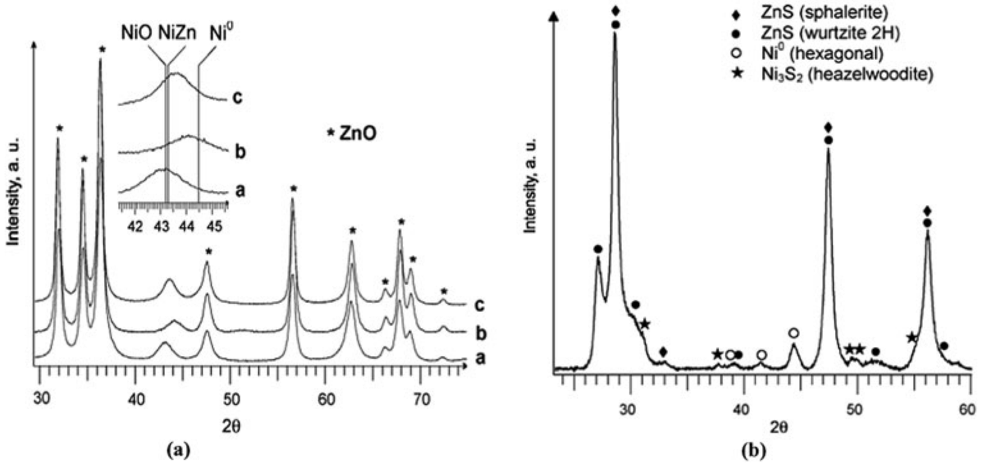


Fig. 6 XRD patterns for (**a**) unreduced and reduced adsorbent before desulfurization (**b**) unreduced sample after reaction with thiophene "Reprinted from Applied Catalysis B: Environmental, 84, Andrey Ryzhikov, Igor Bezverkhyy, Jean-Pierre Bellat, Reactive adsorption of thiophene on Ni/ZnO: Role of hydrogen pretreatment and nature of the rate determining step, 766–772, Copyright (2008), with permission from Elsevier"

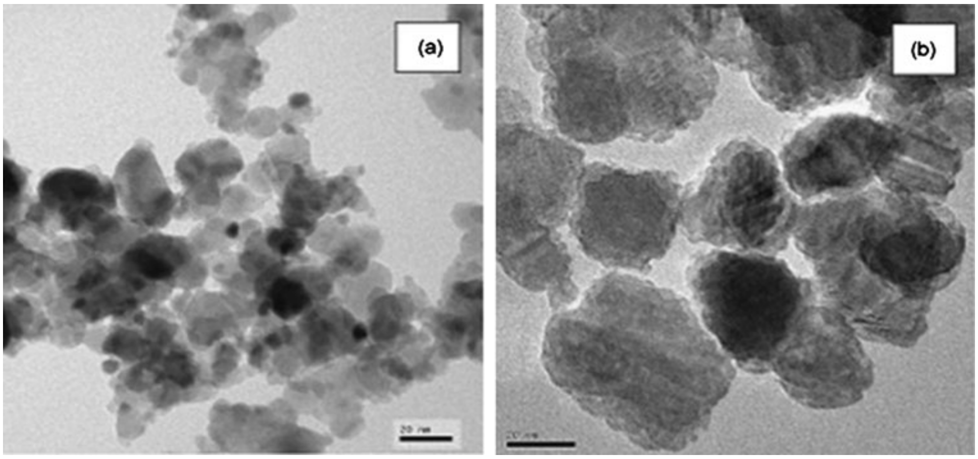


Fig. 7 TEM analysis for adsorbent (**a**) before sulfidation, (**b**) after sulfidation "Reprinted from Applied Catalysis B: Environmental, 84, Andrey Ryzhikov, Igor Bezverkhyy, Jean-Pierre Bellat, Reactive adsorption of thiophene on Ni/ZnO: Role of hydrogen pretreatment and nature of the rate determining step, 766–772, Copyright (2008), with permission from Elsevier"

weight hourly space velocity on the efficiency of desulfurization was also examined. It was finally concluded that Ni/ZnO-SiO_2-Al_2O_3 is highly efficient and can adsorb almost all types of sulfides with just 2.96 wt% sulfur in raw materials. To further analyze the nature of reactive adsorption of thiophene on Ni/ZnO adsorbent, the textural effect of ZnO on the desulfurization activity was investigated (Zhang et al. 2010). More recently, Zhang et al. (2012) have studied the effect of particle size on the reactive adsorption of thiophene. The study revealed that the adsorbent with a small particle size and high catalyst dispersion on its surface provides better overall performance as compared to the adsorbent with comparatively large size and less dispersion. In another study conducted by Huang et al. (2010a), the role of residual sodium in reactive adsorption of sulfur from diesel fuel using Ni/ZnO adsorbent was investigated. The results revealed the negative impact of residual sodium on the overall performance of the adsorbent. The interaction between NiO and ZnO was, therefore, suppressed. Moreover, the residual sodium upon calcination and reduction lead to the formation of catalytically inactive Ni–Zn and $Zn(OH)_3$ which would further interfere with the overall process.

Other reactive adsorbents investigated for desulfurization are chemically modified activated carbon (Jiang et al. 2003); Metal loaded-polystyrene based carbon (Ania and Bandosz 2006a; Wang et al. 2009); Polymer-derived activated carbons (Seredych et al. 2010, 2011), organic waste derived carbon (Ania et al. 2007b); Metal supported activated carbons (Seredych and Bandosz 2007a; Ma et al. 2007); Wood based activated carbons (Seredych et al. 2011; Seredych and Bandosz 2008); 2.8NiO–$H_{1.8}Ni_{0.6}(OH)MoO_4$ composites (Skrzypski et al. 2011); Ni nanoparticles supported mesoporous silica (Park et al. 2008); Zeolites (Chica et al. 2005); Au(III) on mica (Sako et al. 2005; Ma et al. 2005), and organic sulfur adsorbents (Shalaby et al. 2009) (Table 2).

3.1 Mechanism of desulfurization by reactive adsorption

On an industrial scale, the Philipps S-Zorb$^{®}$ process for desulfurization via. reactive adsorption was implemented (Ito and Van Veen 2006) (Fig. 9). The sulfur containing molecules react with metal supported ZnO in presence of hydrogen to form a mixture of sulfides. The adsorbent re-

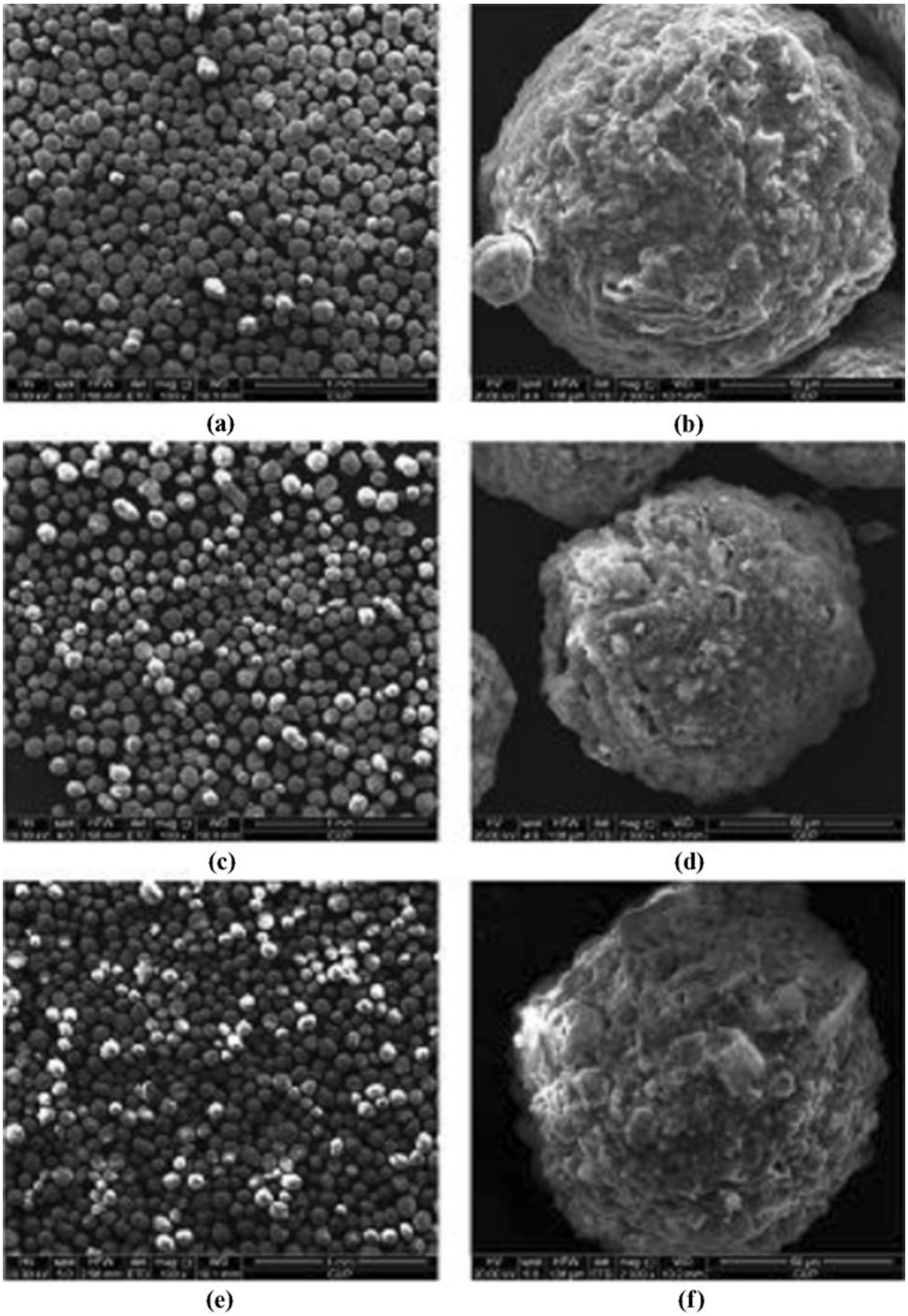

(a) (b) (c) (d) (e) (f)

Fig. 8 SEM micrographs of adsorbents (**a**) fresh adsorbent (100X magnification), (**b**) fresh adsorbent (2000X magnification), (**c**) reduced adsorbent (100X magnification), (**d**) reduced adsorbent (2000X magnification), (**e**) sulfurized adsorbent (100X magnification), and (**f**) sulfurized adsorbent (2000X magnification) "Reprinted with permission from Fan, J., Wang, G., Sun, Y., Xu, C., Zhou, H., Zhou, G., Gao, J.: Research on Reactive Adsorption Desulfurization over Ni/ZnO-SiO_2-Al_2O_3 Adsorbent in a Fixed-Fluidized Bed Reactor. Copyright (2010) American Chemical Society"

generation is accomplished by calcinations of sulfides to produce oxides followed by their treatment with hydrogen in order to obtain the reduced sample. The S-Zorb® process do not affect the octane number of the fuel i.e., it is not associated with the side hydrogenation of hydrocarbons. In addition to S-Zorb® process, other similar processes such as IRVAD® and TReND® are under investigation (Brunet et al. 2005).

Although, various mechanisms have been proposed (Tawara et al. 2000, 2001; Babich and Moulijn 2003), the key points are still under investigation. Babich and Moulijn (2003) made an attempt to describe the overall reaction mechanism. According to them, thiophene is decomposed on nickel surface followed by hydrogenation of NiS sites and transfer of H_2S to ZnO. Ania et al. (2007b) have investigated the mechanism for desulfurization on modified

Table 2 Summary of adsorbent modification for reactive adsorption in desulfurization

Adsorbate	Adsorbent	Modification procedure(s)	Adsorbent characterization method(s)	Adsorbate detection method(s)	Remark(s)	Reference(s)
Dibenzothiophene (DBT)	Modified activated carbon	Chemical modification by H_2SO_4 at 150–270 °C	Nitrogen adsorption, Base titration, FTIR	Sulfur analysis by microcoulometry	The modified AC exhibits high adsorption capacity for large molecules but acts negatively for small molecules as compared to conventional AC	Jiang et al. (2003)
	Metal-loaded polystyrene-based activated carbons	Ion-exchange with nitrates of corresponding metals and Carbonization in nitrogen at 800 °C	Textural and Chemical characterization by N_2 adsorption isotherms at −196 °C, Thermal Analysis, XRF, SEM	UV-Vis spectrophotometer	The metals incorporated act as active centres, structural stabilizers and as catalyst initiators. The sulfur content and acidic groups on adsorbent increase the adsorption capacity	Ania and Bandosz (2006a, 2006b)
	Organic waste derived carbons	Oxidation with $(NH_4)_2S_2O_8$ and nitric acid (20 %) under mild conditions	Textural and Chemical characterization by N_2 adsorption isotherms at −196 °C, Thermal Analysis by MS and FTIR, XRF	UV-Vis spectrophotometer	Adsorption is governed by both physiosorption and chemisorption. Acidic sites on the surface are involved in reactive adsorption whose nature determines the selectivity of the process	Ania et al. (2007a, 2007b)
	Polymer-derived carbon matrices	Sulfur incorporation by high temperature H_2S reduction of oxygen containing groups	Nitrogen adsorption, Thermal analysis, Potentiometric titration, and Elemental XPS analysis	Liquid chromatography with photodiode array detector	Sulfur functionalites increased the DBT selectivity by acid-base and polar interactions	Seredych et al. (2011)
	Template-Derived Mesoporous Carbon modified with transition metals	Ion exchange with metal nitrates followed by subsequent carbonization under nitrogen at 800 °C	Nitrogen adsorption, Thermal analysis, Potentiometric titration, and Elemental analysis	UV-Vis spectrophotometer	A combination of surface acidity and high metallic dispersion enhance the reactive adsorption	Seredych and Bandosz (2007a, 2007b)

Table 2 (*Continued*)

Adsorbate	Adsorbent	Modification procedure(s)	Adsorbent characterization method(s)	Adsorbate detection method(s)	Remark(s)	Reference(s)
	Ni/ZnO	Co-precipitation of $Ni(NO_3)_2 \cdot 6H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ with Na_2CO_3 at 80 °C followed by calcination in air at 350 °C	Nitrogen adsorption, XRD, Thermogravimetric analysis, and XPS	Gas chromatography equipped with Flame photometric detector (FPD)	Residual sodium enriched during calcination and reduction decrease the surface area and pore volume imparts negative effect on the performance of adsorbent	Huang et al. (2010a)
	Ni/ZnO	Co-precipitation of $Ni(NO_3)_2 \cdot 6H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ with Na_2CO_3 at 80 °C followed by calcination in air at 350 °C	Sulfur K-edge XANES, XRD, XAS, and XPS	Gas chromatography equipped with FID detector	Desulfurization catalyzed by active Ni species under hydrogen follows reactive adsorption	Huang et al. (2011)
	Ni-Si-Al_2O_3, Cu(I)Y-Zeolite	–	N_2 adsorption, Elemental Analysis, Temperature programmed reduction experiments	GC_FID, GC-FPD, GC_PFPD, Total sulfur analyzer (TSA)	GC-FPD, and GC_PFPD are not suitable for estimation of total sulfur	Ma et al. (2005)
	Sulfur and oxygen rich wood based activated carbons	Heat treatment with H_2S at 650 °C and 800 °C	Nitrogen adsorption, Thermal Analysis, potentiometric titration, FTIR, MS, Surface pH and Elemental analysis	Liquid chromatography equipped with photodiode array detector	The incorporated sulfur positively affects the selectivity and adsorptivity of carbon. Sulfur aids in oxygen activation and DBT oxidation	Seredych et al. (2011)
	Sulfonic acid based polymer derived carbon incorporated with nitrogen surface functionalities	Carbonization and impregnation of urea solution at 800 °C and at 950 °C under nitrogen	Elemental analysis, XPS, Nitrogen adsorption, Thermal Analysis, and potentiometric titration, CHN analysis	Liquid chromatography equipped with photodiode array detector	Nitrogen enhances the participation of oxygen groups and increases the adsorption potential	Seredych et al. (2010)
Thiophenic compounds	Fe (III) salts supported activated carbon	Mechano-chemical method	Nitrogen adsorption	Gas chromatography equipped with Pulsed flame photometric detector (PFPD), and Total sulfur analysis	Oxidation in presence of molecular O_2 with Fe (III) loaded carbon promotes desulfurization	Ma et al. (2007)

Table 2 (*Continued*)

Adsorbate	Adsorbent	Modification procedure(s)	Adsorbent characterization method(s)	Adsorbate detection method(s)	Remark(s)	Reference(s)
Thiophene	NiO/ZnO	Co-precipitation of $Ni(NO_3)_2 \cdot 6H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ with Na_2CO_3 followed by calcination at 400 °C	XRD, TEM, Nitrogen adsorption	TGA, GC equipped with mass selective detector	Unreduced adsorbent is two times more active than the reduced one	Ryzhikov et al. (2008)
	Au(111) on mica	Evaporation of gold at 673 K	XPS, near edge XAF	Gas chromatography–mass spectrometry (GC–MS)	The presence of solvent considerably affect the adsorption process	Sako et al. (2005)
	Ni/ZnO	Incipient impregnation method	TG-DSC-MS analysis, XRD, TEM, IR BET measurements	Gas chromatograph GC–MS	ZnO plays a crucial role in reactive adsorption	Zhang et al. (2010)
	Zeolites (H-ZSM5, H-Beta, H-Y) with varying Si/Al ratio	Dealumination followed by sequential steaming and acid treatment	SEM, Al MAS NMR spectra	GC-MS using flame ionization and thermal conductivity detection	Thiophene adsorption is affected by zeolite structure but remain unaffected by Si/Al content	Chica et al. (2005)
	Ni/SiO_2 and Ni/ZnO	Co-precipitation followed by reduction in hydrogen	XRD, TEM, BET analysis,	Thermal gravimetric analysis for kinetic study,	Reactive adsorption on different adsorbents proceeds in a different manner	Bezverkhyy et al. (2008)
	Ni/ZnO	Incipient wetness impregnation method	N_2 adsorption, XRD, HRTEM, and TEM	Total sulfur analyzer	A decrease in ZnO particles and high Ni dispersion enhance the adsorption capacity	Zhang et al. Zhang et al. (2012))
Thiophene and H_2S	2.8NiO–$H_{1.8}Ni_{0.6}(OH)MoO_4$ composite	Co-precipitation from mixed Ni-Mo solution induced by evaporation of NH_3	TGA, XRD, TEM, SEM, EXAFS, XAS	GC–MS, TGA analysis	Faster reactive adsorption as compared to Ni/ZnO by virtue of fine dispersion of metals	Skrzypski et al. (2011)
Sulfur from diesel oil	Ni/ZnO	Co-precipitation of $Ni(NO_3)_2 \cdot 6H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ with Na_2CO_3 at 80 °C followed by calcination in air at 350 °C	K-edge-XANES, XRD	GC-FPD chromatogram	The K-edge-XANES and XRD are effective procedures to identify the transfer of sulfur species	Huang et al. (2010b)

Table 2 (*Continued*)

Adsorbate	Adsorbent	Modification procedure(s)	Adsorbent characterization method(s)	Adsorbate detection method(s)	Remark(s)	Reference(s)
Sulfur from digester gas	Wood-Based Activated Carbons Modified with Nitrogen	Impregnation followed by heat treatment	Elemental analysis, Nitrogen adsorption, Boehm titration, Potentiometric titration, FTIR, and Thermal analysis	Electrochemical methods	Nitrogen acts as an activator of the oxygen groups. The prehumidified adsorbent have high capacities for H_2S removal	Seredych and Bandosz (2008)
Sulfur from Gasoline	Ni/ZnO-SiO_2-Al_2O_3	Wet mixing method follwed by reduction in H_2 flow at 723 K	XRF, SEM/EDX, XRD	GC-PFPD chromatogram, GC-MS	The adsorbent exhibits significant desulfurization	Fan et al. (2010)
4,6-dimethyldibenzothiophene	Polymer-derived activated carbons	Carbonization of polymer with subsequent oxidation with nitric acid (70 %)	Potentiometric titration, Nitrogen adsorption, FTIR, SEM/EDAX, Thermal analysis	UV-Vis spectrophotometer	The role of surface chemistry is significant in reactive adsorption	Seredych et al.(2010)
Sulfur compounds from commercial diesel	Ni nanoparticles supported mesoporous silica	Impregnation of nickel nitrate and followed by its reduction	XRD, TEM, nitrogen adsorption	GC equipped with FPD, Total sulfur analyzer	Maximum adsorption capacity obtained depends upon nickel concentration and pore structure of substrates	Park et al. (2008)
Sulfur compounds from commercial diesel	Cu/AC, Cu/Zeolites, Cu/ZSM-5, Cu-FER and Ni based sorbents	Wet Impregnation, wet ion exchange, dry impregnation	EDX, BASF	GC-PFPD	Ni based adsorbents showed the best performance. A commercial diesel below 1 ppm of sulfur was obtained	Pieterse et al. (2011)

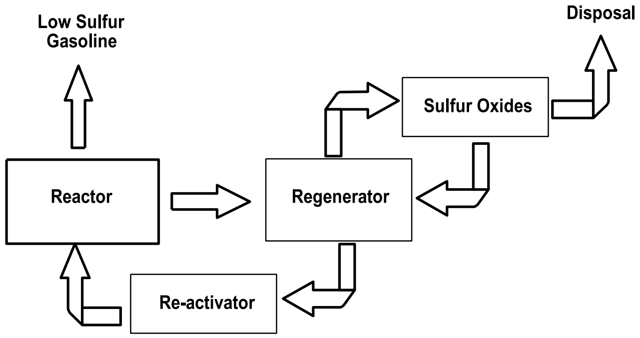


Fig. 9 Schematic representation of Philipps S-Zorb® process for gasoline and diesel fuel

activated carbon by means of reactive adsorption. It was predicted that the sulfur-oxygen interactions are responsible for the enhanced adsorption of the thiophenic compounds. Thermal treatment was employed for adsorbent regeneration. In reactive adsorption, the adsorption of DBT is followed by breaking of its sulfur carbon bonds via polymerization/condensation reactions, thereby, forming sulfur-based intermediates.

A suitable mechanism for the reactive adsorption of sulfur containing compounds present mainly in diesel and gasoline was well presented in separate studies by Huang et al. (2010b) and Fan et al. (2010). The XRD patterns of the fresh, reduced, and sulfurized adsorbents have been presented in Fig. 10 (Fan et al. 2010). Figure 10a presents a diffractogram of the fresh adsorbent. The diffraction peak of ZnO indicates large grain size with a weak diffraction peak for $ZnAl_2O_4$ formed during the calcination process.

Figure 10b, displays an increase in the intensity of diffraction peaks for ZnO, Al_2O_3, and SiO_2 after reduction accompanied by a weak reflection of metallic Ni. No peak of Ni–Zn alloy was observed as was seen in the XRD patterns of Ryzhikov et al. (2008). Figure 10c indicates the reflection mainly related to ZnS. Overall it was stated that sulfur compounds are first decomposed on surface Ni of adsorbent to form Ni_3S_2 followed by its reduction to H_2S. H_2S so formed, is stored in the adsorbent accompanied by the conversion of ZnO into ZnS. The overall mechanism has been pictorially represented in Fig. 11.

Sako et al. (2005) proposed a mechanism for reactive adsorption of thiophene on Au (III) supported mica demonstrating that the solvent plays a crucial role in modification of the adsorption pathway. Seredych et al. (2009) investigated the mechanism of removal of simulated diesel fuel under dynamic conditions using modified polymer-derived urea as adsorbent. It was indicated that nitrogen-containing groups contribute to chemical transformations of DBT and DMDBT and promote the surface oxygen interactions in the process of reactive adsorption. Other possible mechanisms were also investigated by Kim et al. (2006a).

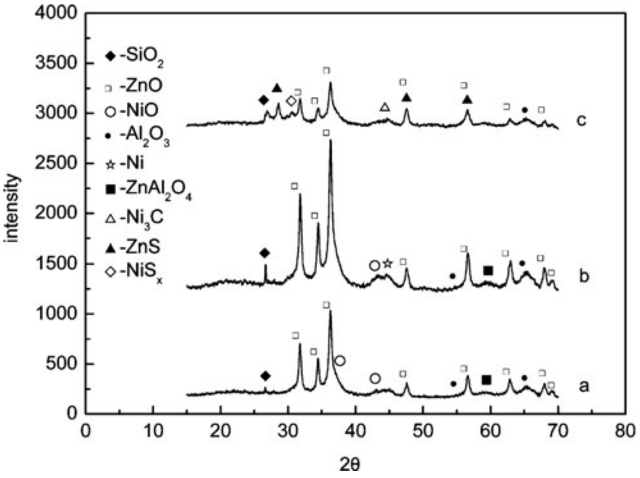


Fig. 10 XRD patterns for adsorbents (**a**) fresh adsorbent, (**b**) after reduction, and (**c**) after sulfidation "Reprinted with permission from Fan, J., Wang, G., Sun, Y., Xu, C., Zhou, H., Zhou, G., Gao, J.: Research on Reactive Adsorption Desulfurization over Ni/ZnO-SiO_2-Al_2O_3 Adsorbent in a Fixed-Fluidized Bed Reactor. Copyright (2010) American Chemical Society"

Many research papers and reviews on desulfurization have been published which also contain a section on reactive adsorption (Song 2003; Ito and Van Veen 2006; Brunet et al. 2005). That is why this section has been dealt in brief. However, the significant contributions made in this area have been listed in Table 2. It has been suggested that different adsorbents are required to accomplish the removal of different sulfur compounds from different streams. Several combinations were used for this purpose but the best performance was observed with Ni–ZnO system.

4 Adsorbent modification for removal of gaseous pollutants by reactive adsorption

Sulfur oxides, nitrogen oxides, carbon monoxide, volatile organic compounds (VOCs), etc. are the major primary gaseous pollutants held responsible to multiple health conditions including respiratory infections, heart disease, and lung cancer. As per WHO statistics, around 1.3 million people die each year from causes directly attributable to air pollution (WHO 2011). There are various air pollution control technologies available to reduce air pollution. Reactive adsorption is an advancement made in this sector.

4.1 Ammonia

Industries like food, rubber, fish, animal husbandry, leather, compost plants, livestock crematoria, wastewater treatment plants etc., are the major contributors of ammonia in environment. It shows toxic effects to both the environment and human health. Several types of adsorbents have been tested

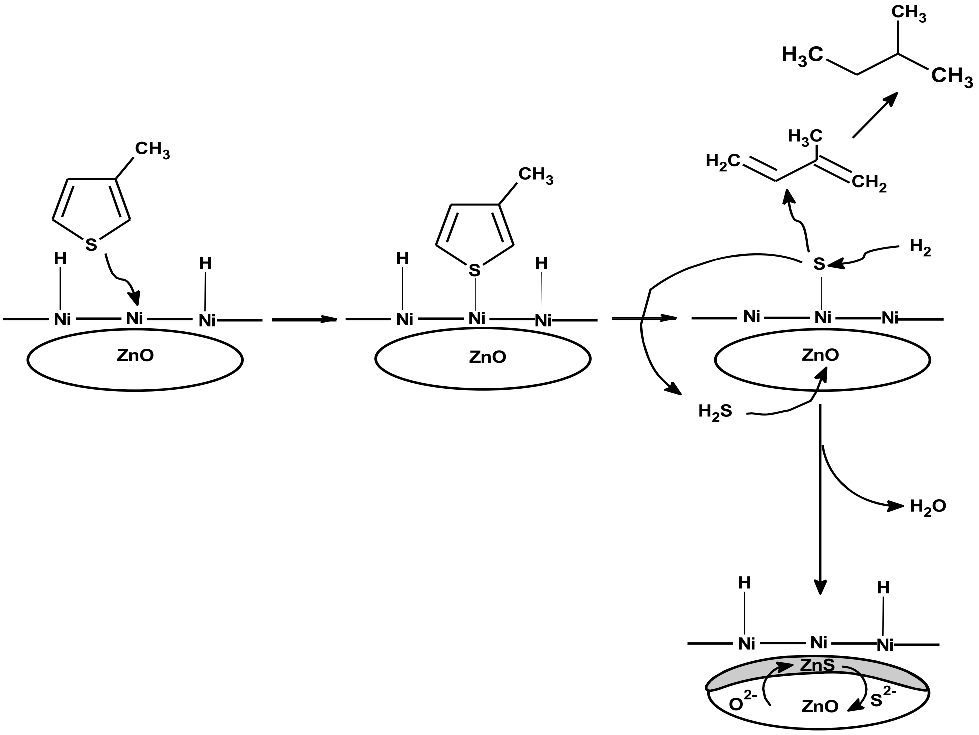


Fig. 11 Reaction mechanism of desulfurization over Ni/ZnO-SiO_2-Al_2O_3 (Fan et al. 2010)

so far for the removal of ammonia. Among them, activated carbon has been a favorable choice (Shin et al. 2001). Recently, it has been shown that activated carbon as an adsorbent for ammonia removal often encounters a problem during desorption of NH_3 (Petit et al. 2010). To overcome this issue, the adsorbent is required to be highly porous and should posses some functional groups to enhance the retention of ammonia on the adsorbent (Bandosz and Petit 2009; Stoeckli et al. 2004). In case of weak dispersive interactions, the molecules are forced to react on the surface of reactant to enhance the adsorption process. This is what is known as Reactive Adsorption (Ania and Bandosz 2005; Bandosz 2002). Le Leuch et al. (2005) have shown that transition metals or their oxides impregnated on the surface of the carbonaceous phase are beneficial for the removal of ammonia. Metals such as Fe, Cu, and Co are reported to be an active participant in the ammonia oxidation process (Cant and Liu 2000; Zawadzki and Wisniewski 2003).

It was shown that the adsorption capacity depends on the source of carbon, nature of compound used for impregnation and experimental conditions (Bandosz and Petit 2009). The reactive adsorption of ammonia is believed to be influenced by either the acid-base interaction or complexation mechanism. Moreover, the role of humidity in the adsorption process, and desorption of ammonia when the bed is purged with air have also been discussed.

Reactive adsorption of ammonia was also examined by Bandosz and Petit (2009) on water stable composites of HKUST-1 and graphene layers. The composite showed high adsorption capacity of ammonia because of increased porosity and dispersive forces. The reactive adsorption of ammonia takes place by physical adsorption followed by binding to the copper sites in HKUST-1 and finally by the reaction with the MOF component. In moist conditions, ammonia get dissolved in a water film present in the pores and thus show higher adsorption as compared to that in dry conditions.

4.2 Nitrogen oxides

Both adsorption of NO_2 and its reduction to NO were observed upon the exposure of activated carbon to NO_2 (Gao et al. 2011). NO_2 adsorption on –C (O) complexes results in the formation of –C (ONO_2) complexes in the micropores. Modified wood based activated carbon was studied for the adsorption/reduction of NO_2 at ambient conditions. NO_2 after adsorption get reduced to NO, whose retention is affected by the presence of moisture (Bashkova and Bandosz 2009). The effect of nitrogen-containing groups and heat treatment on the adsorption of NO_2 and on the retention of NO was also investigated.

Since commonly employed impregnation technique limits the pore accessibility, polymeric Fe-salt carbonization is employed for the effective dispersion of iron on the carbon's surface (Bashkova and Bandosz 2011). It was observed that iron dispersed in the form of Fe_2O_3 with a favorable Fe/C ratio shows excellent results in NO_2 adsorption. More recently, the role of copper in reactive adsorption of NO_2 was investigated by Levasseur et al. (2012). The Cu_2O particles, along with silanol groups, were identified as the active sites for the process. The reactive adsorption of NO_2 was affected by the extent of thermal treatment given to the adsorbent material. Other significant contributions indicating the importance of adsorbent modification for reactive adsorption of NO_x compounds have been presented in Table 3.

4.3 Hydrogen sulfides from biogas

Anaerobic fermentation of organic waste leads to the production of biogas with a major constituent being methane (55–80 vol.%). Other constituents being CO_2 (20–45 vol.%), H_2S (0–1.0 vol.%), and NH_3 (0–0.05 vol.%) (Schomaker et al. 2000). H_2S poses serious problems of odor, toxicity for human and animal health, and corrosion. Moreover, for energy production, biogas has to be conditioned since the combustion of hydrogen sulphide lead to the emission of SO_x, which play a detrimental role in the atmosphere and human health. Biogas can be purified by a variety of methods (Nagl 1996; Schomaker et al. 2000; Vavilin et al. 1994). Adsorption using a H_2S scavenger was analyzed by Truong and Abatzoglou (2005). A combination of iron oxides (Fe_2O_3, Fe_3O_4) and an activator oxide integrated to a calcined montmorillonite carrier matrix was used for adsorption. The activator oxide is thought to be enhancing catalytically the reactive adsorption phenomenon. The results suggested that mosit conditions favor the reactive adsorption of H_2S.

Bandosz and Block (2006) demonstrated the utilization of municipal and industrial wastes as adsorbents of hydrogen sulfide from moist air. Carbonized mixture of industrial sludge and sewage sludge proved to be an effective adsorbent for the reactive adsorption of hydrogen sulfide. The materials obtained are environmentally safe and can be easily disposed off in a landfill. The better performance of these adsorbents as compared to activated carbon can be attributed to the presence of metals and their dispersion on the surface. The sludge can, therefore, be employed in the manufacturing of such cost effective novel composite adsorbents.

A study on removal of hydrogen sulfide from the digester gas was presented by Seredych and Bandosz (2006). Best results were obtained with prehumidified adsorbents. The removal of water prior to desulfurization is not advisable since the sulfurous acid formed during the process deactivates the catalyst. The catalysts based on iron and calcium do not affect the process, therefore, they can be employed for desulfurization of fuels containing CO_2. Later in Seredych and Bandosz (2008), studied the performance of melamine or urea modified wood based activated carbon for the H_2S removal. The introduced nitrogen functionalities revealed high H_2S removal, and unlike the previous results, CO_2 was not found deleterious for reactive adsorption centers. The H_2S adsorbed is then converted to the elemental sulfur by the chemisorbed oxygen and gets further oxidized.

Other modified adsorbents used for the removal of primary pollutants from air have been summarized in Table 3. The results obtained from various literature reveal that in moist conditions, the adsorbent must possess high porosity so that a thin film of water could be formed. Water had been observed to improve the reactive adsorption of gases such as ammonia. However, it is observed to compete with NO_2 to bind to copper, leading to a decrease in the number of reactive adsorption sites. Moreover, it was suggested that the *ex situ* or indirect methods for characterizing particle sizes/dispersions, are not reliable and for the subsequent interpretation of kinetic data (Newton et al. 2007). The active participation of the iron species contributes towards a high NO_2 reduction/retention capacity. The incorporation of amines affects the adsorption of NO_2 and its subsequent reduction to NO.

5 Regeneration of spent adsorbent

For an efficient adsorption process, the reusability of an adsorbent for a longer duration and that too without losing its adsorption capacity is crucial. Desorption can be accomplished either by displacement with a compound of a higher affinity, variation of pressure and/or by increasing the temperature. In case, where the adsorbed component is immediately converted into a product and released back into the bulk, regeneration is not required. That is why, in case of reversible reactions, equilibrium is never attained and thus the adsorbent never gets saturated. While in other cases, where the product formed at the catalyst surface is adsorbed by the adsorbent, regeneration is accomplished simply by displacement or by thermal treatment.

The choice of regeneration method, for any particular system, depends on economic as well as technical considerations. A brief summary of factors governing the choice of desorption methods have been presented by Ruthven (1984). Although thermal regeneration is the preferred method for the regeneration of spent activated carbon, it is associated with high energy consumption and may also lead to thermal aging of adsorbent. Pressure swing desorption is applied to those systems where weakly adsorbed component is required with high purity. To accomplish this, very low pressure may be required and the expenditure involved in mechanical energy is sometimes greater than that required by thermal swing regeneration. On the other hand, displacement desorption involves the product separation and recovery requiring an additional separation step to obtain the purified product. In such a case, the choice of desorption solvent is crucial.

Matatov-Meytal and Sheintuch (1997) employed the low temperature catalytic regeneration procedure. GAC modified with metal oxide catalyst was used as an adsorbent

Table 3 Summary of adsorbent modification for reactive adsorption in gas phase reactive adsorption

Adsorbate	Adsorbent	Modification procedure(s)	Adsorbent characterization method(s)	Adsorbate detection method(s)	Remark(s)	Reference(s)
Ammonia	Modified activated carbon	Incipient wetness impregnation with metal salts followed by calcination at 300 °C	Nitrogen adsorption, Potentiometric titration, Thermal analysis, XRF, SEM and FTIR	Multi-Gas Monitor ITX system (Lumidor) with an electrochemical sensor	The nature of metal deposits, surface functionalities, moisture and acidity of adsorbent determines the adsorption capacity. Highly acidic nature is required for the reactive adsorption of NH_3	Le Leuch and Bandosz (2007)
	Cu-based MOF/Graphene Composites	Process described elsewhere	XRD, FTIR, Nitrogen adsorption, Thermal analysis	Multi-Gas Monitor ITX system (Lumidor) with an electrochemical sensor	The surface characteristics play a major role in reactive adsorption. Adsorption of ammonia is favored in moist condition rather than dry condition	Petit et al. (2010)
	Modified activated carbon	Impregnation/ chemical modification	XRD, FTIR, Nitrogen adsorption, Thermal analysis, and Potentiometric titration	Multi-Gas Monitor ITX system (Lumidor) with an electrochemical sensor	Surface characteristics of adsorbent significantly affect the overall process. Water can have both favorable as well as adverse effects on adsorbent performance	Bandosz and Petit (2009)
H_2S	Iron oxides on calcined montmorillonite	–	SEM, Particle size analysis	Colorimetric method	Gas saturated in water is recommended	Truong and Abatzoglou (2005)
	Sludge mixture	Mixing sludges from various sources followed by carbonization at 950 °C in nitrogen	Nitrogen adsorption, SEM, XRF, XRD, thermal analysis, and surface pH measurements	Electrochemical sensors	A new technology utilizing industrial and municipal wastes as adsorbents for H_2S is proposed. Very high capacity reactive adsorbents are obtained	Bandosz and Block (2006)

Table 3 (*Continued*)

Adsorbate	Adsorbent	Modification procedure(s)	Adsorbent characterization method(s)	Adsorbate detection method(s)	Remark(s)	Reference(s)
	Modified activated carbon	Chemical and Physical activation	TGA, Surface pH measurements	Gas Chromatography equipped with Flame Photometric Detector	The textural, physical, and surface chemical morphology of adsorbent is crucial	Bashkova et al. (2007)
	Catalytic Carbonaceous Adsorbents	–	Nitrogen adsorption, XRF, thermal analysis, and surface pH measurements	Electrochemical sensors	The surface chemistry, porosity and water content determine the capacity of adsorbent used	Seredych and Bandosz (2006)
	Graphite oxide/Zr(OH)$_4$ composites	Graphite oxidation by Hummers method followed by subsequent dispersion of zirchonium chloride	Nitrogen adsorption, IR spectroscopy, Potentiometric titration, XRF, XRD, and thermal analysis	Electrochemical sensor	The reactive adsorption is supplemented by enhanced basicity and features of modified adsorbent	Seredych et al. (2011)
NO$_x$	Al$_2$O$_3$ supported Rh nanoparticles	–	EDE, DRIFTS, and MS	Mass Spectrometry	Divergence in structural, functional and reactive response of adsorbent is observed	Newton et al. (2007)
	γ-Al$_2$O$_3$, α-Fe$_2$O$_3$	–	XPS	Ultra X-ray photoelectron spectroscopy	Humidity and surface oxygen groups affect the overall process	Baltrusaitis et al. (2009)
	Iron-Containing Polymer-Based Porous Carbons	Ion exchange followed by carbonization with N$_2$ at 800 °C	XRD, SEM, TEM, EDX, FTIR, TGA, and nitrogen adsorption	Multiple gas monitor with electrochemical sensors	The dispersion and particle size of iron compounds on carbon affect the reactive adsorption of NO$_x$	Bashkova and Bandosz (2011)
	Activated carbon	Degassification in ultrapure Ar at 900 °C	Nitrogen adsorption, XPS, and TPD	Fourier-transform IR spectrometer	The micropores of AC act as nanoreactor	Gao et al. (2011)
	Composites of Metal Organic Framework and Graphite Oxide	Addition of oxidized graphite to MOF precursor and solvent	Thermal analysis, FTIR, XRD, and nitrogen adsorption	Electrochemical sensor	Though moist conditions are accompanied with less NO$_2$ adsorption and high stability materials	Levasseur et al. (2010)

Table 3 (*Continued*)

Adsorbate	Adsorbent	Modification procedure(s)	Adsorbent characterization method(s)	Adsorbate detection method(s)	Remark(s)	Reference(s)
	$Ce_{1-x}Zr_xO_2$ Mixed Oxides	Co-precipitation in NaOH	Thermal analysis, Potentiometric titration FTIR, XRD, and nitrogen adsorption	Electrochemical sensor	Mixed oxide is better adsorbents than its parent materials. Insertion of $Zr(OH)_4$ enhances the reactive adsorption	Levasseur et al. (2011)
	Sewage Sludge-Derived Materials	Pyrolysis of dry sewage sludge at different temperatures	Thermal analysis, FTIR, XRD, and nitrogen adsorption	Electrochemical sensor	The performance of adsorption depends upon the pyrolysis conditions with maximum efficiency at pyrolysis temperature of 650 °C	Pietrzak and Bandosz (2007)
	Wood based activated carbon	Oxidation with nitric acid and exposure to dimethylamine vapors	Thermal analysis, Potentiometric titration FTIR, Elemental analysis, and nitrogen adsorption	Electrochemical sensor	The performance of adsorbents Modified with amines is significant	Deliyanni and Bandosz (2010)
	SBA-15 modified with copper	Co-precipitation in NaOH	Nitrogen adsorption, XRD, TEM, Thermal Analysis, FT-IR	Electrochemical sensor	Copper significantly affects the adsorption capacity	Levasseur et al. (2012)
Hydrogen cyanide	Modified Activated Carbon	Thermal treatment at 950 °C	Thermal analysis, Potentiometric titration, Elemental analysis, and nitrogen adsorption	Mass Spectrometer, Electrochemical cell and FID	The incorporation of nitrogen in carbon matrix and the basic environment enhance the adsorbent efficiency	Seredych et al. (2009)

Table 4 Summary of adsorbent regeneration in adsorption and reactive adsorption

Adsorbate	Adsorbent	Adsorption/ Reactive adsorption	Regeneration method(s)	Reference(s)
Phenol	Activated Carbon, Anion exchange resin	Adsorption	Acid/Alkali regeneration	Goto et al. (1986)
	Activated carbon	Adsorption	Ultrasound waves	Juang et al. (2006)
	Activated carbon	Adsorption	Caustic regeneration	Ozkaya (2006)
	Fe/CMK-3	Reactive adsorption	Thermal regeneration	Hu et al. (2012)
	Activated carbon supported Cobalt catalyst	Reactive adsorption	Solvent extraction with distilled water	Shukla et al. (2010)
	Cerium incorporated manganese oxide	Reactive adsorption	Oxidative regeneration	Abecassis-Wolfovich et al. (2005)
Carbon monoxide	Pd (100)	Adsorption	Thermal regeneration	Myyrylainen and Rantala (2005)
Phenol and Aniline	Activated carbon	Adsorption	Thermal regeneration	Laszlo et al. (2007)
Phenol and reactive dyes	Activated carbon	Adsorption	Solvent extraction with distilled water	Tanthapanichakoon et al. (2005)
Mercury	Cross linked graft polymer	Adsorption	Selective stripping	Chowdhury et al. (2010)
Pb (II)	Ploy (m-phenylenediamine) powder	Adsorption	Acid regeneration	Huang et al. (2010c)
Water	Zeolite 13 X	Adsorption	Thermal regeneration	Ahn and Lee (2004)
Water soluble dye	Agricultural waste material	Adsorption	Stripping using a solvent	Gupta et al. (2005)
Cu (II)	Variable charge soils	Adsorption	Stripping using a solvent	Xu et al. (2005)
VOCs	Impregnated activated carbon	Adsorption	Thermal regeneration	Kim et al. (2006a, 2006b)
Organic vapors	Activated carbons	Adsorption	Electrothermal regeneration	Luo et al. (2006)
Phenol and Halogenated Phenol	Granular Activated Carbon	Reactive adsorption	Thermal regeneration	Matatov-Meytal and Sheintuch (1997)

for the removal of phenol and halogenated phenols from wastewater. A periodic low temperature catalytic oxidative regeneration was used for regeneration of the spent carbon. Adsorption capacity, in case of phenol, remained unaltered even after many usages. Table 4 describes the various desorption methods employed for a variety of adsorbate-adsorbent system. From the table, it may be inferred that regeneration of adsorbents can be accomplished by different techniques. The major regeneration procedures include: thermal/electrothermal regeneration, solvent extraction, acid/alkali regeneration. Ultrasound wave and oxidative regeneration methods can also be employed. Out of these techniques, thermal/electrothermal regeneration, solvent extraction and oxidative regeneration have been tried in case of reactive adsorption. It can be very well understood that there is a need to adopt/adapt newer regeneration techniques for reactive adsorption. The regeneration techniques that have been used earlier in simple adsorption process i.e. acid/base regeneration, ultrasound regeneration and electrothermal regeneration should be attempted for reactive adsorption. In addition, a couple of novel techniques, potential use of which can be investigated are: electrochemical (anodic/cathodic), pH swing, and microwave regeneration.

6 Modeling of reactive adsorption

Before any process is implemented on a large scale, knowledge of the process behavior is essential. This can be achieved by experimental analysis which is time consuming and at times may be expensive. A most viable alternative is mathematical modeling and simulation. Not only it provides a complete knowledge of the process under different circumstances but also enables the researcher to easily decide upon the fate of the technology. Modeling studies are all the more important for the designing of complex processes such as reactive adsorption. In fact, not much attention has been paid towards modeling and simulation studies in the related area.

Models used to describe a reactive adsorber are simply an extension of the adsorption column with incorporation of the reaction term. A general model of a reactive adsorber incorporates the component mass balance equations for both mobile and stationary phases. A heat balance equation is also required if the process is considered as non-isothermal. For a plug flow through the interparticle voids and neglecting the radial and tangential dispersion, the mass balance on the ith component in the mobile phase can be represented as (Molga 2008):

$$D_L \frac{\partial^2 c_i}{\partial x^2} - u\frac{\partial c_i}{\partial x} + \nu_i r - \frac{6(1-\varepsilon)}{\varepsilon d_p} N_{W,i} = \frac{\partial c_i}{\partial t} \tag{1}$$

The mass flux at the surface of particle can be expressed as:

$$N_{W,i} = D_{e,i}\left(\frac{\partial c_{p,i}}{\partial r}\right)_{r=R} = k_c\big(c_i - (c_{p,i})_{r=R}\big) \tag{2}$$

In the intraparticle voids, the mass balance of the ith component can be expressed as:

$$\frac{D_{e,i}}{\varepsilon_p}\left(\frac{2}{r}\frac{\partial^2 c_{p,i}}{\partial r^2}\right) - S_{p,i} + \nu_i r_p = \frac{\partial c_{p,i}}{\partial t} \tag{3}$$

For adsorption without a simultaneous reaction, the adsorption rate is expressed as:

$$S_{p,i} = k_{a,i}(c_{p,i} - c_{s,i}) = \frac{\partial q_i}{\partial t} \tag{4}$$

For adsorption with a simultaneous heterogeneous reaction, the adsorption rate is expressed as:

$$S_{p,i} = k_{a,i}(c_{p,i} - c_{s,i}) = \frac{\partial q_i}{\partial t} + r_{S,i} \tag{5}$$

For an N component system, the adsorbed concentration of each component is determined by a general equilibrium equation:

$$q_i = f(c_{S,1}, c_{S,2}c_{S,3}, \ldots, c_{S,N}) \tag{6}$$

The rate of heterogeneous reaction $r_{s,i}$, can be calculated using an appropriate kinetic equation as:

$$r_s = k(T)\psi(q_1, q_2, q_3, \ldots, q_N) \tag{7}$$

The significance of stage processes was also discussed based on the statistical moments approach. Another mathematical model was presented by Shukla et al. (2008) to study the effect of various parameters on the reactive adsorption. Modified Butler and Ockerent theory was employed for multicomponent adsorption analysis.

Modeling exercises reported so far appear to be inadequate as modeling of reactive adsorber column can be done by several approaches depending upon the characteristics of adsorbent used, column behavior, and properties of adsorbate. These approaches include the adsorption isotherm models, adsorbate transport models such as axial dispersion model, interpellet mass transfer, intrapellet mass transfer effects, interphase mass transfer, adsorption kinetics and adsorption equilibrium. Table 5 represents a broad classification of various approaches to model liquid adsorption

Table 5 Classification of different model approaches for a liquid adsorption column (Johannsen 2007)

Model	Effects considered
Ideal model	Convection and Adsorption equilibrium
Thomas model	Convection, and Adsorption kinetics
Reactive dispersive model	Convection, Adsorption kinetics, and Dispersion
Transport model	Convection, Adsorption equilibrium, and Mass transfer
Dispersive model	Convection, Adsorption equilibrium, Dispersion
Transport dispersive model	Convection, Adsorption equilibrium, Dispersion, and Mass transfer
General rate model	Convection, Dispersion, Mass transfer, and Adsorption equilibrium or kinetics

columns. The *Ideal Model* is the simplest model with just the convective and adsorption equilibrium effects. The complexity of the models increases as we move towards the general rate model since different effects in addition to those involved in *Ideal Model* are gradually incorporated. These approaches can further be extended for the modeling of a reactive adsorption column.

The knowledge of multicomponent adsorption systems is essential for understanding and predicting the reactive adsorption processes where more than one contaminant is present in the effluent stream. The competition among the adsorbates to adsorb and the interaction between the sorbates and adsorbent increases the complexity of the process. Therefore, modeling of a multicomponent reactive adsorption system may be a little complex, but with the advent of efficient numerical techniques and computer simulation softwares (MATLAB®, g-proms®, FLUENT®, Aspen® etc.), the solution of resultant complex equations could be relatively easier.

7 Conclusions

This review presents the importance and applications of adsorbent modification in reactive adsorption. Adsorbent selection, modification procedure and its effect on the adsorbent performance for different adsorbates and adsorbent regeneration procedures have been discussed. Specific examples on reactivity and the plots showing the dependency on surface characteristics have also been presented. Besides this, potential areas of reactive adsorption have also been emphasized. Investigations on the feasibility of the technology and development of highly selective reactive adsorbents are essential for industrial applications.

From the literature review, following conclusions can be drawn:

1. For an effective reactive adsorption, adsorbent modification and its characterization are recommended.
2. The selection criteria of an adsorbent for a particular adsorbate species depend upon the nature of adsorbate such as its ability to undergo oxidation, hydroxylation, ion exchange, reduction, redox, and electrochemical reactions. For instance, penicillin, in presence of acids, alkalies, oxidizing agents etc. gets oxidized into non-toxic compounds. The surface oxygen introduced on the adsorbent, degrade the penicillin into non-toxic product(s). Such reaction pathways are to be explored in order to achieve enhanced separation.
3. The affinity of reactive adsorbent towards a particular constituent is influenced by the nature of support, nature of solvent, and conditions for modification.
4. Although the reactive adsorbents have exhibited a good performance on laboratory scale, they still need to be applied commercially.

Some of the areas which need attention are as follows:

1. An extensive research is required for the selection and regeneration of reactive adsorbent to make reactive adsorption economically feasible.
2. Parametric analysis of reactive adsorption is required in order to optimize the design of a reactive adsorber.
3. Mathematical modeling and simulation studies on reactive adsorption are scarce. Reactive adsorption has not yet been implemented on a large scale except the S-Zorb technology. Thus, mathematical modeling and simulation can be a viable tool, to optimize the process conditions and predict the process behavior. Various single component (Langmuir, Freundlich, Sipps model etc.) or multicomponent adsorption isotherm models (IAS theory, CDSM theory, Butler and Ockrent model etc.) and various transport models as described above may be incorporated for adsorption analysis.
4. Studies on preparation and/or adsorbent modification to produce reactive adsorbents from conventional/commercial/low cost adsorbents for environmental remediation are not abundantly available.
5. The application of reactive adsorption in areas other than described above should also be explored.
6. Evaluation of the performance of reactive adsorbents for continuous large scale applications is also a potential area.

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