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Natural Bentonite Clay and Its Composites for Dye Removal: Current State and Future Potential

Sadanand Pandey[1, 2, *], James Ramontja[1, 2]

[1]Department of Applied Chemistry, University of Johannesburg, Johannesburg, South Africa

[2]Centre for Nanomaterials Science Research, University of Johannesburg, Johannesburg, South Africa

Email address

sadanand.au@gmail.com (S. Pandey), spandey.uj@gmail.com (S. Pandey)

*Corresponding author

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Abstract

Dye bearing effluent have become one of the most dangerous environmental complications, and the removal of synthetic dyes (e.g., acid dyes, azoic (or naphthol) dyes, basic dyes, chrome (or mordant) dyes, developed (or diazo) dyes, direct dyes, disperse (or acetate) dyes, reactive (or fiber-reactive) dyes, sulphur dyes, Vat dyes) from water and wastewater is of unique concern because they are unmanageable and sustained in the environment. As of late, bentonites and its composite have been moderately applied to the removal of dye bearing effluent from contaminated water through adsorption processes. This paper reviews recent progress in the application of bentonites and its composites for the removal of synthetic dyes from contaminated water. The purpose of this article is to provide a comprehensive literature review of the performance of adsorption process in removing synthetic dyes from water and wastewater by using bentonites and its composites. This study assesses the removal data compare from recent research relating to various dyes during the adsorption process. The paper discusses removal efficiencies, thermodynamics and reaction kinetics. Bentonites are anticipated to have significant potential for comprehensive application to wastewater treatment in the near future. Various challenges encountered in using bentonites and its composite are highlighted and a number of future prospects for the bentonites based adsorbents are proposed.

1. Introduction

Water pollution occurs when pollutants are directly or indirectly discharged into water bodies without adequate treatment. Water pollution are caused by marine dumping, industrial waste, domestic sewage, nuclear waste, oil pollution, underground storage leaks etc. Some of different sources of water pollution are provide in (Figure. 1). Disposal of large amounts of wastewater that contain potentially toxic organic solutes is a problem shared by many companies. These water contaminants are the main cause of life taking diseases like cancer, lungs diseases, skin issues, allergies and many more (Figure. 2).

Figure 1. Sources of water pollution.

Dyes are coloured compounds appropriate for colouring textiles, wool, leather, paper and fibres. Natural dyes for example, indigo have been being used for more than 5000

years. Synthetic dyes have supplanted natural dyes due to their low cost and incomprehensible range of new colours. Today, there are more than 10,000 dyes with various chemical structures available. Nowadays, synthetic dyes are widely utilized as a part of numerous fields, such as (textile industry, leather tanning industry, paper production, food technology, agricultural research, light-harvesting arrays, photoelectrochemical cells, hair colorings etc.).

It is assessed that around more than 10,000 tons of colors are produced every year around the world. And the estimated amount of dyes discharged in the environment are thought to be 1-2% loss during production, and 1–10% loss during uses.
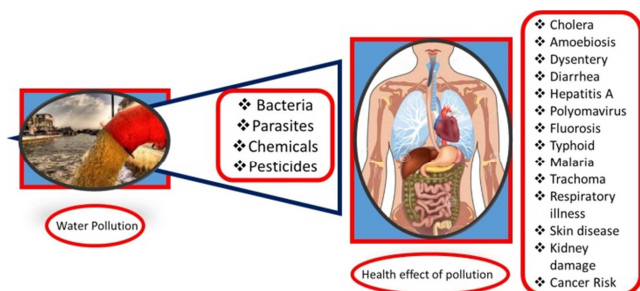

Figure 2. Human effect of water pollution.

It was understood that effluents of textile, paper and pulp, paint, printing and cosmetic industries contain critical amount of these dyes and must be treated to cut down their concentration to permissible limit before releasing into water bodies as required by environmental regulation act [1]. It was observed that high solubility of dyes present in water causes wide dissemination into the environment, thus causing detrimental to crops, aquatic life and human health. The alarming level of synthetic and natural organic substances in natural water led to the value of using adsorption method as one of the most productive methods of removing impurities from wastewater, since most of dyes and its degradation byproducts are very much toxic to living organisms [2]. Thus, removal of dyes is one of the significant part of wastewater treatment before release, as it is hard to expel dyes from effluent because they are not easily degradable and are generally not removed from wastewater by the conventional wastewater purification systems [2].

2. Water Treatment by Adsorption on Bentonite and Its Composites

In view of the importance of water quality and emerging utilities of nanotechnology, attempts have been made to discuss various aspects of water treatment by adsorption using nanoadsorbents. [3-28] Adsorption is a process in which pollutants are adsorbed on the solid surface. Basically, it is a surface phenomenon and adsorption takes place by physical forces but, sometimes, weak chemical bondings also participate in adsorption process. A molecule (pollutant) adhered to the solid surface is called an adsorbate, and the solid surface as an adsorbent. Adsorption is controlled by various parameters such as temperature, nature of the adsorbate and adsorbent, and the presence of other pollutants along with the experimental conditions (pH, concentration of pollutants, contact time, particle size, stirring rate and temperature). An equilibrium is established when the concentrations of pollutant adsorbed and in water become constant. The relationship between amounts of pollutant adsorbed and in water; at equilibrium, is called an adsorption isotherm.

Adsorption is a noteworthy industrial separation method for the purification of effluent media. Adsorption is now recognized as an effective and economic method for wastewater treatment. Among all the different type of methods, removal of pollutants by adsorbents is found to be simple (in terms of operation), cost-effective and efficient methods for the removal of both organic and inorganic pollutants from contaminated waters [29, 30].

This separation technique finds wide application in the removal of dye from aqueous media. Specifically, adsorption finds application in textile, leather, dyeing, cosmetics, plastics, food and paper industries where water recovery is very essential. To achieve and sustain efficient recovery of the desired water quality, a careful selection of adsorbent is of paramount importance

In the last few decades, there are different types of adsorbents had been used for the removal of dyes from wastewater. Mostly use of activated carbon (AC) were exploited a lot for dyes removal. But AC, due to it being a limited natural resource, slow adsorption kinetics and low adsorption capacity of bulky adsorbate because of its microporous nature, disposal problems and also the high cost and difficulty of regeneration, a search for cheap, effective adsorbents such as bantonites clay derivatives has becomes important. Thus keeping the above limitation of AC, Clay minerals have been extensively studied because of their strong sorption and complexation ability.

3. Methods for Modification and Characterization of Bentonite

The preparation and characterization of modify bentonites are the first and foremost steps in water treatment by nanotechnology. The most important methods used for the preparation of modify bentonite including heat treatment [31], acid activation [32], treating the cationic surfactants [33, 34] and polymer modification [35]. The composition and molecular structure of the modify bentonite can be moduled through these methods. The modify bentonite are characterized by Fourier transform infrared spectroscopy (FTIR) [36], thermogravimetric analysis (TGA) [36], X-ray diffraction (XRD) analysis [37], scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Brunauer-Emmet-Teller (BET) surface area analysis [38]. Basically, the reported methods are used for the preparation of different types of modify bentonites for various applications such as biomedical, electronics, optical,

mechanical, environmental science, etc.

There are various methods for modification of clay minerals, such as, acid activation [39], treatment with cationic surfactant [40], clay- rubber composite [41], thermal treatment [31], polymer addition, pillaring by different types of poly (hydroxo metal) cations, intraparticle and interparticle polymerization, dehydroxylation and calcination, delamination and reaggregation of smectites, and lyophilisation, ultrasound and plasma [42] adsorption and ion exchange with inorganic and organic cations, binding of inorganic and organic anions (mainly at the edges) and grafting of organic compounds [43].

Thus in the present article, we are reviewing polymer-clay nanocomposites for dye removal.. Attention is given only to natural clay (Bentonite) for polymer clay nanocomposites synthesis and its application in dye removal from water and wastewater. As we have discuss earlier that the polymer-clay nanocomposites shows some of the significant properties. Because of enhancing these properties, different types of polymer are being used by different workers.

The author believes that this paper will help in understanding the efficiency of the low-cost bentonite clay materials and their abundant availability as an alternative option to otherwise expensive and in few cases toxic treatment technologies being used globally for drinking water treatment.

We hereby sum up some significant contributions made in the adsorption of dyes using bentonites and its composites, highlighting specifically the efficiency of these materials in removing dyes from water and wastewater. The present work aims to summarize some examples of bentonites and its composites used as adsorbents for dyes from aqueous solutions or suspensions.

4. Bentonite and Its Composites for Removal of Dyes

The most widely recognized and best type of clay used in water purification is bentonite which is an adsorbent and is generally impure clay comprise of montmorillonite, although some may comprise of the rare clay minerals, i.e. beidellite, saponite, hectorite and nontronite. The adsorption conduct of organophilic bentonites in contact with aqueous solutions of organic compounds was considered by Stockmeyer [44]. The researched organoclays change in the degree of their total cation exchange capacity (CEC) exchanged by organic counter ions [44]. Bentonites clay offers an attractive and inexpensive option for the removal of dyes. The adsorption of several types of dyes has been reviewd in this section.

Espantaleona et al, 2003 reported the adsorption capacities of Acid yellow 194 are 24.9 and 71.1 mg/g on natural and acid-activated bentonites, respectively, while those of Acid red 423 are 29.1 and 85.2 mg/g, respectively [45]. Besides, the k value for HCl-activated clay is much (2-3 times) smaller than that for pristine clay. Lin et al, 2004 reported the

adsorption of amido black 10B onto pristine and acid-activated montmorillonite (activated with 6 M HCl) from aqueous solution [46]. Özcan et al, 2004 assessed the adsorption of acid red (AR57) and acid blue (AB294) dyes from aqueous solution onto acid activated bentonite [47]. The acid activated bentonite showed very high adsorption capacities for AR57 (416.3 mg/g) and AB294 (119.1 mg/g). Teng et al, 2006 assessed the adsorption of methyl orange onto acid activated MMT clay and reported an improvement of about eight times relative to the natural clay [48]. Li 2007 reported a new adsorbent, EPI-DMA cationic polyelectrolyte/bentonite (EPI-DMA/bentonite), for removal of Reactive Blue K-GL (RBK-GL) dye from aqueous solution by adsorption method. The adsorption capacity (mg/g) is 68.60 at 23°C [49]. The equilibrium adsorption data are better represented by the Freundlich and D–R isotherm models.

Chun-li et al., 2005 synthesis and applied TiO_2 pillared bentonite and TiO_2 pillared bentonite doped with yttrium prepared by sol-gel method with bentonite for removal of Alizarin Yellow R dye from aqueous solution [50]. The XRD results confirm the existing interlayer distance increased to 1.9 µm or more and remained at 1.8 nm or more after being calcined at 500°C. The results shows that TiO_2 pillared bentonite were much faster and higher above all the other types of bentonite. The adsorption isothermal follows equations of Freundlich and Langrnuir. The adsorptions show endothermic process. The adsorption was of physical surface adsorption and ion-exchange type. Xiu qiong, 2000 investigated the removal of reactive red X-3B dye from wastewater by using modifying clay [51]. The results show that it has higher removal efficiency than active carbon. DíazGómez-Treviño et al., 2013 reported the removal of remazol yellow from aqueous solutions onto montmorillonite KSF and iron modified montmorillonite KSF [52]. From the experimental data it is clear that the MMT KSF removed about 10% more remazol yellow dye than the iron modified MMT KSF but the standard deviations of the experiments were very high for the unmodified material. The kinetic experiments showed the pseudo first order model (Lagergren), which is based on a surface reaction. The experimental data could be adjusted better to Freundlich and Langmuir– Freundlich models. Rehman, 2013 reported the adsorption of Brilliant Green (BG) dye on naturally existing red clay (RC) through batch adsorption experiment [53]. Adsorbent characterization showed BET surface area 100.28 m^2/g, pore volume 0.88 cm^3/g, and pore diameter 148.2 Å. Batch studies performed to investigate the effect of different parameter such as pH (2–10), particle size (58–150lm), adsorbent dose (0.3-1.5 g/L), contact time (5–1500 min), initial dye concentration (20–100 mg/L), and temperature (25–65°C) on the adsorption of BG dye. Langmuir (R^2 = 0.993), Freundlich (R^2 = 0.997), Hansley (R^2 = 0.997) and Redlich–Peterson (R^2 = 0.999) isotherms were fitted to describe the equilibrium of BG adsorption process. Adsorption kinetics were well fitted by Pseudo-second order kinetic model (R^2

= 0.999). Thermodynamic study revealed that BG adsorption on RC was spontaneous, favorable and physiosorptive. The maximum adsorption capacity [Qmax] (mg/g) of RC was found to be 125.

Yue et al., 2007 investigated polyepicholorohydrin-dimethylamine/bentonite for adsorption of four disperse dyes; Disperse Yellow Brown S-2RFL (DYB S-2RFL), Disperse Red S-R (DR S-R), Disperse Blue SBL (DB SBL) and Disperse Yellow (DY SE-6GFL) onto organophilic bentonite (polyepicholorohydrin-dimethylamine/bentonite) [54]. The maximum adsorption amount of four dyes was found at pH 1.2 with contact time of 60min. For four dye/bentonite systems, the kinetics of adsorption fitted to the two-step first-order kinetic rate equation with kinetic rate constants (k_1 and k_2) and intra- particle diffusion model with diffusion rate constants (k_{int1} and k_{int2}). Wang and Wang, 2007 reported a series of biopolymer chitosan/montmorillonite (CTS/MMT) nanocomposites for adsorption of Congo red [55]. They investigated the effect of pH and temperature and found that the sorption capacity was increased with increasing the CTS to MMT ratio. Qmax is found to be 81.23 mg/g. The experimental data suggest Langmuir model represented the adsorption data better than Freundlich mode. The Qmax values for the adsorption of CR by CTS, MMT and the nanocomposite were 81.23, 12.70, 54.52 mg/g. Peudo- first order model represents the kinetic data better than the pseudo- second order. Liu et al, 2007 written a review on the adsorption of dyes onto natural clay nano-adsorbents [56]. In this review authors has highlighted different types of clays such as natural, acid activated, calcined and organophilic clays for the adsorption of dyes from aqueous solution. Li et al., 2009 reported bentonite modified by EPI-DMA cationic polymer for adsorption kinetics of two reactive dyes, Reactive Blue K-GL (RB K-GL) and Reactive Yellow K-4G (RY K-4G) [57]. The data for these two dye show a good correspondence with the two-step kinetic rate equation and all the regression coefficients (R^2) = (>0.990). The adsorption capacities at equilibrium Qe (mg/g) for RB K-GL increase from 9.28 to 63.19 and for RY K-4G increase from 9.76 to 110.64 with an increase in concentration from 10 to 150 mg/L with an EPI-DMA/bentonite dose of 2 g/L. The author reported that with increase in pH from 2 to 13, the adsorption amount at equilibrium, Qmax (mg/g) for RB K-GL decreased from 137.53 to 14.14 and for RY K-4G decreases from 99.16 to 4.16. The activation energy of the adsorption process for two dyes increased as RB K-GL>RY K-4G. This suggest that the bigger RB K-GL molecules need more energy to adsorb onto EPI-DMA/bentonite than RY K-4G molecules.

Al et al., 2008 investigated the removal of safranine T from aqueous solutions using starch-*graft*-acrylic acid/Na-MMT (*S*-g-AA/MMT) nanocomposite hydrogels [58]. Effects of various parameters such as treatment time, initial dye concentration, and amount of the Na-MMT were investigated. The Freundlich equations were used to fit the equilibrium isotherms. Almeida et al, 2009 reported the adsorption of cationic dye, methylene blue onto montmorillonite clay from aqueous solution [59]. The montmorillonite clay showed high removal efficiencies with adsorption capacities of about 289 mg/g at 35°C. The experimental results have demonstrated that the equilibrium data are fitted well by a Langmuir isotherm equation (R^2=0.999). The experimental data fitted the pseudo-second-order kinetic model, with activation energy of +28.5 $kJmol^{-1}$. Li et al, 2010 reported adsorption of EPI-DMA/bentonite for two acid dyes, namely Acid Scarlet (AS GR) and Acid Dark Blue 2G (ADB 2G) [60]. Based on the correlation coefficient, Freundlich equation represents a better fit of experimental data (R^2=0.99) than Langmuir, in all cases. The authors also compare the adsorption capacity of three differents bentonite adsorbent towards the two acid dyes with that of EPI-DMA/bentonite, three selected bentonites are: raw bentonite, cationic surfactant-cetyltrimethylammonium bromide (CTMAB) modified bentonite (CTMAB/bentonite) and cationic polymer-polydiallydimethylammonium (PDMDAAC) modified bentonite (PDMDAAC/bentonite). The adsorption capacity Qmax (mg/g) of raw bentonite, CTMAB/bentonite and PDMDAAC/bentonite was 4.12, 30.28 and 42.72, respectively for AS GR; and the adsorption capacity was 3.67, 24.85 and 33.34, respectively for ADB 2G. Whereas, the Qmax (mg/g) of EPI-DMA/bentonite for AS GR and ADB 2G was 45.54 and 35.93, respectively at 303K. This confirm that EPI- DMA/bentonite are best adsorbent for removal of AS GR and ADB 2G. Koswojo et al., 2010 reported Acid Green 25 removal from wastewater by organo-bentonite. kinetic studies was performed by using 0.01 g of organo-bentonite mixed with 150 mL of Acid Green 25 solution at various concentrations (600, 800 and 1000 mg/L) at various time intervals and temperatures (30, 40 and 50°C) for 2 h [61]. The experimental data suggest Langmuir model represented the adsorption data better than Freundlich mode. The adsorption capacity Qmax (mmol/g) was found to be 2.983 at 30°C. Peudo-second order model represents the kinetic data better than the pseudo-first order indicating chemisorption as the controlling step of adsorption with K_2 (($g\ mmol^{-1}min^{-1}$).)= 0.0359 at 30°C.

Jianmin et al., 2010 investigated the adsorption of methylene blue dye by using Na-bentonite from aqueous solution at various contact time, initial pH and temperature [62]. The results obtained showed that the adsorption capacity Qmax (mg/g) of Na-bentonite was 198.71 at 25°C, pH 10, reaction time is 60 min, and it increased with increasing temperature. The thermodynamic parameter such as $\Delta°G$, $\Delta°H$ and $\Delta°S$ at different temperatures confirms that the adsorbing is a spontaneous and endothermic process. Experimental data for adsorption isotherm can be better described by Langmuir isotherm equations. The adsorption kinetic curves follow with the second-order kinetic equations. Yi et al., 2008 modified bentonites by exchanging with an anion surfactant (sodium dodecyl sulfonate, SDS) for removal of methylene blue dye [63]. Yi et al., 2008 study different properties, kinetics and

thermodynamics of methylene blue from water adsorption process on modified bentonites. The characterization of modified bentonite perform by X-ray and FI-IR diffraction show that the modified reagent is intercalated into the layers of bentonite and the spacing of bentonite layers increases from 1.04 nm to 3.52 nm. Result indicat that the isothermal adsorption equations follow Langmuir and Tempkin. The thermodynamic parameter such as $\Delta°H$ and $\Delta°S$ is -25.44 kJmol^{-1} and -50.74 Jmol^{-1} K^{-1}, respectively. It confirms the adsorption exhibits spontaneous surface physical adsorption. The adsorption dynamics follows the laws of pseudo-second-order kinetics with the energy of activation is 3.34 kJmol^{-1}. Zhen-hua & Hao-long, 2010 prepared new kind of modified bentonite by Na-bentonite, cetyl trimethyl ammonium bromide and cationic ammonium salt synthesized by diethylene triamine and epichlorohydrin for treatment of different dyes from wastewater [64]. These modified bentonite are used for was adsorption of dyeing wastewater as adsorbent combined with polyaluminium chloride as flocculant. It can be seen that removal % of dyes; reactive brilliant blue X-BR, reactive brilliant red X-3B and acid red GR was found to be 99.4%, 84.8% and 96.1%, respectively. The removal rate of COD and color were up to 51.6% and 85.9% respectively by using modified bentonite to treat raw water from dyeing wastewater treatment plant. Using it to treat effluent from aerobic tank of dyeing wastewater treatment plant, the COD of effluent could be decreased to 65.4 mg/L from 121.3 mg/L, and chroma could be decreased to below 8 times from 32 times.

As we known that the important problem in dyeing and printing wastewater treatment is to remove its color. Hong et al., 2010 prepared a new type of organic modified bentonite by using 8-hydroxyquinoline as modifier to treat dyeing and printing wastewater [65]. The optimum conditions for treatment are; pH 3.5,7 g/L of modify bentonite, stirred at 125 RPM, for 20 min, centrifugation time was 70 min. The modified bentonite treat the direct sunfast turquoise blue and the acid orange-red dye and the decolorization rate was found to be 94.1% and 74.4%, respectively. Adsorption process of modified bentonite to direct sunfast turquoise blue accorded with quasi-second order rate equations. The modified bentonite was suitable for the decolorization of direct sunfast turquoise blue dye. Guangjun et al., 2004 reported the removal of acidic red-B dye by using inorgano organo montmorillonites was synthesized by titrating Na montmorillonite with hydroxy aluminium solution [66]. XRD data reveal, the interlayer of montmorillonites was increased to 1.9nm and above. It was observed that adsorption ability of inorgano organo montmorillonites was much better than Na montmorillonites. The adsorption dynamics follows the laws of Bangham and Langmuir. The results indicate that the isothermal adsorption equations follow; Langmuir and Freundlich. The adsorption is presented by heat evolution physisorption and organic partion. Jinxu et al., 2005 reported removal of phenol based wastewater from chemical industry by using modify bentonite; Na-bentonite and Ca-bentonite by Al$_2$ (SO$_4$)$_3$ [67]. Different optimum conditions such as adding quantity of modified bentonite, pH, and agitation time are determined. The adsorption experimental results reveal that the removal rate of phenol is 78.5%, and the removal rate of COD and oil in the wastewater is 75.2% and 94.2% respectively. Pei et al., 2007 investigated the removal of methyl orange dye by using anion-cation organobentonite synthesized by incorporating both cationic surfactant bromide cetyltrimethylammonium (CTMAB) and anionic surfactant sodium dodecyl sulfate (SDS) to bentonite [68]. The results show that both the speed and adsorbability of methyl orange by anion-cation organobentonite were much faster and higher. The results indicate that the isothermal adsorption equations follow Langmuir adsoption isotherm. Ruilian, 2008 investigated removal of reactive black dye by using activated and modified bentonite by carbon-entraining and roasting method from wastewater [69]. He optimise the condition for adsorption of dye; the roasting time was 3.5h, the active carbon entrained was 3% and the roasting temperature was 550°C. The results indicated that the CODCr and color of reactive black dyeing wastewater were removed by 88.2% and 96.5% respectively by using modified bentonite.

Mahdavinia, 2012 reported the removal of cationic crystal violet dye from water by using nanocomposite superabsorbents prepared from solution polymerization of sodium acrylate in the presence of carrageenan biopolymer and sodium montmorillonite nanoclay [70]. Solution polymerization of partially neutralized acrylic acid was carried out in the presence of carrageenan biopolymer and sodium montmorillonite nanoclay. APS and MBA were used as initiator and crosslinker, respectively. The persulfate initiator is decomposed under heating to generate sulfate anion-radical. Then, the sulfate anion-radical abstracts hydrogen from H$_2$O molecules to produce hydroxyl radicals. The polymerization of sodium acrylate can initiate in the presence of hydroxyl radicals. In the presence of a cross-linker, i.e. MBA, cross-linking reaction can occur and finally a three dimensional network is produced. Carrageenan biopolymer and dispersed Na-MMt sheets will capture into crosslinked poly (sodium acrylate). It was found that by inclusion of nanoclay into carrageenan-based superabsorbent not only the rate of dye adsorption is increased, but also the removal efficiency is enhanced by 11 %. It depicts that Freundlich isotherm (R^2>0.96) is the best fit of experimental data than the Langmuir model. The adsorption capacity Qmax was found to be 55.8 mg/g.

Mahdavinia et al, 2012 again in the same year reported the adsorption of crystal violet cation dye onto nanocomposite hydrogels based on *kappa*-carrageenan from solution polymerization of acrylic acid monomer in the presence of Na-MMt and Laponite RD nanoclays [71]. In year 2014, Nanocomposite hydrogels were synthesized by solution copolymerization of acrylamide (AAm) in the presence of *kappa*-carrageenan (Carra) biopolymer and

sodium montmorillonite (Na-MMt) nanoclay. The reported XRD profile of pristine Na- MMt shows a diffractive peak at 2θ=7.6 corresponding to the distance of clay sheets with d spacing 11.61 A°. The XRD profile of these nanocomposites hydrogel shown no diffraction peak was observed in nanocomposite containing 5 wt% of clay (Clay0.2) and it can be concluded that the clay layers are exfoliated [72]. To confirm the synthesis of nanocomposites hydrogel, SEM analysis were provided by the author. Where, the microstructure the hydrogels without clay shows a relatively smooth surface, while the nanocomposite contains coarse and undulant surface. This observation can be attributed to insertion of nanoclay into hydrogel. The obtained nanocomposites were examined to remove of MB dye from water. The results showed that the speed of dye removal can affect by clay content. The speed of dye removal was increased by introducing of nanoclay into hydrogel composition. The results showed that the pseudo-second-order adsorption kinetic predominated for the adsorption of methylene blue (MB) onto nanocomposites. The rate constant $k_2 \times 10^{-3}$ (g/mg.min) is found to be 3.43, 5.7, and 4.36 for (Clay0), (Clay3) & (Clay5) respectively. The correlation coefficient is found to be 0.99 in all the three cases. It was observed that the removal efficiency is 99 and 92 % for Clay5 (0.2g) and Clay3 (0.1g), it is only 88 % for hydrogel without clay (Clay0). Langmuir model was obtained as the best model for the adsorption of MB onto nanocomposites. The adsorption capacity Qmax (mg/g) is found to be 303, 322 & 344 for (Clay0), (Clay3) & (Clay5) respectively. The correlation coefficient for Langmuir adsorption is found to be 0.98. The decrease in particle size improved the rate of adsorption and content of adsorbed dye. Thermodynamic parameters $\Delta°H$ (kJ mol^{-1}) & $\Delta°S$ (J K^{-1} mol^{-1}) are found to be +35.5 & +136.7 respectively. The positive value of $\Delta°H$ showed that the adsorption of CV onto nanocomposite was endothermic and positive value of $\Delta°S$ show*s* adsorbent takes place spontaneously.

Tavengwa and Lilian, 2012 investigated removal of pollutants (dyes and heavy metals) from aqueous solution by using composite material based on lignocellulose and montmorillonite clay (MPSgLig-NaMMT) [73]. The MPSgLig-NaMMT composite was prepared by in situ intercalative polymerisation, using methacryloxypropyl trimethoxysilane (MPS) as a coupling agent. The MPSgLig-NaMMT composite showed enhanced adsorption of methyl orange (MetO) compared with the NaMMT or lignocellulose separately. Competitive adsorption studies were carried out from binary mixtures of MetO with Cd^{2+} or Pb^{2+} in aqueous solution. The adsorption process of MetO onto the composite material was found to follow the Freundlich adsorption model. The adsorption of methyl orange from binary mixtures, were found to follow both the pseudo first-order and pseudo second-order models. Sun et al., 2012 reported Natural Na-bentonites were modified with an organic chelating agent, sodium diethyldithiocarbamatre (DDTC), to prepare a new adsorbent (DDTC-bentonite) for mixed

contaminant (Cu^{2+}, Cd^{2+} and phenol) removal [74]. Langmuir model, the sorption capacity of DDTC-bentonite for Cu^{2+}, Cd^{2+} and phenol is calculated to be 52.50, 46.86 and 44.55 mg/g under the experimental conditions, respectively. The large value of K$_f$ (Freundlich model) indicates that DDTC-bentonite has a high sorption affinity towards Cu^{2+}, Cd^{2+} and phenol. Langmuir and Freundlich isotherm equations were applied to the data. Hashem, 2012 reported the removal of basic dyes methylene blue by Fe$_3$O$_4$/bentonite nano composite [75]. The effect of pH on the adsorption was studied by agitated 50 ml of MB solution (2000 mg/L) with 50 mg of Fe$_3$O$_4$/ bentonite nanocomposite at different pH values (2 - 10) with shaking for 24 hours at 25°C. It was observed that increase of pH from 2 to 5 results in increase in adsorption capacity from 200 to 1600 mg/g. study shows that contact time of 150 min are needed for complete adsorption of MB dye. The three models are tested for MB on Fe$_3$O$_4$/bentonite nanocomposites (psedo first order, psedo second order and intra particle diffusion model). The best-fit model is psedo second model with the linear correlation coefficient R^2=0.998. The values of R^2 for Langmuir and Freundlich models are 0.99 and 0.96 respectively. The maximum binding capacity (Qmax) is found to be 1666.7 mg/g.

Tahir et al., 2013 reported the removal of textile dye reactive red 223 (RR 223) by acid treated Modify bentonite clay (MBC) [76]. It shows that maximum optimize removal of RR 223 dye was (95.15%) at 0.9g adsorbent and 20 min contact time. It was founded that Langmuir model is the best fitted isotherm. It was also examin that increase in temp result in decrease in adsorption of dye. Yanru et al., 2013 reported removal of methylene blue from aqueous solution by sorption on lignocellulose-g-poly (acrylic acid)/montmorillonite (LNC-g-PAA/MMT) hydrogel nanocomposites [77]. The results showed that the adsorption capacity for MB increased with increasing contact time, initial dye concentration, and pH value, but decreased with increasing MMT content and temperature. The adsorption kinetics was better described by the pseudo-second-order equation, and their adsorption isotherms were better fitted for the Langmuir equation. By introducing 20 wt% MMT into LNC-g-PAA polymeric network, the obtaining hydrogel composite showed the high adsorption capacity (mg/g) of 1994.38 for MB.

Kun-hong et al., 2012 reported adsorption of methyl orange by using nano-MoS$_2$/bentonite composite was synthesized by calcinating MoS3 deposited on bentonite in H$_2$ [78]. The results show that nano-MoS2 particles are distributed on the surface of bentonite and form layered structures with layer distance of about 0.64 nm. the removal efficiency within 70 min attains a satisfactory level (about 88%) when the dosage of composite is increased to 0.1 g in 150 mL 20 mg/L methyl orange solution. The removal efficiency of methyl is also influenced by temperature and pH value. The composite is more effective on the removal efficiency of methyl orange at a relatively low temperature (20°C). The removal

efficiency of methyl orange is high in acidic (pH 2) solutions but low under alkaline conditions. The adsorption of methyl orange is in accordance with the pseudo-second-order kinetic model.

Sebastian et al., 2014 reported the removal of two dyes Acid Green 25 and Acid Green 27 by Layered anionic clay (MgAl) - sodium alginate (Alg) composites with different alginate concentrations (3 wt%, 5.9 wt%, 11 wt% and 20 wt%) prepared by *in-situ* co-precipitation [79]. SEM image of Pristine MgAl crystals are flake-like with sharp edges, stacked in the form of layers whereas sodium alginate has a smooth surface. Small alginate particles can be seen spread over the clay surface and in-between layers of the clay, at low alginate concentrations. At higher concentrations alginate starts form-ing a smooth continuous/semi-continuous layer on the clay. The clay-alginate composite with 5.9% alginate showed highest adsorption for both the dyes. The maximum adsorption capacity of the composite was enhanced by 51% for Acid Green 25 and 160% for Acid Green 27, compared to the pristine layered clay sample. The isotherm data could be explained well using the Freundlich isotherm model. Adsorption kinetics was analyzed using normal first order and Lagergren first order kinetic models.

Yang et al., 2015 reported adsorption of methylene blue (MB) dye by using TiO_2–WO_3–bentonite composites were synthesized via a hydrothermal route with and without an ultrasonic pretreatment [80]. The maximum adsorption capacity for MB was increased to 70.9 mg g^{-1}. The effect of pH on the adsorption capacity for MB on U/TiW–NB performed at 35°C. It was observed that the adsorption capacity of U/TiW–NB for MB was increased by increasing pH from 3 to 5, approximately kept constant in the pH range of 5–9, and further improved at pH = 11.

Liu et al., 2015 reported Adsorption of an anionic azo dye (Amido Black 10B) by cross-linked chitosan/bentonite composite [81]. Cross-linked chitosan (CCS)/bentonite (BT) composite was prepared by the intercalation of chitosan in bentonite and the cross-linking reaction between chitosan and glutaraldehyde. The adsorption of Amido Black 10B onto the CCS/BT composite was found to be optimal at pH 2, adsorbent dosage: 0.05 g at 293K; contact time: 60 min; dye concentration: 200 and 250 mg/L. The adsorption isotherm was well described by the Langmuir model and the maximum adsorption capacity was 323.6 mg/g at 293K and pH 2. Amido Black 10B adsorption kinetics followed a pseudo-second-order kinetic model. Negative $\Delta°G$ values imply spontaneous adsorption of AB10B onto the CCS/BT composite in the 293–313K range. The positive $\Delta°H$ (kJ/mol) values 15.78, which are supported by increased AB10B adsorption at high temperatures, confirmed that AB10B adsorption onto the CCS/BT composite is endothermic.

Benhouria et al., 2015 reported activated carbon–bentonite–alginate beads (ABA) were prepared for the adsorption of methylene blue (MB) [82]. The optimized conditions a fixed ABA dosage of 0.2 g, pH 6, constant initial concentration of 100 mg/L, and temperature of 30°C.

Results showed that the Qmax of ABA beads for the adsorption of MB were 756.97 mg/g at 30°C. Furthermore, the adsorption kinetics illustrated the suitability of employing the pseudo-second-order kinetic model. The equilibrium adsorption data fitted the Freundlich isotherm well. The values of $\Delta°S$ and $\Delta°H$ were determined from the intercept and slope of plot lnK against 1/T. The values of Gibbs free energy ($\Delta°G$) were 5.920, 5.844, and 5.723 kJ/mol at temperature 303, 313 and 323K respectively. All $\Delta°G$ values were negative and decreases with increasing temperature, indicating that the MB adsorption process on ABA was spontaneous. The negative $\Delta°H$ value (8.897 kJ/mol) of MB adsorption on ABA confirmed the involvement of an exothermic process. The $\Delta°H$ was lower than 84 kJ/mol, indicates the physisorption adsorption process. The $\Delta°S$ value was also negative (9.802 J/mol.K), which explains the decreased randomness at the solid/solution interface during the adsorption process. No significant difference was found in the percentages of desorbed MB in six Sorption–Desorption cycles for ABA (94.42%, 90.33%, 86.07%, 80.14%, 79.15%, and 75.47%). The ABA composite exhibited more than 70% adsorption uptake capacity after six regeneration cycles.

Toor et al., 2015 reported removal of congro red by using thermal activation (TA), acid activation (AA), and combined acid and thermal activation (ATA) bentonites [83]. The best ATA protocol considered here brought a 70% increase in the surface area compared to 65% and 20% for the best AA and TA protocols, respectively. The optimized condition (100 mg L^{-1}), bentonite dosage 1 g L^{-1}, 100°C, 1.4h). The adsorption capacity of raw bentonite was also enhanced by the activations and followed the order: ATA > AA > TA > RB. The overall adsorption capability of bentonite modified by ATA was augmented by more than 25%.

Chinoune et al., 2016 reported magnesium hydroxide coated bentonite, B–Mg(OH)$_2$ composite, and its capacity to remove anionic reactive dyes; Procion blue HP (PB) and remazol brilliant blue R (RB) from aqueous solution [84]. The optimized Conditions are (Dye concentration 100 mg/L; dose = 2 g/L; pH = 2; T = 298 ± 1 K; contact time: 3 h). At pH = 2, the maximum dye adsorption was found as 98.2% for RB and 87.8% for PB. Kinetic studies revealed that adsorption follows a pseudo-second-order model, and rate constants were evaluated. The Langmuir monolayer adsorption capacities of PB and RB in aqueous solution were estimated at 298 K as 40.22 and 66.90 mg/g, respectively. Thermodynamic parameters for the adsorption of PB and RB on B–Mg (OH)$_2$ composite was evaluated results shows $\Delta°H$ (kJ/mol) and $\Delta°S$ (J/mol K) are 27 and 101.28 for PB and 19.46 and 51.55 for RB respectively. A temperature uptake from 278 K to 313 K induced an increase of adsorption for both dyes and the process was found to be physiosorptive, endothermic and spontaneous.

The different adsorption parameter and isotherm studies of several dyes in water or wastewater have been tabulated in (Table 1).

Table 1. Adsorption capacities and other parameters for the removal of organic contaminants from water by different bentonite based adsorbents.

Contaminants	Adsorbents	Conc. range	pH	Contact time	Temp	Adsorption capacity	Ref.
Dyes							
Acid Yellow 194, Acid Blue 349 and Acid Red 423	Natural Bentonite (NB) and acid-activated bentonites (AB)	-	-	3h	25°C	24.9 and 71.1 for Acid Yellow 194; 92.7 and 98.4 for Acid Blue 349; 29.1 and 85.2 mg/g for Acid Red 423, respectively for NB and AB.	[45]
Amido Black 10B	Acid-activated montmorillonite	-	-	-	25°C	-	[46]
Acid Red (AR57) and Acid Blue (AB294) dyes	Acid Activated bentonite	-	2	90 min	20°C	416.3 and 119.1 mg/g for AR57 and AB294 respectively.	[47]
Blue K-GL (RBK-GL)	EPI-DMA /bentonite	0–100 mg/L	1	2 h	23°C	68.60 mg/g	[49]
Brilliant Green (BG) dye	Red clay (RC)	20–100 mg/L	7	4h	25°C	125mg/g	[53]
Disperse Yellow Brown S-2RFL (DYB S-2RFL), Disperse Red S-R (DR S-R), Disperse Blue SBL (DB SBL) and Disperse Yellow (DY SE-6GFL	Polyepicholorohydrin-dimethylamine/ bentonite	50mg/L	1.2	150 min	23°C	45.52, 51.16, 43.94 and 28.46 mg/g respectively	[54]
Congo Red	CTS, MMT and CTS/MMT nanocomposites	400 mg/L	7	720 min	30°C	81.23, 12.70, 54.52 mg/g respectively	[55]
Reactive Blue K-GL (RB K-GL) and Reactive Yellow K-4G (RY K-4G)	Bentonite modified by EPI-DMA cationic polymer	10-150 mg/L	2	120 min	30°C	137.53 and 99.16 mg/g respectively	[57]
Safranine T	Starch-*graft*-acrylic acid/Na-MMT (*S*-g-AA/MMT-0) nanocomposite hydrogels, S-g-AA/MMT-1 and S-g-AA/MMT-3	100–500 mg/L.	-	S-g-AA/MMT-0 & S-g-AA/MMT-1 (24 h) & S-g-AA/MMT-3 (144 h)	-	2300, 2124 and 2237 mg/g respectively	[58]
Methylene Blue	Montmorillonite clay	200 mg/L.	11	30 min	35°C	289 mg/g	[59]
Acid Scarlet (AS GR) and Acid Dark Blue 2G (ADB 2G)	Raw bentonite, cationic surfactant-cetyltrimethylammonium bromide (CTMAB) modified bentonite (CTMAB/bentonite) and Cationic polymer-polydiallydimethylammonium (PDMDAAC) modified bentonite (PDMDAAC/bentonite).	0–100 mg/L	1	120 min	30°C	4.12, 30.28 and 42.72, respectively for AS GR; 3.67, 24.85 and 33.34, respectively for ADB 2G, Whereas, the adsorption capacity (mg/g) of EPI-DMA/bentonite for AS GR and ADB 2G was 45.54 and 35.93, respectively	[60]
Acid Scarlet (AS GR) and Acid Dark Blue 2G (ADB 2G)	EPI-DMA /bentonite	-	1	120 min 120min	30°C	45.54 and 35.93, respectively	
Acid Green 25	Organo-bentonite	600-1000 mg/L		2 h	30°C	2.983 mmol/g	[61]
Methylene Blue	Na-bentonite	-	10	-	25°C	198.71 mg/g	[62]
Direct sunfast turquoise blue and Acid orange-red dye	Organic modified bentonite using 8-hydroxyquinoline	-	3.5	20 min	-	94.1% and 74.4%, respectively.	[65]
Cationic Crystal Violet dye	*kappa*-carrageenan (Carra) biopolymer and sodium montmorillonite (Na-MMt) nanoclay hydrogel	30 mg/g	-	-	-	303, 322 and 344mg/g for (Clay0), (Clay3) & (Clay5) respectively.	[71]
Methyl Orange	MPSgLig-NaMMT composite	2 to 10 mg/L	5	4h	23°C	3.374mg/g	[72]
Cu²⁺, Cd²⁺ and phenol)	DDTC-bentonite	-	-	2h	-	52.50, 46.86 and 44.55 mg/g	[74]
Methylene Blue	Fe₃O₄/ bentonite nano composite	-	5	150 min	25°C	1666.7 mg/g	[75]
Red 223 (RR 223}	Modify bentonite clay (MBC)	-	-	20min	30 ºC	95.15%	[76]

Contaminants	Adsorbents	Conc. range	pH	Contact time	Temp	Adsorption capacity	Ref.
Dyes							
Methylene blue	lignocellulose-g-poly (acrylic acid)/montmorillonite (LNC-g-PAA/MMT) hydrogel nanocomposites	2,500 mg/L	5	120 min.	30 ºC	1994.38 mg/g	[77]
Methyl Orange	Nano-MoS$_2$/bentonite composite	20mg/L	2	70 min	20°C	88%	[78]
Methylene blue	TiO$_2$-WO$_3$-bentonite composite		11		35°C	70.9 mg/g	[80]
Amido black 10B	Crosslinked chitosan/bentonite composite	250mg/L	2	60 min	20°C	323.6 mg/g	[81]
Methylene blue	Activated carbon bentonite alginate beads (ABA)	100mg/L	6		30°C	756.97 mg/g	[82]
Procion blue HP (PB) and Ramazol brilliant blue R (RB)	Magnesium hydroxide coated bentonite (B-M(OH)$_2$) composite		2	3 h	25°C	40.22 and 66.90 mg/g respectively	[84]

5. Conclusions and Future Prospect

A summary of adsorption capacity of various adsorbents for removal of dyes removal from water and wastewater under various experimental conditions has been presented in review article. Recently, bentonite and modified bentonites as adsorbents are gaining wide attention due to their higher potential for dye removal. Review represents the kinetic models and applicable isotherm of dyes adsorption studies respectively, onto various bentonite and its composites. In most studies, pseudo-second-order kinetic model was found to fit well with the experimental data. Furthermore, dyes sorption by various adsorbents has been found to fit well by Freundlich and/or Langmuir isotherm models. Results from the recent advances in using bentonites and its modified composites show the flexible nature of the clay and its ecofriendly nature. They are capable of removing dyes from water. Being natural and their abundance presence makes them a low-cost green, nontoxic adsorbent which can be used for removal of different contaminants from water and making clean and pure drinking water available for developed and developing nations in near future.

From the above review, it was concluded that modifying bentonite by incorporating different polymers and nanoparticles will enhance the adsorption capacity of our natural bentonite for dyes removal. In future more attention in enhancement of sorption capacity of dyes through modification and mechanistic modelling of bentonites clay need to be done. There is need for exploring new and modified methods for separating bentonite from water and improving the dye removal rate. The interaction between adsorbates and the adsorbents must be investigated in more detail to establish the relationships and roles of functional groups in the dye adsorption process. Regeneration of the adsorbent by desorption is not feasible; therefore, cost-effective and feasible regeneration methods must be developed. Some pilot-scale studies to check the feasibility of these clay adsorbents at the industrial level need to be performed in the coming year.

Apart from this, In the near future, scientists and researchers need to focus on removing trace amounts of other contaminants present in safe drinking water. There are very few reports for removal of pathogenic contaminates from wastewater. So pathogenic contaminates removal need to be targeted in coming years, and different bentonite based composites will be the perfect adsorbent that need to exploited for water treatment for removing trace amount of organic, inorganic and pathogenic contaminates from water and wastewater.

References

[1] Aksu Z. Application of biosorption for the removal of organic pollutants: a review. Process Biochem 2005; 40:997–1026.

[2] Abd El-Latif MM, El-Kady MF, Ibrahim AM, Ossman ME. Alginate/polyvinyl alcohol-kaolin composite for removal of methylene blue from aqueous solution in a batch stirred tank reactor. J Am Sci 2010; 6: 280–292.

[3] Pandey S, Mishra SB. Microwave synthesized xanthan gum-g-poly (ethylacrylate): An efficient Pb^{2+} ion binder. Carbohydrate Polymer. 2012; 90 (1): 370-379, 2012.

[4] Pandey S, Mishra SB. Graft copolymerization of Ethylacrylate onto Xanthan Gum, Using Potassium Peroxydisulphate as an Initiator. International Journal of Biological macromolecules. 2011; 49 (4): 527–535.

[5] Pandey S, Mishra SB. Sol–gel derived organic–inorganic hybrid materials: synthesis, characterizations and applications, Sol-gel Science and Technology 2011; 59 (1): 73-94.

[6] Singh V, Singh SK. Pandey S, Kumar P. Sol–gel synthesis and characterization of adsorbent and photoluminescent nanocomposites of starch and silica. Journal of Non-Crystalline Solids. 2011; 357: 194–201.

[7] Singh V, Pandey S, Singh SK, Sanghi R. Removal of cadmium from aqueous solutions by adsorption poly (acrylamide) modified guar gum-silica nanocomposites. Separation and purification technology 2009; 67: 251-261.

[8]   Singh V, Kumari P, Pandey S, Narayan T. Removal of Chromium (VI) using poly (methylacrylate) functionalized guar gum . Bio resource Technology 2009; 100(6): 1977-1982.

[9]   Singh V, Pandey S, Singh SK, Sanghi R. Sol-gel polycondensation of tetraethoxysilane in ethanol in presence of vinyl modified guar gum: synthesis of novel adsorbent materials, Sol-gel Science and Technology 2008; 47(1): 58-67.

[10] Singh V, Pandey S, Singh SK, Sanghi R. Synthesis of Novel Nanocomposites of Silica and Guar Gum: Efficient Zinc Ion Binder, Journal of Fudan University (Natural Science), 2007; 46(5): 155.

[11] Singh V, Tiwari A, Pandey S, Singh SK, Sanghi R. Synthesis and characterization of novel saponified guar graft-polyacrylonitrile/silica nanocomposite materials, Journal of Applied polymer science 2007; 104(1): 536-544.

[12] Pandey S, Goswami GK, Nanda KK. Nanocomposite based flexible ultrasensitive resistive gas sensor for chemical reactions studies. Scientific Reports 2013: (3): 2082. doi: 10.1038/srep02082

[13] Pandey S, Goswami GK, Nanda KK. Green synthesis of polysaccharide/gold nanoparticle nanocomposite: An efficient ammonia sensor. Carbohydr. Polym. 2013: 94: 229-234.

[14] Pandey S, Mishra SB. Chromatographic resolution of racemic α-amino acids: Chiral stationary phase derived from modified xanthan gum. Carbohydr. Polym. 2013: 92: 2201–2205. Pubmed.

[15] Pandey S, Goswami GK, Nanda KK. Green Synthesis of Biopolymer-Silver nanoparticle Nanocomposite: An optical Sensor for Ammonia Detection. Int J Biol Macromol. 2012: 51: 583-589.

[16] Pandey S, Mishra SB. Microwave synthesized xanthan gum-g-poly (ethylacrylate): An efficient Pb^{2+} ion binder. Carbohydr. Polym. 2012: 90(1): 370-379.

[17] Singh V, Tiwari A, Pandey S, Singh SK. Peroxydisulfate initiated synthesis of potato starch-graft- poly (acrylonitrile) under microwave irradiation, xPress polymer letters 2007, 3007: 1(1): 51-58.

[18] Singh V, Tiwari A. Pandey S, Singh SK. Microwave accelerated synthesis and characterization of potato starch-g-poly (acrylamide), Starch/Starke 2006: 58: 536-543. doi:10.1002/star.200600520

[19] Pandey S, Mishra SB. Amorphous mixed oxides: A New and Highly Versatile Class of Materials, Intelligent nanomaterial. 149, 2012 ISBN: 978-0-470-93879-9 Scrivener-Wiley publisher. doi:10.1002/9781118311974.ch4

[20] Pandey S, Nanda KK. One-dimensional Nanostructure Based Chemiresistive Sensor, Nantotechnology, Vol. 10: Nanosensing 2013: 10:1-16. ISBN: 1-62699-010-7, Studium Press LLC, USA.

[21] Pandey S, Mishra SB. Bioceramics: Silica based organic-inorganic hybrid materials for medical applications, "Nanomedicine for Drug Delivery and Therapeutics". ISBN: 9781118414095, 2013: Ch.5: 136-158. Scrivener-Wiley publisher doi: 10.1002/9781118636299.ch5

[22] Pandey S, Mishra SB, Chemical Nanosensors for Monitoring Environmental Pollution. Application of Nanotechnology in Water Research. 309-332 (2014). John Wiley & Sons, Inc. doi:

10.1002/9781118939314.ch12

[23] Singh V, Singh SK, Pandey S, Sanghi R. Synthesis and characterization of guar gum templated hybrid nano silica. Int J Biol Macromol.2011, 49, 233–240.

[24] Pandey S, Mishra SB. Organic-inorganic hybrid of chitosan/organoclay bionanocomposites for hexavalent chromium uptake. J. Colloid Interface Sci. 2011, 361, 509–520.

[25] Pandey S, Tiwari S, Facile approach to synthesize chitosan based composite—Characterization and cadmium (II) ion adsorption studies, Carbohydrate Polymers 134, 646–656, 2015

[26] Pandey S, Nanda KK, Au Nanocomposite Based Chemiresistive Ammonia Sensor for Health Monitoring, ACS Sensors 2016, 1, 55-62.

[27] Pandey S, Ramontja J, Rapid, facile microwave-assisted synthesis of xanthan gum grafted polyaniline for chemical sensor, International Journal of Biological Macromolecules, 2016, 89, 89-98.

[28] Pandey S, Ramontja J, Turning to Nanotechnology for Water Pollution Control: Applications of Nanocomposites, Focus on Sciences, 2016, 2 (2), 1-10.

[29] Nigam P, Banat IM, Singh D, Marchant R. Microbial process for the decolorization of textile effluent containing azo, diazo and reactive dyes. Process Biochemistry 1996; 31, (5): 435-442.

[30] Annadurai G, Juang RS, Lee DJ. Use of cellulose-based waste for adsorption of dyes from aqueous solutions. Journal of Hazardous Materials, 2002; B92: 263–274.

[31] Al-Asheh S, Banat F, Abu-Aitah L. Adsorption of phenol using different types of activated bentonites. Sep. Pur. Tech. 2003; 33: 1-10.

[32] Kara M, Yuzer H, Sabah E, Celik MS. Adsorption of cobalt from aqueous solutions onto sepiolite. Water Res. 2003; 37: 224-232.

[33] Yıldız N, Gönülşen R, Koyuncu H, Calımlı A. Adsorption of benzoic acid and hydroquinone by organically modified bentonite. Colloids Surf. A: Physicochem. Eng. Asp. 2005; 260: 87-94.

[34] Wang L, Wang A. Adsorption properties of Congo red from aqueous solution onto surfactant-modified montmorillonite. Journal of Hazardous materials 2008; 160: 173-180.

[35] Chen R, Peng F, Su S. Synthesis and characterization of novel swelling tunable oligomeric poly (styrene-co-acrylamide) modified clays. J. Appl. Polym. Sci. 2008; 108: 2712-2717.

[36] Kellner R, Mermet JM, Otto M, Widmer HM. Analytical Chemistry, Wiley-VCH, New York, 1998, pp. 541-546, 691-700.

[37] Fischer EW. Small angle x-ray scattering studies of phase transitions in polymeric and oligomeric systems. Pure and Applied Chemistry, 1971; 26 (3-4): 385-422.

[38] Mahboub R, Mouzdahir YE, Elmchaouri A, Carvalho A, Pinto M, Pires J. Characterization of a delaminated clay and pillared clays by adsorption of probe molecules. Colloids and Surfaces A: Physicochem. Eng. Aspects, 2006; 280: 81–87.

[39] Steudel A, Batenburg LF, Fischer HR, Weidler PG, Emmerich K. Alteration of swelling clay minerals by acid activation. Appl. Clay Sci. 2009; 44: 105-115.

[40] He H, Frost RL, Bostrom T, Yuan P, Duong L, Yang D, Xi Y, Kloprogge T. Changes in morphology of organoclays with HDTMA surfactant loading. Appl. Clay Sci. 2006; 31: 262-271.

[41] Dai JC, Huang JT. Surface modification of clays and clay-rubber composite. Appl. Clay Sci. 1991; 15: 51-65.

[42] Paiva de LB, Morales AR, Díaz FRV. Organoclays: Properties, prepration and applications. Appl. Clay Sci. 2008; 42: 8-24.

[43] Liu P. Polymer modified clay minerals: A review. Appl. Clay Sci. 2007; 38: 64-76.

[44] Stockmeyer MR. Adsorption of organic compounds on organophilic bentonites. Appl Clay Sci 1991; 6: 39–57.

[45] Espantaleona AG, Nietoa JA, Fernandezb M, Marsalc A. Use of activated clays in the removal of dyes and surfactants from tannery wastewater, Appl. Clay Sci. 2003; 24:105–110.

[46] Lin SH, Juang RS, Wang YH. Adsorption of acid dye from water onto pristine and acid-activated clays in fixed beds. Journal of Hazardous Materials. 2004; B113: 195–200.

[47] Özcan AS, Özcan A. Adsorption of acid dyes from aqueous solutions onto acid-activated bentonite. Journal of Colloid and Interface Science. 2004; 276: 39–46.

[48] Teng MY, Lin SH. Removal of methyl orange dye from water onto raw and acid activated montmorillonite in fixed beds. Desalination 2006: 201: 71–81.

[49] Li Q, Yue Q-Y, Su Y, Gao B-Y, Fu L. Cationic polyelectrolyte/bentonite prepared by ultrasonic technique and its use as adsorbent for Reactive Blue K-GL dye, Journal of Hazardous Materials. 2007; 147: 370–380.

[50] Chun-li Z, Guang-jun R, En-jun S, Xin W. A Study on the Adsorption of Alizarin Yellow R from Aqueous Solution by TiO_2 Pillared Bentonite. Dyestuffs and coloration. 2005-05.

[51] Xiu-qiong Z. Treating dyeing wastewater of reactive red X-3B with modified montmorillonite clay. Environmental science and technology. 2000-03.

[52] DíazGómez-Treviño AP, Martínez-Miranda V, Solache-Ríos M. Removal of remazol yellow from aqueous solutions by unmodified and stabilized iron modified clay, Applied Clay Science. 2013; 80–81: 219–225.

[53] Rehman MSU, Munir M, Ashfaq M, Rashid N, Nazar MF, Danish M, Han J-I. Adsorption of Brilliant Green dye from aqueous solution onto red clay, Chemical Engineering Journal. 2013; 228: 54–62.

[54] Yue Q-Y, Li Q, Gao B-Y, Wang Y. Kinetics of adsorption of disperse dyes by polyepicholorohydrin-dimethylamine cationic polymer/bentonite, Separation and Purification Technology. 2007; 54: 279–290.

[55] Wang L, Wang A. Adsorption characteristics of Congo red onto the chitosan/montmorillonite nanocomposite J. Hazard. Mater. 2007; 147: 979.

[56] Liu P. Polymer modified clay minerals: A review. Applied Clay Science. 2007; 38: 64–76.

[57] Li Q, Yue Q-Y, Su Y, Gao B-Y, Jing L. Two-step kinetic study on the adsorption and desorption of reactive dyes at cationic polymer/bentonite, Journal of Hazardous Materials. 2009; 165: 1170–1178.

[58] Al E; Güçlü G, İyim TB, Emik S, Özgümüş S. Synthesis and properties of starch-graft-acrylic acid/Na-montmorillonite superabsorbent nanocomposite hydrogels. Journal of Applied Polymer Science. 2008; 109 (1) 16-22.

[59] Almeida CAP, Debacher NA, Downs AJ, Cottet L, Mello CAD. Removal of methylene blue from colored effluents by adsorption on montmorillonite clay. Journal of Colloid and Interface Science. 2009; 332: 46–53.

[60] Li Q, Yue Q-Y, Su Y, Gao B-Y, Sun H-J. Equilibrium, thermodynamics and process design to minimize adsorbent amount for the adsorption of acid dyes onto cationic polymer-loaded bentonite, Chemical Engineering Journal. 2010; 158: 489–497.

[61] Koswojo R, Utomo RP, Ju Y-H, Ayucitra A, Soetaredjo FE, Sunarso J, Ismadji S. Acid Green 25 removal from wastewater by organo-bentonite from Pacitan, Applied Clay Science. 2010; 48: 81–86.

[62] Jianmin R, Yongmin Z, Siwei W, Sheguang D, Peipei G. Thermodynamics and kinetics of adsorption of methylene blue by Na-bentonite, Ion Exchange and Adsorption. 2010-02.

[63] Yi W, Ting Z, Huixia F, Jianhui Q. Study on Adsorption of Methylene Blue from Aqueous Solution by Anion Surfactant Modified Bentonites, Non-Metallic Mines. 2008-02.

[64] Zhen-hua P, Hao-long X, Application of New Type Organobentonite for Treating of Dyeing Wastewater, Guangzhou Chemical Industry. 2010-09.

[65] Hong S, Hong-kang X, Lei W. Study on treatment of dyeing and printing wastewater with 8-hydroxyquinoline-modified bentonite, Textile Auxiliaries. 2010-10.

[66] Guangjun R. et al. Adsorption Behaviours of Pillared-bentonite to Dyeing Acidic Red-B, Non-metallic Mines. 2004-02.

[67] Jinxu N, Xianmin X, Lifan L. Experimental Study of The Modified Bentonite Coagulant for Phenol-based Wastewater, Non-metallic Mines. 2005-02.

[68] Pei W,Wen-jie W, Li-hui Z. Adsorption of Methyl Orange onto Anion-Cation Organobentonite, Technology & Development of Chemical Industry. 2007-11.

[69] Ruilian Y. Treatment of Reactive Black Dyeing Wastewater by Carbon-entrained & Roasted Bentonite. Non-Metallic Mines. 2008-01.

[70] Mahdavinia GR, Zhalebaghy R. Removal Kinetic of Cationic Dye Using Poly (Sodium Acrylate)-Carrageenan/Na-Montmorillonite Nanocomposite Superabsorbents. J. Mater. Environ. Sci. 2012; 3 (5): 895-906.

[71] Mahdavinia GR, Massoumi B, Jalili K, Kiani G. Effect of sodium montmorillonite nanoclay on the water absorbency and cationic dye removal of carrageenan- based nanocomposite superabsorbents. J. Polym. Res. 2012; 19: 9947.

[72] Mahdavinia GR, Baghban A, Zorofi S, Massoudi A. Kappa-Carrageenan Biopolymer-Based Nanocomposite Hydrogel and Adsorption of Methylene Blue Cationic Dye from Water. J. Mater. Environ. Sci. 2014; 5(2): 330-337.

[73] Tavengwa B, Lilian T. Adsorption of Methyl Orange, Pb2+ and Cd2+ from Aqueous Solution by Composites of Lignocellulose-Montmorillonite Modified with Methacryloxypropyl Trimethoxysilane. Macromolecular Symposia. 2012; 313-314(1): 146-156.

[74] Sun Y-X, Ren Z-L, Li Y-Q. Preparation of Organic Chelating Agents Modified Bentonite for Mixed Contaminant Removal from Aqueous Solutions, Geomatics for Integrated Water Resources Management (GIWRM). International Symposium on. 2012; 1–4.

[75] Hashem FS. Adsorption of Methylene Blue from Aqueous Solutions using Fe3O4/ Bentonite Nanocomposite. Hydrology Current Research. 2012; 3: 5.

[76] Tahir H, Sultan M, Qadir Z. Physiochemical Modification and Characterization of Bentonite Clay and Its Application for the Removal of Reactive Dyes, International Journal of Chemistry. 2013; 5(3).

[77] Yanru S, Zhenhua X, Ximing W. Removal of methylene blue from aqueous solution by sorption on lignocellulose-g-poly (acrylic acid)/montmorillonite three-dimensional cross-linked polymeric network hydrogels, Polymer Bulletin. 2013; 70: 1163-1179.

[78] Kun-hong, Zhao Di-fang, Liu Jun-sheng, Synthesis of nano-MoS2/bentonite composite and its application for removal of organic dye HU Trans. Nonferrous Met. Soc. China 22(2012) 24842490.

[79] Sebastian S, Mayadevi S, Beevi BS, Sujata Mandal S. Layered Clay-Alginate Composites for the Adsorption of Anionic Dyes: A Biocompatible Solution for Water/Wastewater Treatment, Journal of Water Resource and Protection. 2014; 6: 177-184.

[80] Yang C, Zhu Y, Wang J, Li Z, Su X, Chunge Niu, Hydrothermal synthesis of TiO_2–WO_3–bentonite composites: Conventional versus ultrasonic pretreatments and their adsorption of methylene blue, Applied Clay Science 2015, 105–106, 243–251.

[81] Liu Q, Yang B, Zhang L, Huang R, Adsorption of an anionic azo dye by cross-linked chitosan/bentonite composite, International Journal of Biological Macromolecules 2015, 72, 1129–1135.

[82] Benhouria A, Islam MA, Zaghouane-Boudiaf H, Boutahala M, Hameed BH, Calcium alginate–bentonite–activated carbon composite beads as highly effective adsorbent for methylene blue, Chemical Engineering Journal 2015, 270, 621–630.

[83] Toor M, Jin B, Dai S, Vimonses V, Activating natural bentonite as a cost-effective adsorbent for removal of Congo-red in wastewater, Journal of Industrial and Engineering Chemistry 2015, 21, 653–661.

[84] Chinoune K, Bentaleb K, Bouberka Z, Nadim A, Maschke U, Adsorption of reactive dyes from aqueous solution by dirty bentonite, Applied Clay Science 2016, 123, 64–75.