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POTENTIAL OF USING NZVI AS A DYE REMOVAL METHOD IN THE CONTEXT OF BANGLADESH

Abstract:

Bangladesh is one of the top garment exporting countries of the world. In FY 2014-2015, 81.69% of Bangladesh’s export industries was comprised of ready-made garments. Dyeing industries are an integral part of most of these garment industries. Unfortunately, majority of the effluents from these dyeing industries are responsible for severe water pollution and environmental degradation as they are often discharged with no or minimal treatment. This has dire consequences as Bangladesh is a densely populated country with a soaring figure of 1252 per km2 as of 2016, based on the latest United Nations estimates. Additionally, it is a chiefly rural and river centric country and 66 % of its population are directly dependent on its rivers for either their livelihood (e.g. fishermen, oarsman) or other household activities such as washing, bathing, cooking and sometimes even drinking. This has led to an outburst of diseases like cholera, dysentery, diarrhea, hepatitis A, lead poisoning, malaria, etc prevailing for the last few years, creating a catastrophic impact on public health. This has made it imperative for wastewater to be treated properly before its release into the water bodies. Although there are a number of techniques available, most of them are expensive and so the local industries are reluctant to use these methods. In this study, it has been attempted to find a cheap and suitable method for removing dyes from these effluents. NZVI (Nano-scale Zero Valent Iron) seems to have a great potential in this aspect. It is cheap, easy to make and has a high efficiency in degrading dyes. Furthermore, only a small amount is sufficient to remove a relatively large amount of dyes, which makes it an attractive treatment method for Bangladesh.

Keywords:

Garment industries, dyeing industries, effluent, Bangladesh, NZVI, public health

Introduction

Bangladesh is one of the most densely populated and poorest countries in the world with approximately 1252 people per square kilometer and as of 2010, 31.5% of the population live below the poverty line (indexmundi, 2015, Agency, 2016). The ready-made garment (RMG) sector has become one of the largest providers of employment in Bangladesh. There are now approximately 42792 registered industrial units in Bangladesh and it is generally accepted that there are an equivalent number of unregistered units ((BSS), 2013). The RMG sector accounts for 80% of Bangladesh's total export, which was approximately $15.6 billion in 2010 ((BSS), 2013). The growth in this sector unquestionably had a positive effect on the national economic development. However, industrialization has also brought along a range of environmental problems. One of the main environmental impacts of these industries is the discharge of the wastewater into the nearby water bodies with little to no treatment. The World Bank estimates that 17 to 20% of industrial water pollution comes from textile dyeing and treatment and 72 toxic chemicals in water come solely from textile dyeing, 30 of which are extremely difficult to remove (Islam et al., 2012). The manufacturing processes involved such as slashing, bleaching, mercerizing and dyeing are the biggest water consumption activities as well as the ones that generate the most amount of wastewater. Among these various stages of textile manufacturing most pollution is generated in the fabric coloring stage (dyeing and bleaching) where chemicals such as oil, grease, ammonia, sulfide, lead, color, heavy metals and other toxic organic substances are released from these processes. It is a legal requirement in Bangladesh for all water polluting factories to establish Effluent Treatment Plants (ETPs). However, there are very few ETPs that are installed and functioning in these polluting industries as they are expensive to install and maintain. The cost of establishing an ETP ranges from US$100,000- US$290,000 and up to 20-30,000 sq. ft. (1,840-2,760 m) of land is required (Chowdhury and Clemett, 2006). Small-scale industries, therefore, cannot afford to install and operate ETPs. The Department of Environment (DoE) of Bangladesh has identified 1200 polluting industrial units of which only 21 have taken environmental clearance (Zafar et al., 2004).

Common Dye Removal Methods

Most dyes are designed to be resistant to environmental conditions like light, water, pH, temperature, microbial attack, etc (Pagga and Taeger, 1994). This characteristic, together with the low concentration of dye molecules in wastewater makes the conventional methods for organic molecule removal from water prohibitive to use at a large scale (Crini and Badot, 2008). Nonetheless, there are various techniques which have been employed for the treatment of wastewaters involving physicochemical, chemical and biological processes, as well as some new and developing techniques. Adsorption is considered to be a very effective physical separation technique in wastewater treatment in terms of its simplicity in design, ease of operation and insensitivity to toxic substances provided the adsorbents used are locally available with little or no value (Dawood and Sen, 2013, Walker and Weatherley, 1997, Pala and Tokat, 2002). The main criteria for selection of adsorbents are based on characteristics like high affinity and possibility of adsorbent regeneration (Golob et al., 2005, Patel and Vashi, 2010, Karcher et al., 2002). The best material for adsorption is activated carbon (AC) (Walker and Weatherley, 1997, Pala and Tokat, 2002). The efficiency of AC as a dye removal material is directly dependent upon the type of carbon material used (Poots et al., 1976, McKay et al., 1980, McKay et al., 1988, Walker and Weatherley, 1997, Gupta et al., 2000). The biggest disadvantage of activated carbon is that it is non-selective and disposal or regeneration of AC can be expensive (Robinson et al., 2001). Zeolite and chitosan are other examples of adsorption material that have been extensively studied for their ability in removing trace quantities of contaminants such as heavy metal ions, phenols and dyes (Armağan and Turan, 2004, Ozdemir et al., 2004, Wu et al., 2001). In general, sorption methods, independently of the inorganic or organic character of the supports, are usually non-selective. Competition between the sorbents can influence the dye-binding capacity of support in an unpredictable manner. Moreover, a sorption process removes the synthetic dyes from wastewater by concentrating them on the surface, without structurally changing them. When the support is regenerated, the fate of the resulting concentrated solution of dyes presents a problem that has not yet been satisfactorily solved (Weber Jr et al., 1970).

One other popular method for dye removal is the filtration technology. Filtration methods such as ultrafiltration and reverse osmosis have been used for water reuse and chemical recovery (Marcucci et al., 2001, Fersi and Dhahbi, 2008). Membrane technology for dye removal from textile wastewater is very effective as reported by various researchers (Ledakowicz et al., 2001, Ahmad et al., 2012). However, the main drawbacks of membrane technology are the high costs of labor and membrane replacement, since membranes are predisposed to clogging and fouling (Ahmad et al., 2012). Proper pretreatment units for removing secondary sludge are almost mandatory to increase the life time of the membranes (Robinson et al., 2001, Akbari et al., 2012).

A popular chemical method for treating dye laden wastewaters is coagulation and flocculation (Golob et al., 2005, Anjaneyulu et al., 2005). Methods based on coagulation–flocculation are effective for the removal of mainly disperse dyes, but show very low capacity for acid, direct, reactive and vat dyes (Vandevivere et al., 1998, Chaturvedi, 2013, Wong et al., 2007). One major limitation of this process is the generation of sludge (Anjaneyulu et al., 2005, Hai et al., 2007). Other chemical methods for the removal of dyes from wastewater involve the use of oxidizing agents such as ozone (O_3), hydrogen peroxide (H_2O_2) and permanganate (MnO_4) (Tchobanoglous and Burton, 1991). Among these oxidants, ozone is widely used because of its high reactivity with dyes and good removal efficiencies (Alaton et al., 2002). It has also been reported, however, that ozone is not effective in degrading insoluble disperse and vat dyes since it has long reaction times (Marmagne and Coste, 1996, Rajeswari, 2000). Also, the decolorization efficiency depends upon the pH. (Munter, 2001, Konsowa, 2003). Fenton reaction is also an example of Advanced Oxidation Process (AOP) in which hydrogen peroxide is added to an acid solution containing ferric ions. The main drawback is high sludge generation due to the flocculation of reagents and dye molecules (Robinson et al., 2001, Azbar et al., 2004). Most of the AOPs for textile wastewaters are highly expensive and its effectiveness varies widely with the type of constituents present in the textile wastewaters (Azbar et al., 2004, Robinson et al., 2001). Electrochemical oxidation process for removal of dyes offers high removal efficiency; with little or no consumption of chemicals, no sludge production and degradation of intractable contaminants such as polyaromatic organic compounds and anthraquinone-based compounds (Panizza et al., 2000, Kim et al., 2002). However, after the several washing processes, unfixed reactive and hydrolysed dyes remain in the dyeing wastewater (Venkataraman, 2012). In addition, there is also a high cost involved because of the electricity required.

Biodegradation methods are also commonly applied to the treatment of dye bearing wastewaters because microorganisms such as bacteria, yeasts, algae and fungi are able to amass and break down different dyes (McMullan et al., 2001). The microbial process is inexpensive and environmental friendly but the treatment entails a long time for microorganism acclimatization. Furthermore, the treatment plant requires a large land area and is constrained by its sensitivity toward diurnal variation and toxicity of some chemicals (McMullan et al., 2001). Though most organic molecules are degraded; complex synthetic dyes are recalcitrant to degradation due to their complex structure. Azo dye biodegradation by white rot fungi has also been studied (Machado et al., 2006). However, application of white-rot fungi for the removal of dyes has some inherent drawbacks such as the long growth cycle and the need for nitrogen limiting conditions. In addition, white-rot fungi are not naturally found in wastewater and hence the enzyme production may be unreliable (Robinson et al., 2001).

Nano-scale Zero Valent Iron

The potential use of nanomaterials for the treatment of polluted waters has sparked a great deal of interest, specially in water treatment (Michael, 1999, Zhang and Fang, 2010, Dastjerdi and Montazer, 2010, Dimitrov, 2006). Due to its cheap cost, availability, environmental compatibility and high reactivity, the most widely studied nanomaterial for water treatment is metallic iron (Zhang, 2003, Nurmi et al., 2005). Nanoscale zero valent iron (NZVI) is an environmentally friendly reducing agent which can break the azo bond, cleaving dye molecules into products that are relatively benign (Nurmi et al., 2005, Chang et al., 2006). Further advantages of the NZVI decolorization process include the ease in use as a pre-treatment process, easy recycling of the spent iron powder by magnetism or filtration as well as low concentration of iron remaining in the resultant mixture and no necessity for further treatment of the effluents (Saxe et al., 2006). Building on the original work by Glavee (Glavee et al., 1995), NZVI was first tested for treating contaminated water by Wang and Zhang at Lehigh University, USA (Wang and Zhang, 1997). NZVI has gained eminence for environmental remediation, especially for the remediation of contaminants that are susceptible to reductive transformation such as halogenated organics (Liu and Lowry, 2006, Song and Carraway, 2008) and high valent heavy metals (Manning et al., 2007, Celebi et al., 2007). Another unique physical property of NZVI is its magnetism - adsorption combined with magnetic separation has been used broadly used in water treatment and environmental cleanup (Ambashta and Sillanpää, 2010, Mahdavian and Mirrahimi, 2010). The ability of NZVI to remove contaminants has been demonstrated at both laboratory and field scale tests (White et al., 2009, Girginova et al., 2010). Current applications of NZVI in contaminated water treatment can be divided into two groups: (a) technologies which use NZVI as a kind of nanosorbent or immobilization carrier for removal efficiency enhancement (adsorptive/ immobilization technologies) and (b) those which use NZVI as photocatalysts to break down or to convert contaminants into a less toxic form (photocatalytic technologies). However, a difficulty in the practical application of NZVI is its inadequate mobility in the environment. Research conducted by Elliot and Zhang showed that only 1.5 % of NZVI introduced into ground water reached the remediation location at the depth of 6 m (Elliott and Zhang, 2001). Therefore, from the practical point of view, it is necessary to increase the mobility of NZVI keeping in mind that increased mobility of NZVI will reduce the possibility of controlling the particles (mobile particles can propagate more easily in the environment and more to undesirable locations) (Saleh et al., 2008, Keane, 2010). It is necessary to conduct research that will take into account not only the toxicity of NZVI prior to the process of remediation, but also address the consequences resulting from the application of NZVI. Of particular importance here would be studies involving various groups of organisms, at various stages of development and at various degrees of transformation of modified NZVI. Also important are the interactions between NZVI and other contaminants and the stability of those complexes in relation to variable environmental conditions and in relation to the degree of transformation of NZVI.

Table 1: Comparison of NZVI to other dye removal methods

Method	Advantages	Disadvantages
Physical (adsorption, ion exchange, membrane filtration, etc)	High adsorption capacity for most dyes with high quality effluent.	High cost of adsorbents Adsorbent disposal problem Low surface area for some adsorbents Not effective for disperse dyes Production of sludge Further treatments required
Chemical (oxidation, coagulation, flocculation, etc)	Effective process No production of sludge	Disposal problems High operational costs Formation of toxic byproducts
Biological (aerobic and anaerobic degradation)	Efficient in the treatment of azo dyes Low operational costs	Very slow process Not effective for all dyes Anaerobic degradation yields hydrogen sulphide
NZVI	High speed in contaminant destruction Works for a wide variety of dyes Cheap Easy to manufacture Very high surface area	Low mobility Numerous coatings, modifiers, catalysts could create complications

Source: Compiled from (Keane, 2010), (Verma et al., 2012) and examples from the text

Conclusion

Nanotechnology is one of the most rapidly growing sectors of the global economy. Over a thousand products using nanomaterials are currently available for a diverse range of applications within the private and public sector. For the treatment of contaminated water, a growing body of theoretical and empirical evidence has proven NZVI as both highly effective and versatile. In recent years there have been significant innovations in terms of manufacture techniques, physiochemical functionalization and enhancements in subsurface stability and mobility.

Thus, for a country like Bangladesh, with an ever growing garment sector, producing tons of wastewater per year, NZVI seems to be the most economical and eco-friendly solution from all aspects.

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