THE EFFECT OF ADSORBENT ADDITIVE ON CLAY BASED ADSORBENT TO THE REMOVAL OF A SINGLE SYSTEM

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ABSTRACT

One of the powerful treatment processes for the removal of dyes from water at low cost is adsorption. This research is studied to identify which one is the best additive used for removal of dyes solution from wastewater. This dyes containing wastewater discharge in stream and river and will cause the major sources of water pollution. The main objective of this research is to study the effect of adsorbent additive on clay base to the removal of a single dye system. Scope of this research are to study the effect of single dye by adding the different ratio of additive with clay and to study the influenced of pH towards dye removal performance. For each parameter studied, clay will keep as a constant parameter and three additives are used to increase the efficiency of dye removal from wastewater which is zeolite, chitosan and powdered activated carbon. Clay and additives are adsorbent but in this research studied for the one of the additive will adsorb more dyes if mixed with the clay. For the pH parameter, stock solution of Methylene Blue prepared and mass of the clay and the additive set to constant. Stock solution then divided into 250ml beaker. The initial and final concentration determined by using the Uv-vis spectrophotometer. Standard curve prepared for this equipment to get the value of the concentration of each sample. The range of pH used between 1 to 14. The results showed that all of three additives are effective at pH 14 for alkali solution. For acidic solution, powdered activated carbon and chitosan effective at pH 3 but zeolite effective at pH 1. For ratio study, the experiments were conducted by adding different amount of additive into a constant amount of clay. From the data collected shows that the powdered activated carbon is the most effective additive compared to chitosan and zeolite which have highest percentage of dye removal at 96.86% for alkali dye solution. This occurs at the weight of 1g clay added with 1.5g powdered activated carbon. However, 90% of dye is removed for acidic solution when ratio of clay and additive are similar. As a conclusion, powdered activated carbon is the most effective additive used for removal of dye in solution compared than chitosan and zeolite. Further research should be studied to look forward the cheaper additives to substitute the powdered activated carbon but the performance of adsorption will not effect.

ABSTRAK

Penyelidikan ini dipelajari untuk mengenalpasti mana yang terbaik aditif yang digunakan untuk menghilangkan larutan zat warna dari sisa cair. Pewarna ini mengandungi pembuangan air sisa di sungai dan sungai dan akan menyebabkan sumber utama pencemaran air. Tujuan utama dari penelitian ini adalah untuk mempelajari pengaruh aditif adsorben pada dasar tanah liat untuk penghapusan sistem pewarna tunggal. Objektif kajian ini pengaruh warna tunggal dengan menambah aditif nisbah yang berbeza dengan tanah liat dan mempelajari pengaruh pH terhadap prestasi penghapusan pewarna. Setiap parameter, tanah liat akan tetap sebagai parameter malar dan tiga aditif yang digunakan untuk meningkatkan kecekapan penyisihan warna dari sisa cair yang zeolite, kitosan dan serbuk karbon. Keputusan kajian menunjukkan bahawa semua daripada tiga aditif yang berkesan pada pH 14 untuk larutan alkali. Untuk larutan asid, serbuk karbon dan chitosan berkesan pada pH 3 tapi zeolite berkesan pada pH 1. Untuk perbandingan, kajiian dilakukan dengan menambah perbezaan jumlah aditif ke dalam jumlah yang konstan dari tanah liat. Dari data yang dikumpul menunjukkan bahawa karbon aktif serbuk adalah aditif yang paling efektif dibandingkan dengan kitosan dan zeolite yang mempunyai peratusan tertinggi removal pewarna pada 96,86% untuk penyelesaian pewarna alkali. Hal ini terjadi di tanah liat berat 1g ditambah dengan karbon aktif serbuk 1.5g. Namun, 90% dari pewarna akan dihapuskan untuk penyelesaian asid ketika nisbah dari tanah liat dan aditif yang serupa. Sebagai kesimpulan, karbon aktif serbuk adalah aditif yang paling berkesan digunakan untuk menghilangkan zat warna dalam larutan berbanding kitosan dan zeolite. Penyelidikan lebih lanjut perlu dipelajari untuk melihat meneruskan aditif yang lebih murah untuk menggantikan karbon aktif serbuk tetapi prestasi tidak terjejas.

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CHAPTER 1

INTRODUCTION

Many of the dyestuff and textile use dyes in order to make their production. These dyes are their raw materials in order to color their product and also consume a large amount of waters. As a result, they generate a large amount of colored wastewaters from production line to the water. Color is the major contaminant to be identified in wastewater (Banattet et al., 1996).

Textile industry effluents exhibit large amount of dye chemicals which create severe water pollution. Therefore, it is important to reduce the dye concentration in the wastewater before discharging into the environment. Discharging large amounts of dyes into water, accompanied by organics, bleaches, and salts can affect the physical and chemical properties of fresh water (Erdem et al., 2004)

Many of dyes are also toxic and even carcinogenic and this will be the factor of a serious hazard to aquatic living organism. However, wastewater containing dyes are very difficult to treat since the dyes are recalcitrant organic molecules, resistant to aerobic digestion and are stable to light, heat and oxidizing agents (Sun and Yang et al., 2003)

Amongst the numerous techniques of dye removal, adsorption is the procedure of choice and gives the best results as it can be used to remove different types of coloring materials (Gregorio et al., 2005). Most commercial systems currently use activated carbon as sorbent to remove dyes in wastewater because of its excellent adsorption ability. Activated carbon adsorption has been cited by the US Environmental Protection Energy Agency as one of the best available control technologies (Derbyshire et al., 2001). However, although activated carbon use is restricted due to high cost. In order to decrease the cost of treatment, attempts have been made to find inexpensive alternative adsorbents (Gregorio et al., 2005).

Among natural minerals clays occupy a prominent position being low cost, available in abundance and having good sorption properties (Gupta et al., 2009). Clay is a soil particle smaller than 0.002 mm or 2 μm with high specific area which mainly influenced the soil colloidal properties as well as stability of soil structure. Besides, is has high stability in both wet and dry conditions and in soil structure class. While colloid is a particle which may be a molecular aggregate with a diameter of 0.1 to 0.001 μm. Clay and soil are organic matter are often called as soil colloids because they have particle sizes that are within or approach colloidal dimensions.

1.2 Problem statement

Many of the dyestuff and textile use dyes in their production lines. These dyes are their raw materials in order to color their product and also consume a large amount of waters. As results, they generate a large amount of colored wastewaters from the production line to water. Color is the major contaminant to be identified in wastewaters (Banattet al., 1996). The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable (Robinson et al., 2001; Banat et al., 1996)

Over 100,000 commercially available dyes exist and more than 7×10^5 tonnes per year are produced annually (Pearce et al., 2003; McMullan et al., 2001). An indication of the scale of the problem is given by the fact that two per cent of dyes that produced are discharged directly in aqueous effluent (Pearce et al., 2003 Robinson et al., 2001). Due to increasingly stringent restrictions on the organic content of industrial effluents, it is necessary to eliminate dyes from the wastewaters before it is discharged. Many of these dyes are also toxic and even carcinogenic and this will be the factor of a serious hazard to aquatic living organism. However, wastewaters containing dyes is very difficult to treat since the dyes are recalcitrant organic molecules, resistant to aerobic digestion and are stable to light, heat and oxidizing agents (Sun and Yang, 2003; Ravi Kumar et al., 1998).

During the previous studies, several physical, chemical and biological decolorization methods methods have been reported. Amongst the numerous techniques of dye removal, adsorption is the procedure of choice and gives best results as it can be used to remove different types of coloring materials (Jain et al., 2003; Ho and Mc Kay, 2003; Derbyshire et al., 2001). Most commercial systems currently use activated carbon as sorbent to remove dyes in wastewaters because of its excellent adsorption ability. Although activated carbon is a preferred sorbent, its widespread low cost adsorbent including natural minerals, biosorbents and waste materials from industry and agriculture. Clay materials such as bentonite, kaolite zeolite and many more can use as a good sorbent into the removal in single dye system. Using of clays with the additives is the best ways to be investigated because the using of clays can reduce the cost of the wastewaters treatment in industry. Table 1.1 below is the price of the additive base on 2009.

ADDITIVE	PRICE, USD / kg
Powdered activated carbon	1.65 – 9.9
Chitosan	0.4 – 0.8
Zeolite	0.56 – 1.0

Table 1.1 Price of additive base on 2009

1.3 Objectives

The research was conducted to study the effect of adsorbent additive on clay base adsorbent to the removal of a single dye system. The objectives of the study are:

1. To study the effect of adding different types of additives (powdered activated carbon, zeolite and chitosan) with clay on adsorption process.

2. To study the influence of pH and ratio toward dye removal performance.

CHAPTER 2

LITERATURE REVIEW

2.1 Adsorption process

One of the effective treatment processes for the removal of dyes from water is adsorption. Adsorption techniques have been proven successful in removing colored organics (Erdem et al., 2004).

Adsorption is the separation of substances from phase accompanied by its accumulation or concentration or concentration at the surface of another. It is the process that takes place when liquid or most commonly a gas known as a adsorbent accumulates on the surface of a solid adsorbent and forming molecular film.

In adsorption processes one or more components of a gas or liquid stream are adsorbed on the surface of a solid adsorbent and a separation is accomplished. In commercial process, the adsorbent is usually in the form of small particle. The fluid is passed through and the solid particles adsorb components from the fluid.

Application of liquid-phase adsorption includes removal organic compounds from water or organic solutions, colored impurities from organics and various fermentation products from ferment or effluents.

Adsorption similar to surface tension is a consequences surface energy. In the bulk material, all the bonding requirements ionic, covalent or metallic of the constituent atoms of the material are filled. However, atoms on the surface experience a bond deficiency because they are not wholly surrounded by other atoms.

2.1.1 Mechanism of adsorption

Adsorption occurs in there steps. Firstly, the adsorbate diffuses from the major body of the stream to the external surface of the adsorbent particle. Secondly, the adsorbate migrates from relatively small area of the external surface to the pores within each adsorbent particle. The bulk of adsorption usually occurs in these pores because there is the majority of available surface area. Finally, the contaminant molecules adhere to the surface in the pores.

Adsorption at a surface is the surface is the results of binding between the individual atoms, ions, or molecules of an adsorbate and the surface of adsorbent. The adsorption process can be classified as a physical or chemical adsorption.

Molecules that are adsorbed by chemisorptions are very difficult to remove from the adsorbent. Whereas, physically adsorbed molecules can usually be removed by either increasing the operating temperature or reducing the pressure.

Chemisorptions is a highly selective process. A molecule must be capable of forming a chemical bond with the adsorbent surface for chemisorptions to occur. Physical adsorption occurs under suitable conditions in most gas-solid or liquid-solid system.

Chemisorptions form only a monolayer of adsorbate molecules on the surface and stops when all reactive sites on the adsorbent surface area reacted. Physical adsorption can form multilayer adsorbate molecules once stop another due to van der waals force. The chemisorptions rate increase with increasing temperature. While, the physical adsorption rate decrease with increasing temperature. The fundamental of a desorption is useful to distinguish between physical adsorption, involving only relatively weak intermolecular forces, and chemisorptions which involves the formation of a chemical bond between the adsorbate molecule and the surface of the adsorbent.

2.1.2 Adsorbent

Adsorption is the adhesion of atoms, ions, biomolecules or molecules of gas, liquid, or dissolved solids to a surface This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent. It differs from absorption, in which a fluid permeates or is dissolved by a liquid or solid. (Anonymous et al., 2009)

Adsorption is present in many natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated carbon, capturing and using waste heat to provide cold water for air conditioning and other process.

However, activated carbon suffers from high cost production and regeneration. Therefore other adsorbents such as natural clay with higher surface areas are alternatives (Wang et al., 2006). Recent investigation has focused on the use of clays to remove dyes.

2.1.3. Factors affecting adsorption

There are several important factors affecting adsorption such as:

a) Surface area of adsorbent.

Large size simply greater adsorption capacity. (Hafiz, 2005).

b) Solubility of solute in liquid wastewater

Substances slightly soluble in water will be more easily removed from water than substances with highly solubility. Also non-polar substances will be more easily removed than polar substances since the latter have greater affinity for water. (Hafiz, 2005)

c) Numbers of carbon atoms.

For substances in the same homologous series a larger of carbon atoms is generally with a lower polarity and hence a greater potrtential for being adsorbed. (Hafiz, 2005).

d) Size of molecule with respect to size of the pores.

Large molecules may be too large to enter small pores. This may reduce adsorption independently of other causes. (Hafiz, 2005).

2.1.4 Dye & pigment

A dye can generally be described as a colored substance that has an affinity to the substrate to which it is being applied. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber. (Anonymous et al., 2009)

Both dyes and pigments appear to be colored because they absorb some wavelengths of light preferentially. In contrast with a dye, a pigment generally is insoluble, and has no affinity for the substrate. Some dyes can be precipitated with an inert salt to produce a lake pigment, and based on the salt used they could be aluminum lake, calcium lake or barium lake pigments. (Anonymous et al., 2009)

An acid dye is a dye in which the coloring component is in the anion or negative charge in its chemistry. They are often applied from an acidic solution in order to intensify the staining. Attachments to the fiber are attributed at least partly, to salt formation between anionic groups in the dyes and cations groups in the fiber. Acid dyes are not substantive to cellulosic fibers. Figure 2.1is the sample of acid dyes structure.

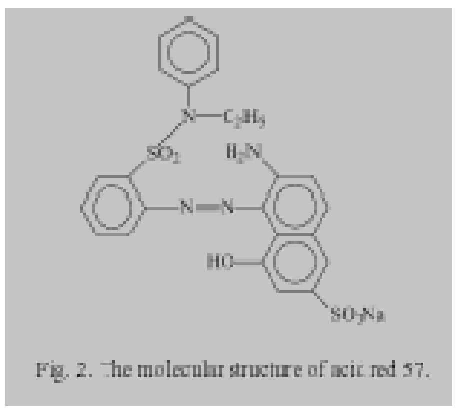

Figure 2.1 Chemical structure of acid dye

Basic dyes are water-soluble cationic dyes that are mainly applied to acrylic fibers, but find some use for wool and silk. Usually acetic acid is added to the dye bath to help the uptake of the dye onto the fiber. Basic dyes are also used in the coloration of paper. Figure 2.2 is the sample of basic dye structure.

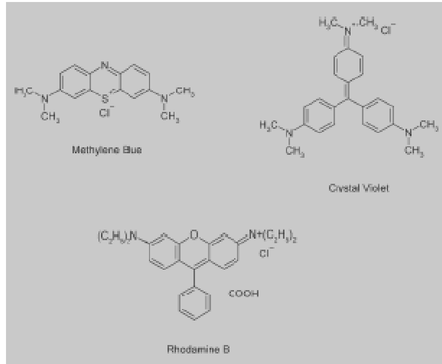

Figure 2.2 Chemical structure of basic dye

Direct dye is normally carried out in a neutral or slightly alkaline dyebath, at or near boiling point, with the addition of either sodium chloride (NaCl) or sodium sulfate (Na_2SO_4). Direct dye is used on cotton, paper, leather, wool and many more. They are also used as pH indicators and as biological stains.

Vat dyes are essentially insoluble in water and incapable of dyeing fibers directly. However, reduction in alkaline liquor produces the water soluble alkali metal salt of the dye which in this liquor form has an affinity for the textile fiber. Subsequent oxidation reforms the original insoluble dye. The color of denim is due to indigo, the original vat dye.

Disperse dyes were originally developed for the dyeing of cellulose acetate, and are water insoluble. The dyes are finely ground in the presence of a dispersing agent and sold as a paste, or spray-dried and sold as a powder. Their main use is to dye polyester but they can also be used to dye nylon, cellulose triacetate, and acrylic fibers. In some cases, a dyeing temperature of 130 °C is required, and a pressurized dye bath is used. The very fine particle size gives a large surface area that aids dissolution to allow uptake by the fiber. The dyeing rate can be significantly influenced by the choice of dispersing agent used during the grinding.

Mordant dyes require a mordant, which improves the fastness of the dye against water, light and perspiration. The choice of mordant is very important as different mordant can change the final color significantly. Most natural dyes are mordant dyes and there is therefore a large literature base describing dyeing techniques. The most important mordant dyes are the synthetic mordant dyes, or chrome dyes, used for wool. These comprise some 30% of dyes used for wool, and are especially useful for black and navy shades. The mordant, potassium dichromate, is applied as an after-treatment. It is important to note that many mordant, particularly those in the heavy metal category, can be hazardous to health and extreme care must be taken in using them. There are three basic classes of pigments:

a) Chlorophylls

The greenish pigments which contain a porphyrin ring. This is a stable ring shaped molecule around which electrons are free to migrate. Because the electrons move freely, the ring has the potential to gain or lose electrons easily and thus the potential to provide energized electrons to other molecules. Thi is fundamental process by which chlorophyll captures the energy sublight.

There are several kinds of chlorophyll. The most important being chlorophyll “a”. This is the molecule which makes photosynthesis possible by passing its energized electrons on the molecules which will manufacture sugars. All plants, algae and cynobacteria which photosynthesize contain chlorophyll “a”. A second kind chlorophyll is chlorophyll “b” which occurs only in green algae and in the plants. A third form chlorophyll which is common is called chlorophyll “c” and is found only in the photosynthetic members of the chromista as well as the dinoflagellates. The dirrfrence between the chlorophyll of these major groups was one of the first clues that they were not as closely related as previously though.

b) Carotenoids.

Carotenoids are usually red, orange or yellow pigments, and include the familiar compound carotene which gives carrots their color. These compounds are composed of two small six-carbon rings connected by a chain of carbon atoms. As a result, they do not dissolve in water and must be attached to membranes within the cell. Carotenoids cannot transfer sunlight energy directly to the photosynthetic energy pathway, but must pass their absorbed energy to chlorophyll. Because of this, they are called accessory pigments. One very visible pigment if fucoxanthin the brown pigment which colors kelps and other brown algae as well as the diatoms.

c) Phycobilins.

Phycobilins are water-soluble pigments and therefore found in the cytoplasm or in the stoma of the chloroplast. They occur only in cynobacteria and thodophyta. The vial on the left contains the bluish pigments phycocyanin which gives the cyanobacteria their name. the vial on the right contains the reddish pigment phycoerythrin which give the red algae their common name.

2.1.5 Additives

There are three types of additives in this research and they are:

a) Powdered activated carbon

Activated carbon (AC) is the carbonaceous material which plays an important role in adsorption process. Its ability to remove organic and inorganic chemical waste, odor, color and taste from any kind of chemical industry process is based on their amazing properties. Activated carbon has high degree of surface reactivity which can influence its interaction with polar or nonpolar adsorbates. Besides, it also has higher surface area and micro porous structure. Activated carbon are widely use in wastewater treatment to remove harmful chemicals and heavy metal, industrial waste water or industrial flue gas. (Bansal, 2005). Their application in industry includes removing organic and inorganic pollutants from drinking water, dye removal, industrial wastewater treatment, decolorizing of syrups and purification of air and pharmaceutical products. Activated carbon's properties are:

i) Chemical porous structure of carbon.

ii) The polarity of the structure.

iii) The carbon surface area.

iv) Pore size distribution.

v) Physical and chemical characteristics of adsorbate.

b) Chitosan

Chitosan are mechanically tough polysaccharides with chemical structures similar to cellulose, studied as adsorbents. Chitin is a fairly abundant natural iopolymer and is generally found in the exoskeletons of crabs and other arthropods and also in the cell wall of some fungi whereas chirosan is a deacetylated derivative of chitin and can be chemically prepared from it. Both chitin and chitosan are being used as a attractive source of adsorbents, especially for metal removal. Nevertheless, they are versatile materials and have been used successfully for the removal dyes. These materials can be used in different forms, from flake types to gels, bead type or fibers. The efficiency of chitosan as a adsorbent to remove acid dyes has been presented by Wong who found the maximum adsorption capacities of chitosan. (Gupta et al., 2009).

Chitosan is natural polysaccharide comprising copolymers of glucosamine and *N*-acetylglucosamine, and can be obtained by the partial deacetylation of Chitin, from crustacean shells (Illum, 1998). The most abundant source of Chitin is in the shells of shellfish such as crab and shrimp. The worldwide shellfish harvest is estimated to be able supply 50,000 tons of Chitin annually (Johnson, 1982). The harvest in United State alone could produce over 15000 tons of chitin each year (Shahram, 1992). Chitosan has been widely used in vastly diverse fields, ranging from waste management to food processing, medical and biotechnology (Savant et al, 1995). Besides, the material is so natural and environmentally safe that has found numerous interesting application in the fields of health care, food and beverages, cosmetics and toiletries, waste and water treatment, product separation and recovery, and immobilization and cell culture (Casimiro et al, 2005).

c) Zeolite

Zeolites are natural volcanic minerals with a number of unique characteristics. Zeolites were formed when volcanic ash was deposited in ancient alkaline lakes. The interaction of the volcanic ash with the salts in the lake water altered the ash into various zeolite materials. Zeolites have an unusual crystalline structure and a unique ability to change ions. A very large number of small channel are present in its structure. These channels have typical diameters of 0.5 to 0.7 nm, only slightly larger than the diameter of a water molecule. These channels are called microporosity. Beside this there are a number of larger pores, the so-called microporosity. Positive ions are present in the channels, which can be exchanged for other ions.

The porous zeolite is host to the water molecules and ions of potassium and calcium as well as a variety of other positively charged ions, but only those of appropriate molecular size to fit into the pores are admitted creating the sieving property. Because of their regular and reproducible structure, they behave in a predictable fashion.

The application of zeolite for dye removal from wastewater has rarely been previously reported. Investigation using polyvinyl chloride zeolite composites for methylene blue adsorption and found that the adsorption capacity of zeolite decreased when it was embedded in composites. (Balkose et al., 2003).

2.2 Clay

Clay is a naturally occurring material composed primarily of fine-grained minerals. Clay deposits are mostly composed of clay minerals, a subtype of phyllosilicate minerals, which impart plasticity and harden when fired or dried. They also contain variable amounts of water trapped in the mineral structure by polar attraction. Organic materials which do not impart plasticity may also be a part of clay deposits. (Anonymous et al., 2010).

There are four or more main groups of clays and they are kaolite, montmorillonite smectite, illite and chlorite. Chlorites are not always considered clay, sometimes being classified as a separate group within the phyllosilicates. There are approximately 30 different types of pure clays in these categories, but most natural clays are mixture of these different types along with other weathered minerals. (Anonymous et al., 2010).

2.2.1 Clay minerals

Clay are widely applied in many fields such as polymer nano-composites, adsorbents for heavy metals, catalysts, photochemical reactions fields and ceramics due to their high specific surface area, chemical and mechanical stabilities and a variety of surface and structure properties.

Clay minerals are hydrous aluminum phyllosilicates, sometime variable amounts of iron, magnesium, alkali metals, alkine earth and other cations. Clays have structures similar to the micas and therefore form flat hexagonal sheets. Clay minerals are common weathering products and low temperature hydrothermal alteration products. Clay minerals are very common in fine grained sedimentary rocks such as shale, mudstone and siltstone and in fine grained metamorphic slate and phylite. (Anonymous et al., 2009)

Clays are ultra fine grained (normally considered to be less than micrometers in size on standard particle size classifications) and so require analytical techniques. Standards include: