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INDUSTRIAL APPLICATION OF CHITOSAN AS PROMISING MATERIAL FOR WASTEWATER PURIFICATION: A REVIEW

Belgis[1*]

[1]*Department of Vocational Study Universitas Airlangga, 60286, Indonesia*

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ABSTRACT

The rapid growth of the industry is giving positive effects for humans by providing daily needs and supporting economic development. However, the industrial process also releases pollution to the environment, which can cause water scarcity, biodiversity loss, and climate change. Removing these pollutants from various industrial wastes is a requirement for ensuring proper water quality for human consumption, agricultural use, and environmental safety. This work aims to explain the use of natural resources as a source of valuable compounds that can be used in wastewater treatment, particularly in Indonesia, by adopting a literature study method reviewing both national and international references. Chitosan is an effective bio-absorbent pollutant because of its high level of deacetylation and free amino groups, making it polycationic which is capable of being bound to metals, proteins, and dyes. Chitosan membranes can be applied only with chitosan material and composites: chitosan-Polyethylene Glycol (PEG), chitosan-Poly Vinyl Alcohol, chitosan-biosilica, chitosan-PVA-silica, chitosan-alginate, chitosan-cellulose, and chitosan-silica. Chitosan has the ability as a coagulant and reducing water turbidity. Chitosan can absorb metal ion (Cr (VI), Cs+, Pb(II), Fe, Cu(II)), dyes (anthraquinone dyes, brilliant blue, yellow dye, methylene blue, disperse orange, disperse blue, rhodamine B), drug residue, and hazardous materials, and can be used as raw material or in a film form. Since there is a high abundance of chitosan raw material in Indonesia, it is supposed to be able to support the application of chitosan as a natural purifying agent considering its high ability to absorb heavy metal and some dangerous materials.

Keywords: adsorbent; chitosan; membrane; wastewater

1. INTRODUCTION

The rapid development of the industry plays a vital role in economic growth since it denotes an indicator of the positive growth of the country. However, industrial growth also harms our environment because the residue from the industrial production process is dangerous. Pollution released by the industrial process releases to the environment can cause water scarcity, biodiversity loss, and climate change. The disposal of unsafe industrial and municipal wastewater containing various chemicals such as solvents, dyes/paints, pesticides, and medicines, can harm the river systems. The release of untreated dye waste, which also contains organic matter, metals, bleach, and salt, not only changes the physicochemical parameters of surfaces and groundwater bodies but also adversely affects aquatic and human life (Markandeya et al., 2017).

The sewage sludge that accumulates at the wastewater treatment center is a mixture of various

*Corresponding author's email: belgis@vokasi.unair.ac.id
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organic and inorganic materials containing substances and microorganisms from various sources (Bratina et al., 2016). The composition of liquid waste consists of 99.9% water, and the rest is solid material (Lessa et al., 2018). The final waste from the industrial process is discharged into the waters and rivers after passing through wastewater management. Some industries do not have standard waste disposal; hence they cause water pollution in river areas (Karimifard & Alavi Moghaddam, 2018; Li et al., 2019). The problem of waste must be overcome in order to be corresponding to the environmental sustainability issue, particularly in wastewater treatment, in which only hygienic material can be released into the environment. At present, the technology for the separation and recovery of water purification using organic materials has progressed, is easily accessible, and is generally inexpensive. Liquid waste is released as a suspension or granules in liquid media (Li et al., 2019).

Various waste management methods are being used to separate the pollution of liquid waste in physical, chemical, and biological forms from waste treatment or in combination. In general, chemical wastewater treatment is a separation process with a coagulation-flocculation system (Karimifard & Alavi Moghaddam, 2018). Some chemicals can be used efficiently and effectively but still somehow produce other residues that contain hazardous substances. Providing an effective, efficient, and harmless liquid waste management system is an effort to minimize pollution residues on water. One of the wastewater treatment technologies that are widely used today is membrane technology. The current use of membranes can be carried out on a large scale to produce drinking water from seawater in the desalination process by reverse osmosis, constituent recovery by electrodialysis, fractionation of macromolecules in the food and beverage industry by ultrafiltration processes and removing poisons and other poisons from human blood by dialysis in artificial kidneys (Karimifard & Alavi Moghaddam, 2018). Chitosan is a cationic polymer that is non-toxic, biodegradable, and biocompatible. Chitosan is an effective bio-absorbent pollutant because of its high level of deacetylation and free amino groups, so it is polycationic which is capable of binding to metals, proteins, and dyes. However, chitosan also has weaknesses. The use of chitosan as bio-absorbent dissolves in low pH so that it cannot absorb Cr (III) at low pH (Al-Manhel et al., 2018). This is caused by the active site (amine group) of chitosan that undergoes protonation, and the adsorption ability is influenced by anions in the waters.

Previous experiments have examined biopolymers that can bind heavy metal waste through the formation of complex compounds so that biopolymers can act as adsorbents to separate heavy metals from water even in deficient concentrations. One of the potential biopolymers as heavy metal adsorbents from wastewater is chitosan, the research of which has been extensively conducted for these last 25 years (Al-Manhel et al., 2018). Currently, chitosan has been widely used in industry as the absorbent of heavy metals in the water purification process, a preservative and anti-cholesterol in the food industry, a fertilizer factory, for cosmetics, and a surface coating for photo paper (Ma et al., 2018).

In Indonesia, chitosan has been researched for its application to enhance water quality (Ruswahyuni Hartoko, Agus, 2010). The experiments have been done to optimize the function of chitosan for purifying wastewater, but only a few industries have applied it to their waste management, despite it being in high abundance in Indonesia (Arifin et al., 2017; Noralia & Dina Kartika, 2013; Utami, Umi Barorh Lili Irawati, Utami, 2011). The increasing demand for safe drinking water, particularly in developing and underdeveloped countries, is a serious challenge because the sources of clean water available are epidemically polluted. Therefore, removing these pollutants from various industrial wastes, before being discharged into water bodies, is a requirement for ensuring proper water quality for human consumption, agricultural use, and environmental safety (Nurdjannah, 2016).

In this context, this paper aims to explain the use of natural resources as a source of valuable compounds that can be used in wastewater treatment. This technology can not only solve the problem of environmental pollution caused by industrial residues but also identify alternative natural resources that can be used optimally. Future research opportunities are shown for extensive use to minimize harmful environmental impacts.

2. LITERATURE STUDY

Chitosan is a 2-amino-2-deoxy-D-glucose polymer with β-1,4-glycoside bonds. Naturally, chitosan contains acetyl groups in some of its monosaccharides. The physical and chemical characteristics of chitosan are white and crystalline, soluble in organic acid solutions, but not soluble in other organic solvents. High-grade chitosan dissolves in acetic acid. Chitosan is slightly soluble in water, slightly dissolvable in HCl and HNO_3, 0.5% H_3PO_4, whereas in H_2SO_4, it is not soluble. Chitosan has a strong positive charge, which can bind the negative charge of other compounds, and is easily subjected to biological degradation. The viscosity of chitosan in acetic acid tends to increase with increasing acid concentration or decreasing pH (Al-Manhel et al. 2018). Polymers obtained from renewable resources or valorization of agro-industrial and marine waste and by-products are considered attractive alternatives. Crustacean shell waste is the most abundant source of Chitin, but also the most available source to support commercial production of chitosan.

Chitosan is one of the most abundant organic materials after the amount of cellulose produced every year through the biosynthesis process, in which Chitin is its raw material. This is an essential constituent of the exoskeleton in animals, especially in crustaceans, mollusks, and insects. It is also the primary fibrillar polymer in particular fungal cell walls (Yavuz et al., 2009). The glucosamine content in chitosan is called the degree of deacetylation (DD). Depending on the source and preparation procedure, the molecular weight can range from 300 to more than 1,000 kD with DD from 30% to 95% (Kumari et al., 2015; Kumari & Rath, 2014). In general, chitosan has three types of reactive functional groups, amino groups, and primary and secondary hydroxyl groups, respectively in positions C (2), C (3), and C (6). These groups allow chitosan modifications such as graft copolymerization for specific applications, which can produce a variety of scaffolds that are useful for tissue engineering applications. The chemical properties of chitosan, in turn, provide many possibilities for a covalent and ionic modification that allow extensive adjustment of mechanical and biological properties. Chitosan is a natural material that has very high economic value and use-value. The use of chitosan as a material to purify liquid waste, especially industrial waste, needs to be increased, given the high impact resulting from disposed of liquid waste that is not appropriately refined. The advantage of chitosan as an easily formed and easily obtainable material is the opportunity for researchers to experiment and create the right formula to overcome the problem of liquid waste.

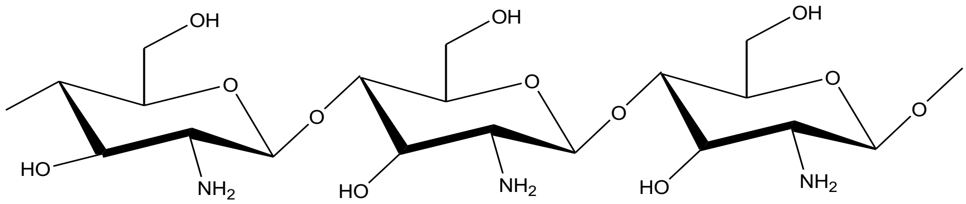

Figure 1 Chemical structure of Chitosan

3. METHODS

This study is conducted using literature study methods. The national references gathered from google scholar (30%) and international references (70%) gathered from ScienceDirect and Scopus resources. The review performed in the thematical section, where each topic or issue was organized by theme approach and discussion. A similar issue will be summarized within each thematic section and illustrated comprehensively.

4. RESULTS AND DISCUSSION

4.1. The Application of Chitosan

4.1.1. Filtrate membrane materials

The chitosan membrane is a semi-permeable thin layer between two phases that has different characters. The first phase is the feeder solution, while the second phase is the permeate or separation results. The most important thing about membranes is the ability to control the size of particles that passing off through membranes. The chitosan membrane is often widely used for various separation processes because of the membrane properties and the ability. Chitosan membranes can absorb heavy and dangerous metal ions.

Chitosan membrane is made by dissolving chitosan in 0.75% acetic acid then stirring it using a stirrer for 3 hours to form a dope (clear thick liquid). Chitosan membrane can also be added with crosslinker compounds such as formaldehyde and glutaraldehyde, to enhance its bonding strength when it is further composited with other materials.

Chitosan membrane can be applied only with chitosan material (Ramadhanur & Sari, 2015) and composites. Some chitosan composites include chitosan-Poly ethylene Glycol (PEG) (Wahyuni et al., 2017), chitosan-Poly Vinyl Alcohol (Wahyuni et al., 2017), chitosan-biosilica (Zulfi et al., 2014), chitosan-PVA-silica (Chodijah,Siti & Liza,Novriani, 2018), chitosan-alginate (Evaani & Cahyaningrum, 2012), chitosan-cellulose (Nurdin & Maulana, 2016), and chitosan-silica (Noralia & Dina Kartika, 2013).

4.1.2. Coagulant materials

Coagulation is the process of forming clots using coagulant material. Coagulation is also a colloidal clumping into a more substantial form. Sediments can be obtained from colloids by heating, so that larger particles develop and encourage smaller particles (Aulia et al., 2016). Particle size affects the deposition of particles in aqueous media. Colloids require coagulant substances to form deposits and also need sufficient time to settle ultimately. If the deposition time is less, then the suspended solids can be shifted so that coagulation and flocculation processes can occur so that the larger particle size and deposition occur quickly (Kumari & Rath, 2014).

The use of coagulants in processing industrial waste has become a common thing to do. Coagulants reduce turbidity and bind solids in water (Fatombi et al., 2013). Chitosan has the ability as a coagulant and has the function of lowering wastewater pollution so that it becomes more apparent by 43% to 50.5% (Arifin et al., 2017; Susanto, Joko Prayitno, 2000; Utami, Umi Barorh Lili Irawati, Utami, 2011).

4.1.3. Adsorbent materials

Adsorbents are very porous materials, and the adsorption process occurs mainly in pore walls or specific areas in a particle. Adsorbents are considered as suitable adsorbents if the absorption and drying time is fast (Hameed et al., 2008). Contact time is crucial in the adsorption process.

Adequate contact time allows the diffusion and adhesion process of absorbing molecules to take place better (Mohd Din et al., 2009; Yavuz et al., 2009).

As an adsorbent, chitosan can be applied alone or in combination with other suitable materials to increase its effectiveness. The function of chitosan as an adsorbent is to absorb harmful substances and colors (Hui et al., 2018; Markandeya et al., 2017; Nitayaphat, 2017; Nuralam, Endoraza & Arbi, 2012; Shaida et al., 2018) that can be improved by using a combination of materials such as activated coconut shell charcoal, chitosan-silica bead (Susilowati, Endang & Mahatmanti, 2018), chitosan-rubber (Phasuphan et al., 2019), chitosan-Fe_3O_4 salt (Liu et al., 2016), chitosan-epichlorohydrin (Yan et al., 2018), chitosan-carbon (Yong-hong Huang, 2018), and chitosan-lignin (Nair et al., 2014).

Pal et al. (2013) showed excellent adsorbent activity from a large number of chitosan gel beads. Its diverse biocompatibility makes bio gel beads more attractive. Chitosan hydrogel beads that have a synergistic effect play an essential role in increasing the efficiency of adsorption. Dyes materials that have been absorbed by chitosan hydrogel beads can be recovered quantitatively using acetone. This positively supports an environmentally friendly process that implements a 'zero waste' management strategy.

4.2. Utilization of Chitosan for Purification Waste

4.2.1. Metal Ion Waste

Metal-containing liquid waste is produced from several industrial activities such as oil mining at sea, liquid clothing dye residues, liquid preservative residues, moisture content metals, Tempe waste, tofu waste, and other chemical wastes (Al-Manhel et al., 2018).

A gel made from chitosan-multiwall carbon nanotube (MWNT)-poly(acrylic acid)-(PAA)-poly(4-amino diphenylamine) (PADPA) can be used to remove hexavalent chromium (Cr (acrylic acid) (PAA)-poly(4-amino diphenylamine) (PADPA) by eliminating hexavalent chromium (Cr(VI)) (Kim et al., 2015).

Chitosan-alkali lignin composites can be used to eliminate the harmful effects present in potential wastewater from the paper industry and the bioreactors today (Nair et al., 2014). Studies demonstrated that chitosan-alkali lignin composites (50:50) show the maximum percentage removal of Cr(VI) compared to other composites.

A simple polymer crosslinking method can be used to remove anionic Cr(VI) compounds efficiently and quickly through adsorption in liquids (Yimin Huang et al., 2018). Modifications to carboxylated multi-wall carbon nanotubes (MWCNTs-COOH) with chitosan were carried out to increase the adsorption of Cr(VI) in acidic solutions. Chitosan/MWCNTs-COOH composites were proved to be successfully applied in several Cr(VI) adsorption cycles, without limited performance loss (98-100% adsorption until the 4th cycle).

Chitosan obtained from seafood processing waste (shrimp shells) and characterized physicochemically was used in a study, in which it is then synthesized using tripolyphosphate (Dima et al., 2015). The synthesis results were then tested for the ability to remove hexavalent chromium Cr(VI) from contaminated water, at different initial chromium concentrations. Chemical analysis carried out showed that the Cr(VI) removed from the solution was bound to chitosan as Cr(III). The conversion of toxic Cr(VI) to less (or non-toxic) Cr(III) by micro-chitosan / reticulated nanoparticles can be considered as a very efficient detoxification technique for treating Cr(VI) contaminated water.

A novel chitosan-Al_2O_3-SiO_2 hybrid composite was used and applied to remove hexavalent chromium [Cr(VI)] from the liquid, the condition of which was in the acidic pH range hence it was conducive to Cr(VI) adsorption (Zhang et al. 2018). It only took ten minutes to achieve 80% adsorption activity. Furthermore, the adsorption ability of this material does not decrease even after five usage cycles.

In another study, Magnetic bentonite-chitosan hybrid beads (Bn-CTS) that were easily obtained and made by immobilizing bentonite in the porous structure of chitosan beads was used to achieve the effect of hybrid adsorption as remover cesium, Ion (Cs^+) from water (Wang et al., 2019). The adsorbent used has excellent selectivity to adsorbs Cs^+ in the presence of other cations (Li^+, Na^+, K^+, and Mg^{2+}). It can be used again by immersing the beads with 0.1 mol L^{-1} of $MgCl_2$ to absorb Cs+ from the beads quantitatively. Bentonite-magnetic chitosan beads can be used as highly efficient adsorbents for the disposal and management of radioactive waste.

Magnetic composites Fe_3O_4-chitosan-bentonite (Fe_3O_4-CS-BT), synthesized natural materials can be applied to restore acid mine drainage for the disposal of heavy metals, especially Cr(VI) in the fluid was examined (Feng et al., 2019). The findings of this study showed that Fe_3O_4-CS-BT composite could function optimally at pH 2.0 and can be used repeatedly by adjusting the magnetic field. Its adsorption capacity was reduced by only 3% after five successive adsorption processes. Furthermore, Fe_3O_4-CS-BT composite also has excellent adsorbent capabilities for AMD remediation containing Cd, Cr, Cu, Fe Zn, Ni, and Pb.

Chitosan and its derivative modifications can be used to improve the adsorption properties of magnetic materials to remove Pb(II) metal ions (Zhang et al., 2018). The material used is a modification of chitosan-Fe_3O_4. The application of this material showed that the initial adsorption results of Pb(II) metal were rapid and equilibrium was achieved in 105 minutes. The maximum absorption capacity is 86.20 mg / g Chitosan-Fe_3O_4.

An adsorption technique can be used to eliminate hexavalent Chromium (Cr(VI)) using chitosan grafted graphene oxide (CS-GO) nanocomposite in batches nanocomposite material was prepared using ultrasonic irradiation techniques (Samuel et al., 2019). The results of the CS-GO adsorbent nanocomposite were analyzed by X-ray (XRD), Fourier transforms infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and Tunneling electron microscopy (TEM), followed by Cr(VI) adsorption studies. The nanocomposite adsorption ability has an adsorption capacity of 104.16 mg / g, which was achieved at an acidic pH of 2.0, at a contact time of 420 minutes. It showed that CS-GO nanocomposite material could be used repeatedly for up to 10 cycles with a very minimum capacity reduction.

In another research, chitosan-grafted magnetic bentonite (CS-g-MB), which was synthesized through the plasma induction method, was investigated (Yang et al., 2016). The CS-g-MB composites showed good magnetic properties, low turbidity performance, and high stability in aqueous solutions, also indicated a significant adsorption capacity for Cs^+ ions. The ability of Cs^+ adsorption by CS-g-MB depends on the pH atmosphere and ionic strength. For some Mg^{2+}, K^+, Li^+, and Na^+ ions, the Cs^+ exchange is limited in the order of $Li^+ \approx Mg^{2+} < Na^+ < K^+$, especially as the hydration energy of these cations in aqueous solutions. CS-g-MB composite stability tests have been carried out in simulated groundwater media and actual seawater, and the results showed that increased coagulation could be achieved by modification of plasma for wastewater management. This adsorbent can also reduce the level of turbidity of water and can be used repeatedly.

According to Lasindrang, et al. (2015), activated coconut shell charcoal Chitosan is more effective in absorbing heavy metal Cr (total) at pH 4, more effective in BOD adsorption at pH 6, and has more influence on COD adsorption at pH 1. The concentration of activated coconut shell charcoal coated with chitosan. The adsorbent C (K3A1) is the adsorption of Cr (total), BOD, and

COD, which is more effective than adsorbent A (K1A1) and adsorbent B (K2A1) (Lasindrang et al., 2015).

Crosslinked chitosan/Waste Active Sludge Char (WASC) beads were developed as a novel composite adsorbent for the removal of Cu(II) ions from aqueous solution (Dandil et al., 2019). A study conducted using Cu(II) adsorbed from aqueous solutions quickly and efficiently by the xanthate Fe_3O_4-CS-GO complex, suggested that xanthate Fe_3O_4-CS-GO may be an ideal candidate for removing Cu(II) from wastewater (Liu et al., 2016). A summarized list of those aforementioned metal ion waste adsorbed by chitosan can be seen in Table 1 below.

Table 1 Metal ion waste adsorbed by chitosan

Metal ion	References
Cr (VI)	(Dima et al., 2015; Feng et al., 2019; Yimin Huang et al., 2018; Kim et al., 2015; Lasindrang et al., 2015; Nair et al., 2014; Noralia & Dina Kartika, 2013; Samuel et al., 2019; Zhang et al., 2018; Zulfi et al., 2014)
Cs^+	(Wang et al., 2019; Yang et al., 2016)
Pb (II)	(Nuralam, Endoraza & Arbi, 2012; Susilowati, Endang & Mahatmanti, 2018; Utami, Umi Barorh Lili Irawati, Utami, 2011; Yan et al., 2018; Zhang et al., 2018)
Fe	(Hui et al., 2018; Nuralam, Endoraza & Arbi, 2012; Nurdin & Maulana, 2016)
Cu (II)	(Dandil et al., 2019; Liu et al., 2016; Susilowati, Endang & Mahatmanti, 2018)

4.2.2. Drug and Hazardous Material Waste

Medicinal waste and hazardous substances are industrial waste that can have long-term adverse effects. This waste also causes environmental damage and endangers the health of the living population. A study by Ramadhanur et al. (2015) used chitosan as a membrane filtration of phosphate compounds in the detergent waste industry (Ramadhanur & Sari, 2015), that can absorb phosphate residue up to 97.40%. Another study used a membrane based on chitosan, PVA, and silica as a filter material for palm oil liquid waste that can reduce BOD levels up to 92.59%, COD 92.59%, and TDS 31.098% (Chodijah, Siti & Liza, Novriani, 2018). Meanwhile, this study indicated that bentonite-chitosan could be used as the removal of cesium radioactive elements in waste (Wang et al., 2019).

Composites that are made from coffee-grounds (WCG) waste combined with chitosan (Cs) and poly (vinyl alcohol) (PVA) was used in a study conducted by (Lessa et al., 2018). At 5% by weight of WCG, the adsorption carried out by composites showed a marked increase (from 10 to 44%) of the adsorption of drugs (metamizole (MET), acetylsalicylic acid (ASA), acetaminophen (ACE), and catalyst compared to samples pure. The highest transfer efficiency was listed at pH six, and the transfer followed the sequence ASA> CAF> ACE> MET. Overall, WCG showed good interaction with polymer matrices and excellent dispersibility of up to 10% by weight. Experiments showed that composites containing WCG present extraordinary reusability in at least five successive adsorption/desorption cycles.

A coal-chitosan composite was used as an adsorbent to remove diethyl phthalate (DEP) through adsorption in a study by (Shaida et al., 2018). The coal used as coal with low carbon content and high silicate. This is also the use of low-quality coal waste. The 9: 1 weight ratio is the ratio that functions optimally from the coal-chitosan composite. This composition can absorb as much as

91.1% DEP under optimal conditions of pH 5.8. The dose of adsorbent used is 4 mg / mL, and the contact time required is 4 hours. The application of coal-chitosan composites as an adsorbent can be used easily and has been proven by repeated use.

Another research indicated that a modification of chitosan polymer could be used in used tire rubber as the removal of anti-inflammatory drugs ibuprofen, diclofenac, and naproxen from aqueous solutions. Modified capacity adsorbents were 70.0, 17.7, and 2.3 mg / g, respectively, for ibuprofen, diclofenac, and naproxen. Various methods have been used to optimize the parameters that affect the efficiency of drug removal to obtain pH 6 as the optimal pH to eliminate all three drugs simultaneously (Phasuphan et al., 2019).

4.2.3. Dye Removal Waste

The dye waste can cause problems because the low amount of color can be highly visible in water and may be toxic to aquatic organisms (Markandeya et al., 2017). The primary source of releasing color content to the environment is related to the imperfect use of dyes in the textile, food, leather, and paper industries. Waste of textile color content is a particular concern because textile consumption will always increase following population growth. Most dyes are made to have resistance to environmental influences such as the effects of pH, temperature and microbial invasion; thus processing of color levels becomes difficult due to the aromatic structure of the dyes which is challenging to be biodegraded, primarily reactive dyes due to the formation of strong covalent bonds between the C atom of the dyestuff with the O, N or S atoms of the hydroxy, amine or thiol groups of the polymer. Chitosan and iron precursor can be used as desorption of congo red for anionic dye wastewater (Hui et al., 2018).

Chitosan-alkali lignin composites can be used to eliminate the harmful effects present in wastewater. Batch adsorption studies showed that chitosan-alkali lignin composites (50:50) showed the maximum percentage removal of anthraquinones dyes, Remazol Brilliant Blue R (RBBR), and Cr(VI) compared to other composites, chitosan, and alkaline lignin. This can be used to utilize lignin residue, which is a potential waste by-product of the paper industry and bio-refractory (Nair et al., 2014).

Chitosan fibers extracted from shrimp shells with high adsorption capacity were used in a study to remove acid yellow dyes from water. Under acidic conditions, the protonated amino groups (positively charged polymer chains), which show attraction with negative ions, are anionic dyes (Iqbal et al., 2011).

The study conducted by (Nitayaphat, 2017) utilized the adsorption of chitosan beads with a combination of coffee residue mixture to remove Reactive Red 152 as an anionic dye. The results showed that the mass ratio of chitosan to coffee residue 60/40 was the most useful for increasing dye removal. While a study by (Sohni et al., 2019) used the new chitosan / nano-lignin composite material as a highly efficient adsorbent (~ 83%) to remove methylene blue (MB) dyes. The adsorption mechanism carried out was one-color adsorption with a maximum adsorption capacity of 74.07 mg g^{-1}. Chitosan composites with nano-lignin also showed better performance in dye decontamination compared to original chitosan and chitosan / bulk-lignin composites. These chitosan-nanolignin composites can be repeated in up to four cycles of adsorption/regeneration, with the results showing recovery as high as 89%.

Two studies by Markandeya et al. conducted efficient, economical, and effective wastewater treatment based on the response surface methodology for removing dyes using cenosphere, waste products, in the form of nanocomposites with chitosan. Chitosan-cenospheres (10: 3) nanocomposite was synthesized using glutaraldehyde, a crosslinking agent, deposited in an alkaline solution to adsorb Disperse Orange 25 (DO) and Disperse Blue 79: 1 (DB). The maximum percentage of dyestuff removal found was 97.30% and 94.22% for DO and DB, respectively (Markandeya et al., 2017, 2018).

Chitosan-PVA composite membrane was used as a filter in waste of rhodamine B dye, in which the best membrane has a pore size of about 0.01-0.15 mm with 75%: 25% chitosan-PVA composition. The membrane can separate the waste of rhodamine B dye up to 87.029% (Novi et al., 2016). Another study (Lou et al., 2018) used a natural polymer-based flocculant that has attracted more attention, in which chitosan and lignin ingredients were mixed by microwaves. The flocculation study indicated that the chitosan-acrylamide-lignin polymer (CAML, 2 g: 2 g: 2 g) showed a maximum removal percentage of 99.3% and 67.0% respectively for C-3R reactive oranges and methyl oranges which reacted actively at acidic pH.

5. CONCLUSION

Chitosan membranes which can only be applied with chitosan material and composites: chitosan-Poly ethylene Glycol (PEG), chitosan-Poly Vinyl Alcohol, chitosan-biosilica, chitosan-PVA-silica, chitosan-alginate, chitosan-cellulose, and chitosan-silica, has the ability to be a coagulant and reduce water turbidity. Chitosan which is used as raw material or in a film form can also adsorb metal ion (Cr (VI), Cs^{+}, Pb(II), Fe, Cu(II)), dyes (anthraquinone dyes, brilliant blue, yellow dye, methylene blue, disperse orange, disperse blue, rhodamine B), drug residue, and hazardous materials. The high abundance of chitosan raw material in Indonesia should be able to support the application of chitosan as a natural purifying agent consider its high ability to adsorb heavy metal and some dangerous materials.

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