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(54) **Title:** EFFLUENT TREATMENT PROCESS

(57) **Abstract:** A process for the treatment of an effluent stream from a pulp mill having one or more liquor streams and one or more recovery processes for recovering useful components from spent liquor, wherein the effluent stream is contacted with anion exchange resin to remove organic compounds from the effluent stream of the mill and, after contact with the effluent stream, anion exchange resin loaded with organic compounds removed from the effluent stream is regenerated with a regeneration solution obtained from a liquor stream used within the mill and, after contact with the loaded anion exchange resin, the spent regenerant solution contains the organic compounds separated from the resin during the regeneration process and is used as feedstock in one or more of the recovery processes of the pulp mill.

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EFFLUENT TREATMENT PROCESS

Field of the Invention

The present invention relates to the sustainable use of anion exchange resins in water treatment systems to remove pollutants from aqueous waste streams. More particularly, the invention relates to the pulp and paper mill industry and an integrated manufacturing and effluent control system.

Background of the Invention

Pulp and paper mills are a significant cause of pollution. Some studies suggest the pulp and paper industry is the leading cause of contaminant discharge (on a mass basis) in the USA.

In general pulp and paper mills use the Kraft process and modifications thereof to chemically pulp wood chips and form cellulose fibres for use in paper manufacture. Environmental concerns and legislative changes have in general resulted in more strict discharge requirements both now and for the future. Of the contaminants, one of the most difficult to reduce in a cost-effective manner is colour. The black colour of discharge is predominantly caused by the action of the caustic chemicals on lignins separated from the wood fibres during the pulping process.

Although the discharge of the coloured contaminants is thought to be safe by those in the industry, it is a highly visible pollutant and an extremely sensitive issue with downstream residents and environmental activists. The resultant political pressures have threatened the continuing operation of pulp and paper mills. For example in New Zealand the political pressures have resulted in legislative change with set environmental targets. A critical target was to reduce the colour impact on the Tarawera River.

This issue of coloured effluent is not limited to New Zealand or even pulp and paper mills. Global environmental concerns have resulted in a general need to reduce the colour impact in water waste streams around the world. Maximum limits on water colorant pollutants have been proposed or set in Australia, New Zealand, United States of America and throughout Europe.

It is believed that the processes known to date will not be sufficient to meet the reduced colour impact targets in some countries. Despite improved environmental practices and improvements in water recycling within pulp and paper mills it is still necessary to use large quantities of water and flush colorants into the environment. Modern effluent treatment methods can remove readily biodegradable organic wastes and separate solids but are not cost effective for use in removing colour.

Known methods for removing organics or colours from water effluent streams include the use of anion and non-polar resin beds, activated carbon, ultraviolet light, ultrafiltration membranes, biological and / or chemical degradation. However, none of these methods are considered to be commercially useful to remove colour in the pulp and paper industry. A number of the methods shift the pollutant from a liquid phase to solid, gas or another liquid phase and may result in additional unacceptable pollutants.

As described in the Final Project Report 2001-26, entitled Colour and Chloride Removal from Pulp Mill Effluent using Ion Exchange by Giyeon Yun and Ian D. Buchanan from the Sustainable Forest Management Network, batch and column tests have shown ion exchange resin beds containing weak base anion exchange resins such as Amberlite® IRA 958, have been found to effectively decolour paper mill effluent. However, it is not economic to simply use the resin once and as such the resin needs to be regenerated in order to restore or recover colour removal functionality. The regeneration process typically involves using substantial qualities of brine as the regenerant and will release the bound colorants into the regenerant containing solution. In effect it will form a new effluent stream containing the colorant together with a new pollutant of namely sodium chloride from spent regenerant solution.

The volumes involved do not make it efficient to regenerant the resin by the above process. By way example, the process would require a large inflow of sodium chloride for use in forming the brine in order to treat 15 megalitres per day of very highly coloured effluent. More critically this process would result in the need to dispose 200-250 cubic metres per day of highly coloured concentrated brine effluent.

Derwent Abstract Accession No. 76-89547X/48 and the associated Japanese patent publication JP51-116205 (Ahlstrom A Oy) relate to the recovery and re-use of sodium chemicals from waste streams from the manufacture of cellulose. The patent includes a description of sulphite and sulphate treatment processes. Two effluent streams are described, a water wash from cleaning the cellulose after digestion and the effluent from an oxygen bleaching process.

The described process is focussed on reducing the loss of sodium from the system by recovering the effluent from the oxygen bleaching and returning it into a combustion furnace (the effluent contained approximately 4% of the pulp). The soda (sodium carbonate) in the combustion residue is separated by recrystallisation for conversion into sodium hydroxide for reuse in oxygen bleaching. The same process was repeated with the effluent obtained from the waste stream after regenerating an ion exchanger of an unspecified type with sodium hydroxide. The ion exchanger was used to clean the water stream which had been used to wash and clean the cellulose after digestion. The source of the sodium hydroxide was not specified.

Derwent Abstract Accession No.75-52740W/32 relates to method for reducing the emission of organic substances from cellulose plants. The associated invention may be described in more detail in Canadian Patent No 1036723 (780815) in the name of Mo och Domsjo Aktiebolag. The Canadian patent describes a process for removing colorants and other organics from the waste streams of cellulose plants, particularly sulphite plants, by using an organic anion exchange resin to treat aqueous waste liquor having a low content of inorganic anions, and by using an adsorption resin on the aqueous waste liquors from any chlorinating and chlorine dioxide bleaching processes. The resins are used in stationary or movable beds (eg a carousel arrangement) and are regenerated and re-used by contact with an aqueous alkali solution.

The regenerant solution used to regenerate the resins was evaporated and combusted with the cooking waste liquor. The regenerant was aqueous sodium hydroxide used to make up losses from the process or aqueous sodium carbonate obtained from the melt after the combustion of waste liquor by separating solid sodium carbonate from sodium sulphite by a fractionated water leaching process, followed by aqueous sodium hydroxide (50g NaOH per litre).

Although resin systems were suggested in 1970's for use in the treatment of effluent from cellulose plants, the applicants believe that the large costs associated with such processes have prevented its adoption to date. Commercial cellulose plants can produce large volumes of effluent containing a low concentration of colorant and can require large quantities of resin to treat the effluent. The costs are increased by the need to have reserve resin beds and flow switching systems for processing the effluent whilst the resin from the primary bed is regenerated. The additional plant equipment, inventory resin and resin storage and regenerant storage requirements significantly increases the cost associated with building and operating a resin treatment system. There is also the risk of breakthrough events if there are changes in concentration of the colorants or as the resin ages reducing the functionality of resin.

It will be appreciated that ionic exchange resins have been relatively recently commercially used to remove non-process elements (NPE) such as chloride and potassium ions from kraft mills. These are very different treatments to the removal of organics from the effluent and may involve the use of cationic exchange resins at various locations in the process to remove potassium ions from more concentrated process streams. Such systems are used in closed kraft mills to control the build up of NPEs. These treatments do not need to operate continuously.

Membrane systems may be used to filter the effluent but can quickly become blocked. Also membrane systems have high capital and operation costs.

Activated carbon has been found to remove a wide range of organic pollutants but can not be easily regenerated and spent carbon is typically disposed in landfill or by incineration.

Biological treatment is not very efficient in the treatment of selected types of organic compounds such as colorants. It takes substantial time and thus would require large storage areas, typically treatment ponds, with the attendant risk of overflow during periods of rainfall. Biological treatment is typically limited to the oxidation of easily oxidised biodegradable organics and can increase the concentration of colorants due to the formation of coloured metabolites from the biological processes.

Other systems such as that proposed in US Patent No. 6,491,827 (Temple et al) use flocculants / agglomerants. A composition of aluminium chlorohydrate and high molecular weight branched epichlorohydrin amine condensate polymers was proposed for use to reduce colour in waste liquids. The composition forms agglomerates containing the coloured lignin which can be filtered from the waste stream.

A current focus of research has been chemical treatment methods such as bleaching the colorant with hydrogen peroxide. Unfortunately, there may be colour reversion downstream depending on local conditions if the colorants are subsequently chemically reduced. It may also result in toxicity issues and potentially increase the concentration of chlorinated organics present in the effluent. Despite these issues and the substantial ongoing costs with using peroxide, there has been considerable interest with such methods because of the real need to reduce the colour impact and the lack of other commercial alternatives.

Brief Description of the Invention

In an embodiment of the invention there is provided the use of anion exchange resin to remove organic compounds, preferably colorants, from an effluent stream of a pulp mill wherein a liquor stream from within the mill is used to provide a regenerant solution for regenerating resin containing bound organic compounds (loaded anion exchange resin) and wherein the regenerant solution after use to regenerate loaded anion exchange resin (spent regenerant solution) contains the removed organic compounds and feeds into a recovery process used within the pulp mill.

In an embodiment of the invention there is provided the use of anion exchange resin to remove organic compounds from an effluent stream of a pulp mill in combination with the use of a liquor stream from within the mill to provide a regenerant solution for regenerating the anion exchange resin loaded with organic compounds removed from the effluent wherein the loaded anion exchange resin is regenerated by contact with the regenerant solution to provide regenerated anion exchange resin for re-use to remove organic compounds from the effluent stream, and wherein the regenerant solution after use to regenerate loaded anion exchange resin (and containing the organic compounds separated from the resin) is fed into a recovery process used within the pulp mill.

Preferably a portion of the liquor stream is directly used as the regenerant solution or is diluted with water before use as the regenerant solution.

In another embodiment of the invention there is provided a process for the treatment of an effluent stream from a pulp mill having one or more liquor streams and one or more recovery processes for recovering useful components from spent liquor, wherein the effluent stream is contacted with anion exchange resin to remove organic compounds from the effluent stream and, after contact with the effluent stream, the anion exchange resin loaded with organic compounds removed from the effluent stream is regenerated with a regeneration solution obtained from a liquor stream used within the mill and, after contact with the loaded anion exchange resin, the spent regenerant solution which contains the organic compounds separated from the resin during the regeneration process is used as feedstock in one or more of the recovery processes of the pulp mill.

In another embodiment of the invention there is provided a pulp manufacturing process which has one or more liquor streams used in process steps in the manufacturing process and one or more recovery processes for recovering useful components from spent liquor and an effluent stream from the manufacturing process containing organic compounds; the manufacturing process further including an effluent treatment process wherein

(a) organic compounds are removed from the effluent stream by contacting the effluent stream with fresh anion exchange resin capable of binding to organic compounds in the effluent stream and forming loaded resin having organic compounds bound thereto;

(b) regenerating at least a portion of the ion exchange resin loaded with the bound organic compounds by contact with a regeneration solution obtained from one or more of the liquor streams used in the manufacturing process to provide regenerated resin and a spent regenerant solution eluate containing the organic compounds;

(c) reusing the regenerated resin as fresh ion exchange resin in step (a);

(d) using the eluate as feedstock in one or more recovery processes of the manufacturing process.

Preferably the anion exchange resin is a weak or strong base anion exchange resin, and preferably is a macroporous resin. Preferably the resin contains magnetic or magnetisable material and more preferably the resin contains magnetic particles dispersed throughout the resin.

Preferably the pulp mill or manufacturing process is a kraft pulp mill or includes the kraft process. Preferably the regenerant solution is obtained from the white or green liquor stream of a mill incorporating the kraft process or the pink liquor stream of a mill incorporating a neutral sulphite semi chemical (NSSC) process.

<u>Detailed Description of the Invention</u>

The present invention is predicated on the realisation that it is not necessary to regenerate anion exchange resin with a separate regenerate solution of brine. Instead it is possible to use regenerant solutions obtained from suitable liquor streams used in a pulp manufacturing process to regenerate the resin.

The regenerant solution can be the liquor itself as used in the process or may be directly obtained therefrom without any significant processing before use as the regenerant. Significant processing includes fractionation processes or chemical treatments to separate chemicals moieties present within the liquor stream. Such steps are not necessary and increase the operation costs associated with the effluent treatment process. It can be sufficient to directly use a process liquor stream ordinarily present in the pulp mill, or a portion thereof diluted by the addition of water before use regenerant. Suitable liquor streams include the green or white liquor streams of the kraft pulping process, or the pink liquor stream of a pulp mill incorporating a NSSC process.

Capital and operation costs can be further reduced by the use of non-fixed column systems having an appropriate resin separation and return system. This includes continuous flow resin systems including fluidised and semi-fluidised bed systems. An example of such a system is a water treatment process using MIEX®DOC resin, as described in more detail below.

These changes may address the significant cost problems associated with the previous use of ion exchange resins in the treatment of effluent streams.

The present invention is also based on the realisation that manufacturing processes may include one or more recovery processes for the recovery of useful compounds from spent liquor streams. The spent regenerant solution containing the unwanted colorants may be fed into suitable recovery processes thereby addressing the disposal problem of the spent regenerant.

The identification and use of suitable liquor streams will depend in part on the type of resin required to remove the organics from the effluent. The selection of a suitable recovery process for the disposal of the spent regenerant requires an assessment of the pulp manufacturing process. Well established manufacturing processes have clearly identifiably recovery processes for the spent liquor streams.

The process should allow for the integration of an effluent treatment process for organics, and in particular colorants, into a wide range of pulp manufacturing processes with resultant environmental benefits.

The invention will now be described with reference to the kraft pulp process as used for manufacturing pulp. The kraft process was first used in the 1880's and is used by most pulp mills to produce pulp for subsequent manufacture of paper in a paper mill. Typically the kraft pulp mill and the paper mill will be adjacent allowing the pulp to be pumped into the adjacent paper mill.

The kraft pulp process is an efficient process and operates with a number of liquor streams and recovery processes. One of the reasons why it dominates the pulp and paper industry is that it can recover approximately 95% of the pulping chemicals and also produce energy for powering part of the operation of the mill. However, it also produces a highly coloured (black) effluent from the wash of the digested wood chips and environmental concerns have made the removal of colorants from the effluent a critical issue which threatens the viability of a number of established kraft pulp mills.

The kraft process uses a caustic mixture for pulping the wood chips. This mixture is known as white liquor and has as major components sodium hydroxide and sodium sulphide but it may also include significant amounts of carbonates. The process involves cooking wood chips under pressure in the white liquor (also known as cooking liquor). This is done in digesters, essentially large pressure tanks. The hydroxides work on and dissolve the lignin component into the liquor and soften the wood chips. The sulphides act to buffer the system and provides additional hydroxide as required. The contents of the digesters are transferred into a blow tank where the softened chips are disintegrated releasing the individual wood fibres known as pulp.

The impact of the lignin organics on the liquor is to turn it into a highly coloured solution, called black liquor. The now very dark spent cooking liquor with pulp suspended therein is sent to a bleach plant where the pulp is separated from the liquor, washed and screened by a series of brown stock washers and the brown pulp is then bleached to a required brightness. The separated spent cooking liquor, known as weak black liquor is collected from the brown stock washers and used in the chemical recovery process area.

The weak black liquor is a dilute solution (approximately 12 to 15 percent solids) of wood lignins, organic materials, inorganic compounds such as sodium sulfate, sodium carbonate, sodium hydroxide and sodium sulphite. The cost effectiveness of the kraft process is determined by the ability to recover the cooking liquor chemicals from the weak black liquor.

The separated black liquor is typically sent to a storage tank prior to being concentrated by evaporation. This is typically done via direct contact evaporation through multiple effect evaporators. This increases the solids content of the black liquor to around 45-50% by weight.

The strong or heavy black liquor may then be oxidised in black liquor oxidation systems or simply further concentrated or evaporated. The oxidation process (used in some mills) reduces the emissions of total reduced sulphur (TRS) compounds. The control of the production of TRS compounds is another important pollutant limitation.

The solids content of the black liquor following the final evaporation or concentration step is in the order of 65 to 68%. The black liquor is then spray injected into a recovery furnace. The organic component of the liquor is burnt and provides the energy source for the boiler / furnace which operates at around 800-1000°C. An additional benefit of this system is that high pressure steam is generated by the boiler / furnace and may be used to drive a power generation turbine, thus also providing power and heat for the plant and may be used to cook the wood chips and to evaporate / concentrate the black liquor.

The flue gases contain particulate matter exiting the furnace and is primarily sodium sulphate. This may be collected with electrostatic precipitators and may be added into the black liquor prior to burning the organics in the furnace.

As the organics burn off, a residue collects in the base of the hearth. The molten residue is known as smelt and is primarily a mixture of sodium sulfide and sodium carbonate, with some sodium oxide, at around 1000°C.

Smelt is drawn off from the base of the hearth and then dissolved into a weak caustic solution to provide green liquor, due to the dark green colouring. The green liquor is essentially a solution of sodium carbonate, sodium sulfide, and some sodium hydroxide, with combined solids of 12-15% by weight and a pH of approximately 13 to 14. The green liquor will also contain some insoluble unburnt carbon which is removed through a series of clarification tanks and/or filters.

The green liquor is reacted with slaked lime ($Ca(OH)_2$). Slaked lime is manufactured on-site utilising a lime kiln where calcium carbonate from lime-rock and together with lime mud is burnt to form lime (CaO) then dissolved in water (slaked). The slaked lime reacts with the sodium carbonate component of the green liquor to form sodium hydroxide and calcium carbonate increasing the alkalinity of the liquor. The reduced solubility of the carbonate in an alkaline medium results in the precipitation of the calcium carbonate in the clarifier and the precipitate (known as lime mud) is washed to recover any last traces of sodium and sent back to the lime kiln. The green liquor becomes white liquor for use to further cook wood chips. The mud wash solution known as weak wash may be used to dissolve the smelt.

By using recovery processes used in the kraft process it is possible to achieve approximately a 95% recovery of the pulping chemicals. Small amounts of make up chemicals still need to maintain the process. Typically sodium metabisulfite, sodium sulphate and sodium hydroxide may be added to the kraft process as make up chemicals.

Some kraft mills also include neutral sulphite semi chemical (NSSC) pulping in addition to the above described digestion process for the wood chips. Other pulp mills simply use the NSSC system.

The NSSC process involves treating the wood chips in a solution of sodium sulphite and sodium bicarbonate. This softens up the wood chips before they are pulped by a mechanical means. NSSC may offer some cost savings but may not provide as good quality pulp fibres. The absence of a large solution of sodium hydroxide means the fibres are not badly damaged by the hydroxides thus improving paper strength. However, the absence of hydroxide also means that it is more difficult to dissolve and remove all of the lignins joining the fibres together reducing paper strength.

The effluent from the pulp extraction step of the NSSC process alone does not tend to be a coloured as the effluent from the pulp extraction step of the kraft process, as the lignins and degradation products are normally obtained in other process stages. However, the NSSC process may be operated together with the kraft processes. The spent sodium sulphite and sodium bicarbonate liquor, known as pink liquor, is inter-mixed with the kraft black liquor and burned in the recovery furnace. The NSSC process can be used in combination with the kraft process to replace most or all of the make-up chemicals required for the ongoing operation of the kraft process, but significantly increases the sulphur emissions.

The organics in the effluent stream include highly coloured lignins. The organics are a type of dissolved organic carbon (DOC). The organics can be removed by using suitable ion exchange resins. As the organics are generally weakly anionic it is preferred to use anionic exchange resins to remove the organics, and in particular the colour causing organics from the effluent stream. Due to the weak anion nature of the organics it can be better to use strong base anion exchange resins, such as type I and type II anion exchange resins.

Anion exchange resins require a source of anions to replace the organic compounds bound to the resin and regenerate the resin. Many anion exchange resins are regenerated with brine due to the ease of use and availability of brine. However, it is not necessary to regenerate all exchange resins with chloride ions to restore resin functionality. Other ionic compounds may be used to regenerate ion exchange resins.

The suitability of liquor streams within the manufacturing process for use to provide the regenerant solution depends on the nature and type of the exchange resins.

White liquor contains hydroxide anions but these anions may not be useful for regenerating a number of types of anion exchange resins. This was shown in the earlier mentioned final report 2001-2006 where a 1 M NaOH solution was not capable of removing the colour from Amberlite IRA 958, a strong base (quaternary ammonium chloride), anion exchange resin from Rohm and Haas, used for the removal of colour and organics and also for cane sugar treatment. Brine was also required to effectively regenerate the resin.

The concentration of hydroxide in white liquor is significantly greater than the 1 M solution used in the 2001-2006 Final report and it is thought that the white liquor solution may be capable of regenerating the Amberlite 958 resin. Further, a skilled addressee would be capable of identifying other resins suitable for removing organics and suitable for regeneration with hydroxides, such as Dowex and other Amberlite strong base (type 1 or 2) anion exchange resins, gel or macroporous.

The white, green and pink liquor streams also contain sulphite anions and may also have carbonate anions and these anions could also be used to regenerate anion exchange resin. Thus it is possible to use these liquor streams in the production of a suitable regenerant solution for regenerating loaded resin.

Thus a portion of the white, green or pink liquor streams of a kraft mill or a kraft and NSSC mill may be used as the regenerant solution or to form a suitable regenerant solution. Depending on the resin used and organic compounds in the effluent, it may be beneficial to dilute the liquor to form the regenerant solution. It may also be beneficial to combine liquor from two or more of the liquor streams.

Depending on the type of resin, it may be damaged by the caustic conditions present in the white or green liquors. The concentrated hydroxide ions may damage ester links used in some polymers. When high pH liquor streams are used to regenerate the resin then it is preferred to use a resin capable of withstanding those conditions.

Alternatively, it may be possible to dilute the liquor for use as a regenerant solution to decrease the pH. This could be done with new water or with water or liquor streams from elsewhere in the manufacturing process.

The white and green liquor streams are effectively buffered solutions and very large amounts of water or acid may be required to reduce the overall pH which is 14 for the white liquor and around 13.8 for the green liquor. This may not be viable with the white and green liquors due to the need to subsequently evaporate a large amount of water. Instead it would be preferable to use a resin capable of resisting the damage caused by the hydroxide ions.

It is preferred to use the green liquor to form the regenerant solution for regenerating loaded resin. The pH of the green liquor is less caustic than the white liquor and should do less damage to hydrolysable resins. If it is particularly desirable to use resins which may be damaged by the regenerant, because of other properties of the resin, then it may still be cost and process effective to accept an operating loss of resin during the regeneration process and simply add virgin resin to offset any reduction in the ion exchange capacity of the system.

It is also preferred to use the pink liquor to form the regenerant solution for the resin. This stream contains sulphide ions for use in the anion exchange and is at lower pH than the white or green liquors and thus may be less damaging to hydrolysable resins.

It may also be possible to tap into the make-up chemical liquor stream and use those chemicals to form the regenerant solution for the resin. Sodium metabisulfite and/or sodium sulphate are normally used to make up sodium and sulphur losses in the process and could first be used to regenerate the resin before being added to a weak black liquor stream like a pink liquor stream. The use of the make-up liquor stream may avoid the pH damage done to the resin.

The amount of regenerate solution required to regenerate the resin will depend on a number of factors including the regeneration method used and the anions in the regenerant and the concentration of the regenerant solution. Some regeneration methods may produce significant qualities of spent regenerant solution. However, in a kraft mill, the disposal of significant amounts of spent regenerant solution should not be a major problem. The spent regenerant solution may be added to the weak black liquor for processing and recovery as black liquor particularly since the spent regenerant solution includes the same or similar compounds as those present in the weak black liquor. It also avoids the need to separately process the regenerant and the associated plant costs. However, it is envisaged that it would be beneficial to use regeneration methods which do not produce large qualities of dilute spent regenerant in order to reduce the extent of the evaporation / concentration processing of the weak black liquor stream.

In respect of the present invention the regenerant solution may also be brine, if brine is used in a liquor stream in a process within the overall manufacturing process. In respect of a kraft mill, the regenerant solution would not be a brine solution as such solutions are not normally used in the kraft process. It will also be appreciated that it is not desirable to add chloride into liquor streams in the kraft process. Chloride is a NPE and it is generally desirable to remove chloride for the kraft process.

The rate at which the regenerant solution loses its effectiveness and becomes spent regenerant will vary depending on the individual processes, the liquor used and the amount of organics in the effluent. It is expected that the regenerant could be used for two or more regeneration cycles before becoming spent and being sent to the black liquor recovery cycle. It will depend in part on the type of regeneration process used. If a counter current system is used and the initial fraction containing the largest amount of organics is separated and sent to recovery then it may be possible to use the regenerant solution for more regeneration cycles than would otherwise be the case.

It is considered that the inclusion of the additional organic compounds in the black liquor will be beneficial. The compounds should, like the other organic compounds in the black liquor stream, be burnt in recovery furnace, and the heat of combustion could contribute to the energy output of the mill instead of polluting the waterways.

Thus in a preferred embodiment of the invention there is provided a process for removing colour from an effluent stream from a pulp mill using the kraft pulp process having white, green and black liquor streams and optionally a pink liquor stream, wherein anion exchange resin is used to remove the colorants from the effluent stream and the ion exchange resin is regenerated with a regenerant solution obtained from the white, green or pink liquor stream and the spent regenerant solution is added to the black liquor.

In another preferred embodiment of the invention there is provided a method of reducing the amount of organics in effluent from a pulp process having a digester, cooking liquor, black liquor, a recovery process for recovering chemicals from the black liquor for use in the manufacture of cooking liquor and an effluent stream containing organics, comprising the steps of:

(a) removing organics from the effluent stream by contacting the effluent with anion exchange resin in a contactor;
(b) separating resin loaded with organics from the contactor;
(c) regenerating the loaded anion exchange resin with a regeneration solution obtained from the cooking liquor or intermediate liquors used in the recovery process to provide regenerated resin and used regenerant containing separated organics;
(d) returning the regenerated resin from step (c) to the contactor; and
(e) adding the used regenerant from step (c) to the black liquor.

One of the benefits of the present invention is it allows the use of known ion exchange resins, known water treatment systems and resin regeneration systems. There are established ion exchange treatment systems for use for treating and purifying water. Such systems may be used or water treatment systems used in the production of potable water from raw water may be adapted for use in the treatment of the effluent stream.

Raw water supplies often contain organic compounds and materials known as natural organic matter (NOM). A fraction of the NOM in the raw water supply is dissolved organic compounds (DOC) but the removal of DOC has presented particular difficulties. DOC is one of the main causes of water discolouration. DOC often includes compounds such as humic and fulvic acids which are water soluble at certain water pH levels. Humic and fulvic acids are not discrete organic compounds but mixtures of organic compounds formed by the degradation of plant residues. DOC also includes the colorant compounds such as lignins present in the effluent of the kraft process and as such it is expected that systems for the removal of DOC from raw water may be used to remove colorants from the effluent of the pulp and paper industry. However, the DOC which may be present and removed in water will generally be present at a concentration less than 25mg/L. The concentration of lignins in the waste streams of the kraft pulp mills can be in excess of 500 mg/L and this may create other problems of the use of systems intended for use for the removal of DOC.

Conventional ion exchange techniques involve passing the water through a packed bed or column of ion exchange resin. The vessel containing the resin may be known as a contactor. The target organic species such the colorants in the effluent stream are removed by being adsorbed onto the ion exchange resin. By this method the ion exchange resins may remove up to 90% of the organics from the water. Further improvements in the efficiency of colorant removal may be obtained by passing the water through a series of beds or columns and thereby increasing overall exposure of the water to resin and contact time.

The use of different types of resins may further improve the overall removal efficiency. This includes the use of resins from different suppliers or resins of different types from the same supplier. In some arrangements the water may be treated with anion exchange resin and also with cation exchange resin, although the cation exchange resin would be used to remove other types of chemicals in the water such as NPE in a closed mill.

Ion exchange resins may also be used in conjunction with other methods of water purification including those mentioned previously in the background of the invention such as activated carbon, membrane filtration and coagulants to further improve the overall effectiveness.

The use of the ion exchange resin may also reduce the cost of other effluent treatments by improving the effectiveness of other treatment steps on the effluent. By way of example, in the purification process involving coagulation, a coagulant is applied to destabilise and combine with suspended matter and organic compounds so that they coalesce and form a floc, which can then be physically removed by methods such as floating, settling, filtration or a combination thereof. Coagulants such as alum (aluminium sulphate), various iron salts and synthetic polymers are commonly used in processes for water treatment. However, the effluent may have high levels of organics present that react with the coagulant and would require a higher coagulant dose than would be required for removal of suspended matter alone. The inclusion of the ion exchange process may allow for the more efficient use of flocking agents. The bulk of the floc formed may then be removed by sedimentation or flotation and the water containing the remainder of the floc passed through a filter for final clarification.

In the membrane filtration process the effluent would be filtered through a membrane. There are four commonly available membrane processes currently in use for water treatment. Microfiltration (MF) and Ultrafiltration (UF) are two processes generally used to remove turbidity and solid particles from water. However, where the water contains high levels of organic colorant compounds these membranes may be fouled by the colorants, thereby reducing the flux across the membrane, reducing the life of the membranes and increasing operating costs. The inclusion of ion exchange resin may also aid in significantly reducing the capital and operating costs of membrane filtration.

Ion exchange resins incorporating magnetic particles (magnetic ion exchange resins) readily agglomerate due to the magnetic attractive forces between them. This property renders them particularly useful as recyclable resins as the agglomerated particles tend to settle quickly and are therefore more readily removable from the water.

The magnetic ion exchange resin particles can have a discrete magnetic core or have magnetic particles dispersed throughout the resin particles. In resin particles which contain dispersed magnetic particles it is preferred that the magnetic particles are evenly dispersed throughout the resin particles. A particularly useful magnetic ion exchange resin for the treatment of raw water is described in WO96/07675 and the related Australian patents 704376 and 744706, the entire content of which are incorporated herein by reference. The resin disclosed in these documents has magnetic particles dispersed throughout the polymeric beads such that even when they become worn through repeated use, they retain their magnetic character. Ion exchange beads of the type disclosed in this document are available from Orica Australia Pty. Ltd., under the trademark, MIEX® DOC.

WO 96/07615 and the related Australian patents 705434 and 749656, the entire contents of which are incorporated herein by reference, describe a process for removing DOC from water using an ion exchange resin which can be recycled and regenerated. This process is particularly useful in treating water with magnetic ion exchange resin of the type described in WO96/07675. The described process may be adapted for use to remove organics such as colorants from the effluent stream of pulp and paper mills.

The ion exchange resin may be dispersed in the water in a contactor tank so as to provide the maximum surface area of resin to adsorb the DOC including the colorant compounds from the pulp mill or process. Dispersal of the ion exchange resin may be achieved by any convenient means. Typically the resin may be dispersed by mechanical agitation such as stirrers and the like, mixing pumps immersed in the water or air agitation where a gas is bubbled through the water. Sufficient shear needs to be imparted on the water to achieve dispersal of the resin.

In some small scale operations the ion exchange resin may be dispersed in a semi-fluidised bed. The use of a semi-fluidised bed is not only a convenient means for dispersal of the ion exchange resin but provides for the ready separation of the loaded resin from the water once DOC is adsorbed onto the ion exchange resin.

Separating the resin loaded with DOC for regeneration from the water may be achieved by settling or screening or a combination thereof. Screening of the loaded resin from the water may be achieved by any convenient means. The screens may be selected with consideration for the size of resin particles to be removed from the water. The configuration of the screens may be such that clogging of the screens is reduced.

Separation may also be achieved by removing the shear, at which point the magnetic particles in the resin cause the resin to agglomerate. The agglomeration may be facilitated by the use of tube settlers and other means known to those skilled in the art. The resin may then be collected by various means including vacuum collection, filtration through a mesh of appropriate porosity, magnetic filtration, and magnetic transport such as belts, discs, drums, and the like. It is preferable that the separation and collection means do not cause mechanical wear which may lead to attrition of the resin. In one embodiment, resin is removed from the process container by means of a resin separator such as a high gradient magnetic filter.

When a continuous fully suspended system is used, the resin may conveniently be separated from treated water by gravity settling. Based on resin characteristics, very effective (>99% solids removal) gravitational settling is achieved in high-rate settling modules with retention times less than 20 minutes.

In a preferred process for separating the ion exchange resin from the water the bulk of resin particles settle out in the first quarter of a separating tank (which may be the contactor tank) length which is devoid of settler modules ("free-flowing" settling). Further removal of resin particles ("enhanced" settling) from treated water is performed in the settler compartment filled with modules which may be either, tilted plates or tubular modules. The bottom of the settler is designed for collection of resin particles in cylindrical, conical or pyramidal hoppers from which the resin particles are pumped back to the front of the process. In this preferred process some mixing of the settled resin in the hoppers may be required to keep it in a fluid condition and to ensure a uniform concentration of the resin within the resin recycling and regeneration system.

The ratio of water to magnetic ion exchange resin in the contactor is preferably kept between about 12.5:1 and 200:1, more preferably between about 20:1 and 33:1.

Process parameters, i.e., resin dose, contact time, and regeneration rate, can be determined by one skilled in the art for any given process, applying art-known principles and the teachings of this specification and the specifications incorporated by cross-reference.

The contacting of the resin with the effluent is not limited to tanks but may be done in any container known to the art for treating water and including tanks used for batch-wise or continuous processes, as well as conduits and piping. The effluent water may flow into the process container by any means known to the art, e.g., by pumping or gravity feed.

The preferred ion exchange resins disclosed in WO96/07675 are magnetic ion exchange resins which have, throughout their structure, cationic functional groups which provide suitable sites for the adsorption of DOC and the other organic compounds in effluent streams, such as those from pulp and paper mills. The cationic functional groups possess negatively charged counter-ions which are capable of exchanging with the negatively charged compounds such as DOC or the colorants in the effluent stream of a kraft pulp mill. The negatively charged organic compounds are removed from the water through exchange with the resin's negative counter ion. Accordingly, these types of resins may be referred to as anion exchange resins, where anion indicates the type of compounds that will exchange and bind to the cationic functional groups of the resins. MIEX® is a strong base anion exchange resin.

When the organic compounds bind to the ion exchange resin, the functionality (activity) of the ion exchange resin is reduced. Such resins can be referred to as used, spent or loaded resins. The loaded resin need not be wholly exhausted (but such resins are also included as loaded resin) and may still retain some functionality but the overall ability of the resin to bind to the resin has reduced.

The ion exchange resins used in the process should be regenerable and also recyclable. Regenerable resins are capable of being treated to remove adsorbed organics restoring activity, at least in part, so that the regenerated resins can be re-used in the treatment process. Recyclable resins can be used multiple times without regeneration and continue to be effective in adsorbing the organics.

It is not necessary for all ion exchange sites in a resin to be regenerated for an ion exchange resin to be considered "regenerated" for the purpose of the present invention. It is sufficient that the regeneration process has occurred to an extent that the ion exchange resin is useful in subsequent ion exchange processes in a water treatment plant. Preferably more than 80% of the ion exchange sites previously taken up by the DOC are regenerated, more preferably greater than 90% and most preferably greater than 98%. The expressions "regenerated ion exchange resin" or "regenerated resin", as used herein refers to resin in which the ion exchange capacity of a loaded (also referred to as spent or used) ion exchange resin has been returned to a level whereby it is rendered suitable for use in a subsequent ion exchange process.

Fresh ion exchange resin may comprise regenerated resin and also resin which has not previously been used in the process. It is common place to make up for loss of resin from the process, e.g., resin leaving the contactor or damaged beyond recovery. The make-up resin may be added directly to a contactor container for contacting the effluent or may be added to a fresh resin holding container also containing regenerated resin, from which fresh resin is supplied to the contactor container.

WO 96/07615 also describes processes for regenerating magnetic ion exchange resin and such processes could be used in the present invention with a suitable regenerant. The regeneration process may involve passing the regenerant through a packed column or bed of loaded resin. Fixed filtering bed systems may be regenerated by retaining the resin within large treatment vessels and the resin is regenerated by taking the treatment vessel offline and washing the loaded resin with a suitable regenerant to regenerate the resin. Whilst this is occurring effluent for treatment could be stored and processed in due course once the resin has been regenerated or the effluent may be pumped through an alternative treatment vessel containing regenerated resin.

The regeneration can also be affected by a mixing or agitation process. In practice, such regeneration processes are typically performed in large batch wise operations. When magnetic ion exchange resin is used, it can be removed from a contactor tank by settler underflow and generally transferred to one of two large regeneration vessels. When one vessel is filled the settler underflow stream is directed to the second regeneration vessel while the one that has been filled undergoes regeneration. The regeneration is performed either in:

(i) a mixing tank where a mechanical agitator mixes the regenerant solution with the resin (agitated tank regeneration), or

(ii) a tank where the regenerant solution is passed through a stationary bed of resin with the ion exchange occurring while the regenerant is in contact with the resin (column regeneration or plug flow regeneration).

It will be appreciated various regeneration systems may be used to regenerate the resin. The regeneration system may be used alone or in conjunction with membrane filtration regeneration systems, if required. One of the benefits of using resins containing dispersed magnetic particles is that it can permit the use of a number of new regeneration processes which can have a significant impact on costs. Magnetic ion exchange resins tend to be significantly smaller than the resins used in fixed bed or column systems but can agglomerate and settle when required due to the magnetic interaction. The smaller resin size permits these types of resins to be fluidised and thus can be pumped from one location to another. This can allow the use of regeneration systems where a portion of the resin is removed from a contact tank, regenerated and returned to the tank.

When magnetic ion exchange resins are used the process may include contacting the effluent with an ion exchange resin, or blend of ion exchange resins with different ion exchange site chemistry, in a contactor, removing a portion of ion exchange resin from the contactor and regenerating at least a portion of the removed resin and returning any remaining separated resin and the regenerated resin to the contactor container.

It also permits the use of counter current systems such as those described in US Provisional Application No. 60/567381 and plug flow systems such as those described in AU Provisional Application No. 2004904207, the entire contents of these applications being incorporated herein by reference. Continuous regeneration systems such as those described in the above mentioned applications can provide significant benefits particularly when used in conjunction with other continuous processes such as the kraft process used in pulp and paper mills. It may reduce the inventory costs, capital costs and the footprint for the regeneration system. Fluidised regeneration systems such as those made possible by the use of magnetic ion exchange resins may also prevent or reduce the extent of fouling of the ion exchange resin because the movement of the resin particles in circulation in the process lines and containers reduces the opportunity for the polymerization and fouling which can occurs on packed, stationary resin beds and columns.

In a typical process, no more than about 0.1% percent of the magnetic ion exchange resin will be lost in the treated effluent stream, and preferably no more than about 0.01% percent of the resin that is added to the contactor will be lost. Make-up resin (new resin added to the system) is then added to the contactor as needed to replace the resin that is lost. The balance of the fresh resin required for the ongoing process is recycled, regenerated resin. Resin lost to the process may be further reduced by use of a filter unit to capture resin in the stream exiting any container used to contain resin and from which resin could be lost.

Typically, resin can be regenerated and reused indefinitely without having to change the total resin inventory, since the small amount of resin loss to the system and its replacement with new resin maintains the condition of the total inventory over the long term. However, the replacement rate may need to be increased when the regenerant solution damages the resin.

The effluent stream may include sensors for assisting in the regulation of the regeneration process. If there is an insufficient amount of fresh resin then the effectiveness of the ion exchange process may be reduced resulting in break throughs of undesirably organic compounds. For column and fixed bed systems when a sensor indicates that the resin is no longer effective then the effluent stream may be switched to another column or bed or into a holding tank for subsequent treatment. The column or bed could then be subjected to a regeneration process. When a fluidised regeneration system is used then flow rates could be adjusted to increase effluent contact time with the resin and increase the production rate of regenerated resin.

The contaminating ions in the effluent could be removed down to a desired concentration. If a single pass through the process container does not remove sufficient amounts of the contaminating compounds, more resin can be added to the system, a greater portion of the resin can be regenerated during a given time period, an additional process container could be added in series or the passed effluent could be passed back through the system. Other parameters may also be changed as will be appreciated by those of skill in the art and as taught herein, in order to reduce concentrations of contaminating ions in the effluent.

The type of resin used, its characteristics and regeneration process will depend on the compounds to be removed from the effluent and the manufacturing process and liquors and recycling processes therein.

The amount of ion exchange resin necessary to remove organic ions from the effluent is dependent on a number of factors including the level of organic ions initially present in the effluent to be treated, the nature of the organic ions, the desired level of organic ions in the treated water, type and concentration of competing ions, salinity, alkalinity, hardness, temperature, pH, and the rate at which it is desired to treat the effluent to remove the organic ions.

It is preferred that the ion exchange resin particles be macroporous in order to provide the particles with a large surface area onto which the organic ions can be adsorbed. Macroporous (or macroreticular) is a term applied to the bead structure of certain ion exchange resins which have a rigid structure with large discrete pores. However, gel resins may still be useful for the removal of DOC in some applications.

Strong base ion exchange resins are preferred, and in particular the MIEX® DOC ion exchange resin, which has a proven capability for adsorbing DOC.

For a kraft mill, the resins used may be selected one or more of from a broad range of resins which a skilled addressee would be able to determine by routine research. The resins could be selected from the following anion exchange resins:

MIEX®DOC from Orica Australia Pty Ltd;
Dowex® strong base anion exchange resins from Dow, such as Dowex Marathon A, Marathon A LB, Marathon 11, Marathon MSA, Upcore 500, 600, 625, Monosphere 550, 700, 725 and Dowex MSA or SBR resins;
Purolite resin from Purolite, such as A420S or A500P;
Amberlite anion exchange resins from Rohm and Haas, such as Amberlite FPA40 Cl, FPA90 Cl, FPA98 Cl or FPA53.
or Lewatit resins from Lanxess, such as S4228, S4268, or S4328.

A number of these resins, such as Marathon A, can withstand pH 14 and may be regenerated with hydroxide ions and may therefore be suitable for regeneration with the white liquor from the kraft process.

The size of the resin used will vary depending on the type of resin. It is preferred that the ion exchange resin particles are magnetic and that they have a diameter less than about 250 µm, more preferably in the range of from about 50 µm to about 200 µm. Particles in this size range can be readily dispersed in the water and are suitable for subsequent separation from the water. The size of the resin particles affects the kinetics of adsorption of organic ions and the effectiveness of separation. The optimal size range for a particular application can be readily determined by one skilled in the art without undue experimentation. Significantly larger sized resins are normally used in fixed bed systems.

The process of the present invention may be readily incorporated into existing Kraft mills. For example, it may be used in combination with any existing effluent treatment processes such as conventional coagulation, sedimentation, filtration, membranes or any combination of processes as the water quality, treatment requirements or other circumstances dictate.

Example

A sample of the green liquor from the Carter Holt Harvey Tasman Kraft Mill was collected for use in bench top tests. Two samples taken on successive days off the effluent steam from the Tasman were also used in the tests.

MIEX® DOC brand magnetic anion exchange resin was used as the ion exchange resin.

Example 1. – Colour removal

The ability of MIEX® DOC resin to remove colorants from the effluent samples was assessed by contacting a fixed bed volume (BV) of resin (120 mls) with effluent. The contact time was 15 minutes at the end of which the colour of the effluent at 465 nm was assessed and the effluent removed. The cycle was repeated with the same (non-regenerated) resin used for each cycle. The results are shown in table 1 below.

Table 1.

Number of BV of effluent to one BV resin	Colour Removal
17	100%
33	99%
50	94%
67	81%
83	79%
100	83%
117	75%
133	64%
150	54%
167	54%
183	47%
200	45%

The experiment was repeated with the second sample of effluent and there were no significant differences in colour removal.

Subsequent lab work indicated that 80-90% of the colour could be removed using resin concentrations of 40-50mls/L and a contact time of 15 to 30 minutes.

From the above results it was concluded that MIEX® resin can be used to effectively remove colorants from a kraft mill effluent stream.

Example 2. – Regeneration Effectiveness

Tests were conducted on loaded resin from example 1. The resin (120 mls) was stirred in 360 mls (3 bed volumes) of green liquor for 15 minutes and green liquor was separated and the resin was then rinsed with 2 litres of water.

The resin was then used with a further 200 bed volumes of effluent, regenerated again with the same green liquor and used a third time to remove colorants from effluent. The effectiveness of the resin after regeneration is shown below in table 2.

Table 2.

Number of BV	Colour removal after first regeneration.	Colour removal after second regeneration.
33	60%	88%
67	33%	52%
100	56%*	52%
133	73%	32%
167	53%	
200	20%	

* New effluent sample used which distorted results.

The colour (at 465 nm) of a sample of the green liquor at 1/200 dilution after each regeneration was determined. The results indicated that the green liquor contained 30800 mg/L of colourant compounds after the first regeneration, 46020 after being used for a second regeneration and 65160 after the third regeneration.

Additional regeneration cycles suggested the green liquor was saturated with colorant after three regeneration cycles and spent as a regenerant and should be forwarded to the black liquor stream.

The results from table 2 also suggest that the standard MIEX® DOC resin had a reduced capacity for colour removal after regeneration, suggesting damage or organic fouling. It is believed that the use of a caustic resistant non-hydrolysable anionic exchange resin should address this issue.

The invention has been illustrated and described with reference to specific embodiments, including specific reagents, ion exchange resins, effluents and organic and competing ions, and process steps and process apparatus. However, as will be appreciated by those of ordinary skill in the art, equivalent reagents, ion exchange resins, waters and organic and competing ions, process steps and apparatuses can be substituted for those described herein

The claims defining the invention are as follows:-

1. A process for the treatment of an effluent stream from a pulp mill having one or more liquor streams and one or more recovery processes for recovering useful components from spent liquor, wherein the effluent stream is contacted with anion exchange resin to remove organic compounds from the effluent stream of the mill and, after contact with the effluent stream, anion exchange resin loaded with organic compounds removed from the effluent stream is regenerated with a regeneration solution obtained from a liquor stream used within the mill and, after contact with the loaded anion exchange resin, the spent regenerant solution contains the organic compounds separated from the resin during the regeneration process and is used as feedstock in one or more of the recovery processes of the pulp mill.

2. A pulp manufacturing process which has one or more liquor streams used in process steps in the manufacturing process and one or more recovery processes for recovering useful components from process streams and an effluent stream from the manufacturing process containing organic compounds; the manufacturing process further including an effluent treatment process wherein

(a) organic compounds are removed from the effluent stream by contacting the effluent stream with fresh anion exchange resin capable of binding to organic compounds in the effluent stream and forming loaded resin having organic compounds bound thereto;

(b) regenerating at least a portion of the ion exchange resin loaded with the bound organic compounds by contact with a regeneration solution obtained from one or more of the liquor streams used in the manufacturing process to provide regenerated resin and a spent regenerant solution eluate containing the organic compounds;

(c) reusing the regenerated resin as fresh ion exchange resin in step (a);

(d) using the eluate as feedstock in one or more recovery processes of the manufacturing process.

3. The process according to claim1 or 2 wherein the organic compounds removed from the effluent are colorants.

4. The process according to any one of claims 1 to 3 wherein a portion of the liquor stream is directly used as the regenerant solution or is diluted with water before use as the regenerant solution.

5. The process according to any one of claims 1 to 4 wherein anion exchange resin is a weak or strong base anion exchange resin.

6. The process according to any one of claims 1 to 5 wherein the anion exchange resin is a macroporous resin.

7. The use or process according to any one of claims 1 to 6 wherein the pulp mill is kraft pulp mill or the pulp process includes the kraft pulp process.

8. The process according to any one of claims 1 to 7 wherein the regenerant solution is obtained from the white or green liquor stream of a kraft pulp mill or the pink liquor stream of a pulp mill incorporating a neutral sulphite semi chemical (NSSC) process.

9. The process according to any one of claims 1 to 8 for removing colorants from an effluent stream of a pulp mill which uses the kraft pulp process and which has white, green and black liquor streams and optionally a pink liquor stream, wherein the effluent is contacted with anion exchange resin to remove the colorants from the effluent, and the loaded anion exchange resin having bound colorants is regenerated by contact with a regenerant solution obtained from the white, green and / or pink liquor streams, after which the regenerant solution containing the colorants separated from the loaded resin is added to the black liquor stream and the regenerated resin is re-used to contact effluent.

10. The process according to claim 1 or 2 for reducing the amount of organics in effluent from a pulp mill or process having a digester, cooking liquor, black liquor, a

recovery process for recovering chemicals from the black liquor for use in the manufacture of cooking liquor, and an effluent stream containing organics, comprising the steps of:

(a) removing organics from the effluent stream by contacting the effluent with anion exchange resin in a contactor;

(b) separating resin loaded with organic from the contactor;

(c) regenerating loaded anion exchange resin with a regeneration solution obtained from the cooking liquor or intermediate liquors used in the recovery process to provide regenerated resin and used regenerant containing separated organics;

(d) returning the regenerated resin from step (c) to the contactor; and

(e) adding the used regenerant from step (c) to the black liquor.

11. The process according to any one of claims 1 to 10 wherein the resin contains magnetic or magnetisable material.

12. The process according to claim 11 wherein the resin contains magnetic particles dispersed throughout the resin.

13. The process according to any one of claims 10 to 12 wherein the effluent contacts the resin in a contactor, loaded resin is separated from the effluent by using a separator, a portion of the separated resin is regenerated with the regeneration solution, and the regenerated resin and the remainder of the separated loaded resin is returned to the contactor.

14. The process according to claim 13 wherein the effluent continuously flows through the contactor and resin is separated from the effluent and returned to the contactor by agglomerating the resin by using the magnetic properties of the resin.