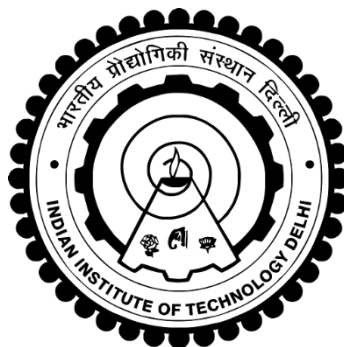


HEAVY METAL SOLUBILIZATION USING ACIDOGENESIS DURING ANAEROBIC DIGESTION

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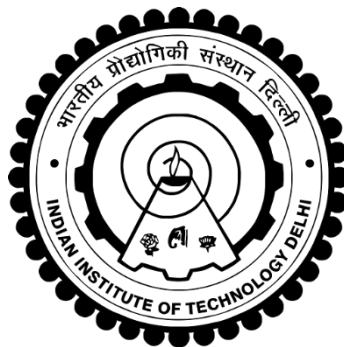
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CERTIFICATE

This is to certify that the thesis titled “**Heavy Metal Solubilization using Acidogenesis during Anaerobic Digestion**” submitted by **Mr. Ashish K. Lohar** is worthy of consideration for fulfilling the requirements for the award of the degree of **Doctor of Philosophy** at **Indian Institute of Technology Delhi**. The thesis is a record of the bonafide research work done by him under my supervision and has been prepared according to the institute’s rules and regulations. The contents of the thesis have not been submitted in whole or in part for the award of any other degree or diploma in any other university or institution.

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ABSTRACT

A large amount of sewage sludge is generated by various wastewater treatment plants. Secondary sludge or waste-activated sludge generated after the secondary treatment is usually dried first and then used as a fertilizer in many parts of India. However, the presence of heavy metals in the sludge limits its use on the land application. In the history of sludge treatment for removing heavy metals, the focus has always been only on the solubilization of heavy metals without considering the cost of operation and the environmental aspect. Therefore, the aim of the current work is to develop a cost-effective and environment-friendly process for the solubilization of heavy metals and the stabilization of the sludge.

The current work proposes a novel approach for the solubilization of heavy metals as well as the stabilization of the sludge using the acidogenic phase of the anaerobic digestion process. The anaerobic digestion process is a cost-effective and environment-friendly process. In the course of the acidogenic phase, various organic acids are produced that lowers the pH of the sludge. The current study is based on the hypothesis that when pH decreases due to organic acid production during the acidogenic phase, it can help in solubilizing heavy metals. Along with pH reduction, bacterial activity also helps in the solubilization of heavy metals.

For the production of organic acids in high concentrations during the anaerobic digestion process, a new inoculum with high acidogenic activity was developed. When organic acids are present in high concentration, the reduction in the sludge pH is also high, and the heavy metals are solubilized in high concentration. All the experiments were carried out without adding any leaching agent and without producing any harmful compounds. Various factors, such as pH, solids concentration, carbon source, and pretreatment of sludge, were studied, which could affect heavy metal solubilization during the anaerobic digestion process.

Heavy metal solubilization was greatly affected by the sludge pH. Heavy metals were efficiently solubilized when the sludge pH was dropped below 4. Similarly, solids concentration also affected the solubilization of heavy metals. When the solid concentration was less than 30 g/l, the pH also decreased. When the solid concentration was greater than 30 g/l, the pH of the sludge did not decrease due to the increase in the buffering capacity of the sludge. When glucose was provided as an external carbon source, the concentration of organic acids inside the reactor increased, and the pH of the sludge was decreased below 4.5. After the treatment process, 52.06 % less land area was required for the disposal of the sludge according to the guidelines provided by the US-EPA.

Pretreatment of sludge also helped in the higher production of organic acids. The pretreatment of the sludge was done using two different methods. The first was ultra-sonication, and the second was heat-treatment. When the ultra-sonicated sludge and heat-treated sludge were used to solubilize heavy metals present in the sludge, 68.78 % and 54.08 % land area were decreased, respectively, for the disposal of the sludge according to the guidelines provided by the US-EPA.

A separate experiment was performed to replace glucose as a carbon source with waste food because the utilization of glucose for the waste treatment process is not a cost-effective process. By using waste food as a carbon source helped in the treatment of both sludge and waste food. After the treatment process, 81.23 % of the land area was decreased for the disposal of the sludge according to the guidelines provided by the US-EPA.

The findings from the current work have shown that it is possible to solubilize heavy metals as well as stabilize sludge without the addition of any leaching agents and the production of any harmful compounds. The present study has demonstrated a process that is cost-effective and environment-friendly.

सारांश

विभिन्न अपशिष्ट जल उपचार संयंत्रों द्वारा बड़ी मात्रा में कीचड़ उत्पन्न होता है। द्वितीयक उपचार के बाद उत्पन्न द्वितीयक कीचड़ (अपशिष्ट-सक्रिय कीचड़) को आमतौर पर पहले सुखाया जाता है और फिर भारत के कई हिस्सों में उर्वरक के रूप में उपयोग किया जाता है। परंतु, कीचड़ में भारी धातुओं की उपस्थिति भूमि पर इसके उपयोग को सीमित करती है। भारी धातुओं को हटाने के लिए कीचड़ के उपचार के इतिहास में, हमेशा संचालन की लागत और पर्यावरणीय पहलू पर विचार किए बिना ही भारी धातुओं के घुलनशीलता पर ध्यान केंद्रित किया गया है। इसलिए, वर्तमान कार्य का उद्देश्य भारी धातुओं के घुलनशीलता और कीचड़ के स्थिरीकरण के लिए एक लागत प्रभावी और पर्यावरण के अनुकूल प्रक्रिया विकसित करना है।

प्रस्तुत कार्य में अवायवीय पाचन प्रक्रिया के अम्लजनिक चरण का उपयोग करके भारी धातुओं की घुलनशीलता के साथ-साथ कीचड़ के स्थिरीकरण के लिए एक नए दृष्टिकोण का प्रस्ताव रखा गया है। अवायवीय पाचन प्रक्रिया एक लागत प्रभावी और पर्यावरण के अनुकूल प्रक्रिया है। अम्लजनिक चरण के दौरान, विभिन्न कार्बनिक अम्ल उत्पन्न होते हैं जो कीचड़ के पीएच को कम करते हैं। वर्तमान अध्ययन इस परिकल्पना पर आधारित है कि जब अम्लजनिक चरण के दौरान कार्बनिक अम्ल के उत्पादन के कारण पीएच कम हो जाता है, तो यह भारी धातुओं को घोलने में मदद कर सकता है। पीएच में कमी के साथ साथ जीवाणुओं की गतिविधि भी भारी धातुओं की घुलनशीलता में मदद करती है।

अवायवीय पाचन प्रक्रिया के दौरान उच्च सांद्रता में कार्बनिक अम्लों के उत्पादन के लिए, उच्च अम्लजनिक गतिविधि वाला एक नया इनोकुलम विकसित किया गया था। जब कार्बनिक अम्ल उच्च सांद्रता में मौजूद होते हैं, तो कीचड़ के पीएच में कमी भी अधिक होती है, और भारी धातुएँ उच्च सांद्रता में घुल जाती हैं। सभी प्रयोग बिना किसी निक्षालन तत्व को डाले और बिना किसी हानिकारक यौगिकों के उत्पादन के किए गए। पीएच, ठोस सांद्रता, कार्बन स्रोत और कीचड़ के पूर्व उपचार जैसे विभिन्न कारकों का अध्ययन किया गया, जो अवायवीय पाचन प्रक्रिया के दौरान धातुओं की घुलनशीलता को प्रभावित कर सकते हैं।

भारी धातुओं की घुलनशीलता कीचड़ के पीएच से बहुत प्रभावित हुई थी। जब कीचड़ का पीएच 4 से नीचे गिर गया था तो भारी धातुएं कुशलतापूर्वक घुल गई थीं। इसके साथ ही, ठोस सांद्रता ने भी भारी धातुओं की घुलनशीलता को प्रभावित किया। जब ठोस सांद्रता 30 ग्राम/लीटर से कम थी, तब पीएच भी कम हुआ। जब ठोस सांद्रता 30 ग्राम/लीटर से अधिक थी, तब कीचड़ की बफरिंग क्षमता बढ़ने के कारण कीचड़ का पीएच कम नहीं हुआ था। जब ग्लूकोज को एक बाह्य कार्बन स्रोत के रूप में प्रदान किया गया, तो रिएक्टर के अंदर कार्बनिक अम्लों की सांद्रता बढ़ गई, और कीचड़ का पीएच 4.5 से कम हो गया। उपचार प्रक्रिया के बाद, यू.एस.-ई.पी.ए. द्वारा प्रदान किए गए दिशानिर्देशों के अनुसार कीचड़ के निपटान के लिए 52.06 % कम भूमि क्षेत्र की आवश्यकता रह गई।

कीचड़ के पूर्व उपचार से भी कार्बनिक अम्लों के उच्च उत्पादन में मदद मिली। कीचड़ का पूर्व उपचार दो अलग-अलग तरीकों का उपयोग करके किया गया था। पहला पराध्वनि-उपचार था, और दूसरा तापोपचार था। जब कीचड़ में मौजूद भारी धातुओं को घोलने के लिए पराध्वनि-उपचारित कीचड़ और तापोपचारित कीचड़ का उपयोग किया गया, तो यू.एस.-ई.पी.ए. द्वारा प्रदान किए गए दिशानिर्देशों के अनुसार कीचड़ के निपटान के लिए क्रमशः 68.78 % और 54.08 % कम भूमि क्षेत्र की आवश्यकता रह गई।

ग्लूकोज को कार्बन स्रोत के रूप में अपशिष्ट भोजन से बदलने के लिए एक अलग प्रयोग किया गया था क्योंकि अपशिष्ट उपचार प्रक्रिया के लिए ग्लूकोज का उपयोग एक लागत प्रभावी प्रक्रिया नहीं है। अपशिष्ट भोजन को कार्बन स्रोत के रूप में उपयोग करने से कीचड़ और अपशिष्ट भोजन दोनों के उपचार में मदद मिली। उपचार प्रक्रिया के बाद, यू.एस.-ई.पी.ए. द्वारा प्रदान किए गए दिशानिर्देशों के अनुसार कीचड़ के निपटान के लिए 81.23 % कम भूमि क्षेत्र की आवश्यकता रह गई।

वर्तमान कार्य के निष्कर्षों से पता चला है कि बिना किसी निक्षालन तत्व को डाले और किसी भी हानिकारक यौगिक के उत्पादन के बिना भी भारी धातुओं को घोलना और साथ ही कीचड़ को भी स्थिर करना संभव है। वर्तमान अध्ययन ने एक ऐसी प्रक्रिया का प्रदर्शन किया है जो लागत प्रभावी और पर्यावरण के अनुकूल है।

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NOMENCLATURE

AAS	Atomic Absorption Spectroscopy
AD process	Anaerobic Digestion process
amu	atomic mass unit
BOD	Biological Oxygen Demand
CSTR	Continuous Stirred-Tank Reactor
EDTA	Ethylene Diamine Tetraacetic Acid
FDS	Fixed Dissolved Solids
FID	Flame Ionized Detector
FSS	Fixed Suspended Solids
GC	Gas Chromatograph
Glc.	Glucose
HRT	Hydraulic Retention Time
ICP	Inductively Coupled Plasma
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
NTA	Nitrilotriacetic Acid
ppb	parts per billion
ppm	parts per million
rpm	revolutions per minute

SCFA	Short-Chain Fatty Acid
STP	Sewage Treatment Plant
TCD	Thermal Conductivity Detector
TDS	Total Dissolved Solids
TS	Total Solids
TSS	Total Suspended Solids
US-EPA	United State-Environmental Protection Agency
VDS	Volatile Dissolved Solids
VFA	Volatile Fatty Acid
VSS	Volatile Suspended Solids
WAS	Waste Activated Sludge